

# 1 Levulinic acid: a novel sustainable solvent for lignin dissolution

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## 14 15 **Abstract**

16 Lignin is a natural macromolecule with potential to be used as a fossil resource to produce  
17 fuels, value-added chemicals, and novel biomaterials and composites. Due to its complex  
18 structure, its efficient dissolution is still challenging, which hinders the applicability of this  
19 natural resource at larger scale. The challenge becomes harder considering the current need  
20 of sustainable and environmentally friendly solvents. This work reports, for the first time, the  
21 dissolution of lignin in levulinic acid, a solvent that can be produced from renewable sources,  
22 and compares its efficiency with common carboxylic acids and sulfuric acid. Levulinic acid  
23 was found to dissolve 40 wt. % kraft lignin; remarkably, the dissolution efficiency was

24 maintained when adding up to 40 wt% of water. The addition of water decreases the  
25 concentration of levulinic acid and the viscosity of the solutions formed which is benefic for  
26 large-scale processing. The Kamlet-Taft  $\pi^*$  parameter of the different acidic solvents was  
27 estimated and found to correlate well with their solubility performance. Lignins previously  
28 dissolved in levulinic and formic acids were selected to be regenerated and minor differences  
29 were found in the content of functional groups, thermal stability, and their morphological  
30 structure, when compared to native kraft lignin. The high dissolution performance and  
31 favorable sustainable features makes this solvent highly appealing for future large-scale  
32 dissolution and manipulation of lignin into novel biomaterials.

33

## 34 **1. Introduction**

35 The concern to reduce the consumption and dependence of fossil fuels has led to an increase  
36 in the demand for products manufactured from renewable and sustainable sources, such as  
37 lignin. Lignin is an amorphous, polyphenolic polymer, being the second most abundant  
38 renewable biomaterial on Earth [1]. Today, the main source of lignin available is isolated from  
39 spent pulping liquors produced after chemical pulping of wood. By far, the most important  
40 pulping methods are kraft and sulfite cooking. The content of the most important functional  
41 groups presents in the lignin materials, such as the phenolic hydroxyl, carboxyl, and sulfonate  
42 groups, varies with the pulping process applied. Due to its high carbon content, high thermal  
43 stability, biodegradability, antioxidant activity and favorable stiffness, there is a great interest  
44 of using lignin to produce value-added products for various applications, such as  
45 reinforcement fillers, antioxidants, UV adsorbents, antimicrobial agents, carbon fibre precursors,

46 and biomaterials for tissue engineering and gene therapy [2,3]. The solubility in the water-based  
47 cooking liquors is governed by the number of dissociating groups available in the lignin and  
48 pH values approaching and exceeding the pKa value of the dissociating functional group [4–  
49 6]. For example, in kraft lignins the pKa value for the main dissociating phenolic moieties is  
50 close to 10, while in sulfite lignins the sulfonate groups have pKa's around 1-2. Like for other  
51 polymers, the polydispersity introduces differences in the solubility characteristics within the  
52 size distribution, which make low molecular fragments much easier to dissolve than larger  
53 molecules. The reason is that the lower the molecular weight, the stringer is the entropic  
54 driving force contribution for dissolution. These considerations refer to the translational  
55 entropy of mixing. Moreover, due to the most frequent depolymerization reaction in kraft  
56 cooking, the number of free phenolic groups increases when the molecular mass decreases  
57 [7]. It has been found that it is possible to re-dissolve aggregated lignin if certain surface  
58 active additives are introduced to a lignin dispersion;. small additions of bile acid salts have  
59 been shown especially efficient to re-dissolve kraft lignin in aqueous solutions[8]. The effect  
60 of bile salts can, most likely, be assigned to an association at hydrophobic sites in the lignin  
61 structure, which then increases the hydrophilicity of the lignin. Moreover, in water the  
62 dissolution and colloidal stability of lignin can be increased by additions of certain  
63 electrolytes (so called “salting in” effect), which shows that ion specific effects are also  
64 important for solvency [9].

65 The ideal scenario would be the development of a solvent that, besides being highly efficient  
66 and easily tuned to fit different types of lignin, should be also inexpensive, nontoxic, low  
67 volatility, and viscosity [10]. In this respect, the use of sustainable solvents, such as,  $\gamma$ -

68 valerolactone and levulinic acid, can represent an interesting approach for lignin dissolution  
69 [11].  $\gamma$ -valerolactone has already been successfully included in binary solvent mixtures with  
70 water, dimethyl sulfoxide, and dimethylformamide for lignin dissolution [10]. The amount of  
71 lignin that can be dissolved in these  $\gamma$ -valerolactone–based mixtures was greater than most  
72 common organic solvents [13]. However, at the best of our knowledge, the use of levulinic  
73 acid as a direct solvent for lignin dissolution has never been described. This green organic  
74 compound, has ketone and carboxylic groups which provides a wide range of functionality  
75 and reactivity [16]. Levulinic acid has been used in many applications, such as textile dyeing,  
76 pharmaceutical products, antifreezing agent, resin, food flavoring additive, coating material,  
77 and animal feed [17]. Despite nowadays the use of renewable materials still carry reasonable  
78 expensive precursors, low yields, and lack of efficient separation procedures [18], there is a  
79 growing interest on this “green” acid. Levulinic acid has a large potential to be obtained from  
80 different renewable sources, such as sugars (e.g., glucose, sucrose and fructose) and biomass  
81 (e.g., wood, starch and agricultural wastes), through different dehydrating acid treatment  
82 [19].

83 In this work, we intend to evaluate the performance of levulinic acid as a direct dissolution  
84 system for lignin and shed light on the mechanisms involved in lignin dissolution. Therefore  
85 Kraft lignin was dissolved with levulinic acid, and a set different of carboxylic acids (e.g. 2-  
86 methylbutyric, 2-methylvaleric acid, glacial acetic acid and propionic acid) and a strong  
87 inorganic acid (i.e. sulfuric acid), and their dissolution efficiency was compared. The effect of  
88 diluting levulinic acid with water is also evaluated in regard of its dissolution performance.  
89 The Kamlet-Taft  $\pi^*$  parameter was estimated for the dissolution systems and correlated with

90 lignin solubility. Additionally, lignins dissolved in levulinic and formic acids were regenerated  
91 and analyzed by infrared spectroscopy, thermogravimetry and scanning electron  
92 microscopy.

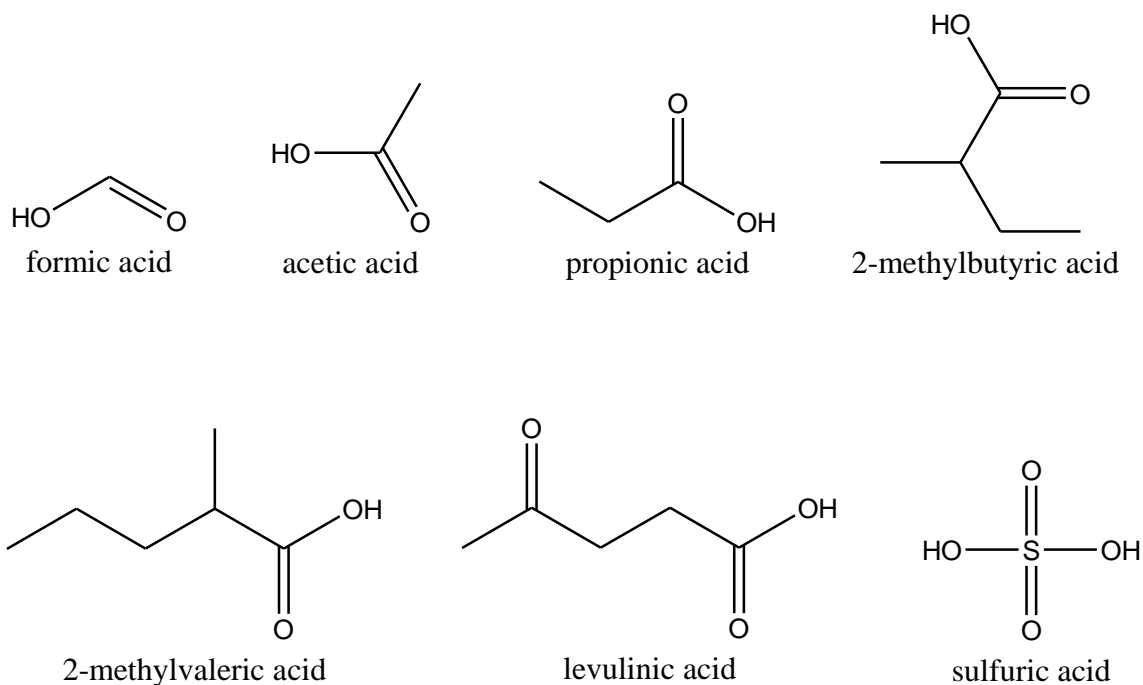
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## 94 **2. Materials and methods**

95

### 96 **2.1. Materials**

97 Kraft lignin (selected as the model lignin) and 2-methylbutyric acid were purchased from  
98 Sigma-Aldrich. Levulinic and formic acids were obtained from Merck and 2-methylvaleric acid  
99 from Lancaster Synthesis. Acetic acid glacial and sulfuric acid were acquired from Panreac  
100 while the propionic acid was obtained from Honeywell - Fluka. Sodium hydroxide (NaOH) was  
101 purchased from José Manuel Gomes dos Santos, Lda., (Porto, Portugal). The 4-nitroanisol  
102 (4NA) was acquired from Dagma. All the chemicals were used as received. The chemical  
103 structures of different acids are depicted in the Figure 1.



104

105 Figure 1. Molecular structures of the acids used .

106

## 107 2.2. Dissolution efficiency of lignin

108 Dispersions of kraft lignin were stirred with a magnetic stirrer for 24 h at 25, 40 and 60 °C.

109 After centrifugation for 1 h at 14000 rpm (17968 g), the supernatant was removed and

110 diluted with 1 wt. % NaOH(aq.) to determine the total content of dissolved lignin. The

111 amount of lignin was estimated by measuring the absorbance at 288 nm using a UV-Vis

112 spectrophotometer (Shimadzu UV-2450). Calibration curves (i.e. nine solutions with

113 concentrations from 0.0001 to 0.004 wt. % kraft lignin in 1 wt. % NaOH(aq.) solvent) were

114 previously prepared. Samples were left to equilibrate and inspected over time by naked eye

115 and under optical microscopy (Linkam LTS 120 microscope equipped with a Q imaging station

116 (Qicam) Fast 1394 camera).

117

### 118 2.3. Solvatochromic Kamlet-Taft measurements

119 The solvatochromic probe 4-nitroanisole (4NA) was used to estimate the Kamlet-Taft  
120 parameter  $\pi^*$  (polarizability index). A stock solution of the dye in DCM was prepared to a  
121 concentration of 4 mM. The dye stock solution was added to the solvents under study to a  
122 final concentration of 0.1 mM, that enables to obtain the absorbance values within the  
123 required measurable range, and DCM was removed by evaporation at room temperature.  
124 The absorption spectra of the solvatochromic probe was recorded from 250 nm to 500 nm  
125 in a quartz cell with a 10 mm path length, using a Shimadzu UV/Vis spectrometer UV-1700  
126 at 1 nm stepwise. The wavelength at maximum absorption  $\lambda_{max}$  was determined for the  
127 probe in each solvent. The  $\pi^*$  parameter was determined according to Kamlet and Taft [20],  
128 using the equation:

$$129 \quad \pi^* = \frac{(34.12 - \lambda_{max})}{2.343} \quad (1)$$

130 The constant values were obtained from multiple correlation equations that set  $\pi^*$  at zero  
131 for cyclohexane and unity for dimethyl sulfoxide [21].

132

### 133 2.4. Rheometry

134 The rheological measurements were carried out on a Haake Mars III (Thermo Fisher  
135 Scientific) set with the cone-plate geometry (1°, 35 mm, 0.052 mm gap). A Peltier unit was  
136 used to ensure strict temperature control, which was set to  $20.0 \pm 0.1$  °C. The Newtonian  
137 viscosity was accessed by nonlinear rotational tests from 0.1 to 50 Pa.

138

### 139 2.5. Fourier transform infrared spectroscopy (FTIR)

140 Infrared spectra were recorded with a Thermo Nicolet 380 FT-IR apparatus (Thermo  
141 Scientific) equipped with Smart Orbit Diamond ATR system. The FTIR analysis was performed  
142 within the wave number range of 4000-400  $\text{cm}^{-1}$ . A total of 68 scans were used for each  
143 spectrum at a resolution of 8  $\text{cm}^{-1}$  in the absorbance mode. The background spectrum was  
144 subtracted before each analysis. All the samples were freeze-dried before FTIR assays.

145

## 146 **2.6. Thermogravimetric analysis (TGA)**

147 Thermograms were measured using a thermogravimetric analyzer, TG 209 F Tarsus (Netzsch  
148 Instruments). Previously lyophilized samples were weighed in aluminum pans (ca. 3 mg) and  
149 subsequently heated from 25 to 1000  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  under  $\text{N}_2$   
150 atmosphere (flow rate of 50  $\text{mL}\cdot\text{min}^{-1}$ ).

151

## 152 **2.7. Scanning electron microscopy (SEM)**

153 A VEGA3 SBH from TESCAN scanning electron microscope equipped with a selected energy  
154 dispersive X-ray microanalyser (EDX) was used to access the microstructural features of the  
155 regenerated lignins. Before the SEM analysis, the samples were freeze dried, deposited  
156 directly over the carbon tape on the support and sputtered with an approximately 6 nm thin  
157 Au/Pd film, by cathodic pulverization using a SPI Module Sputter Coater, during 90 s at a  
158 current of 15 mA. The accelerating voltage used ranged from 5 to 15 kV, and the work  
159 distance (WD) was set to 10 mm.

160

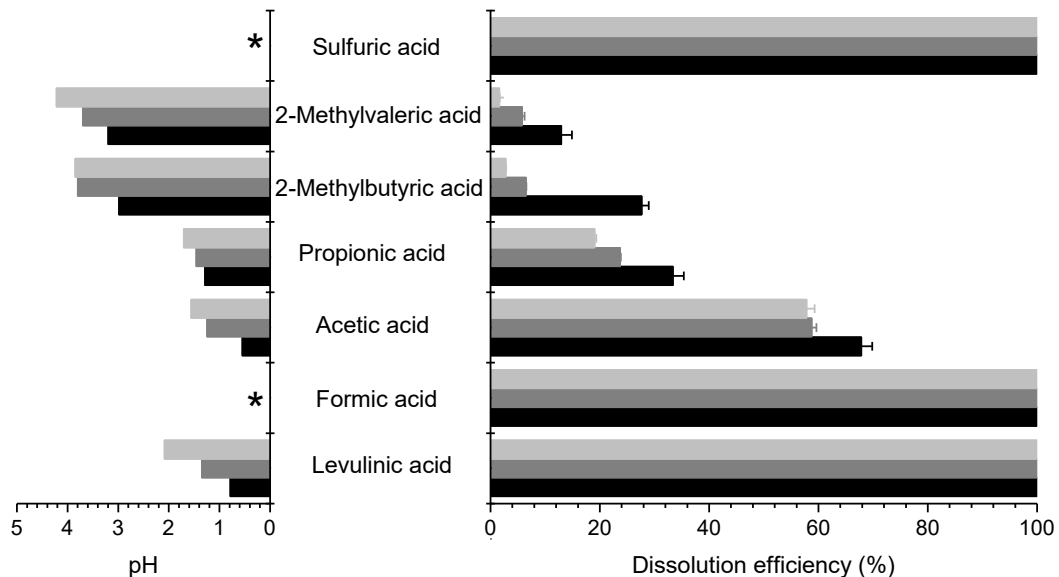
## 161 **3. Results and discussion**



162

163 **3.1. Dissolution efficiency and Kamlet-Taft parameters**

164 The efficiency of levulinic acid to dissolve 10 wt. % kraft lignin was evaluated and compared  
165 with five carboxylic acids and sulfuric acid. For all carboxylic acids, an increase of dissolution  
166 efficiency of lignin is verified with the reduction of the carbon chain length (Figure 2). A  
167 similar trend was previously found for alcohols [22]. Surprisingly, levulinic acid does not  
168 follow this trend since, despite having a long carbon chain, it can dissolve up to 40 wt. % kraft  
169 lignin. This sustainable solvent shows a similar dissolution performance to formic acid, but  
170 much higher than the carboxylic acids of similar chain length (e.g., 2-methylbutyric acid). This  
171 higher solubility efficiency might be due to the presence of an additional ketone group in the  
172 levulinic acid structure. The sulfuric acid was able to fully dissolve lignin until a concentration  
173 of 10 wt. %. Its dissolution efficiency strongly decreases for higher amounts of lignin, as can  
174 be observed in Figure 3. The pH value of each lignin solution was analyzed, and it is reported  
175 in Figure 2. The data suggests that the efficiency of the dissolution does not have a direct  
176 relationship to the pH value. In all cases, the samples were prepared in a pH region below  
177 the pKa of the acids, and the dissolution performances are strikingly different. Note that,  
178 levulinic, acetic, and propionic acids have a rather similar pKa, ca. 4.8, [23,24].

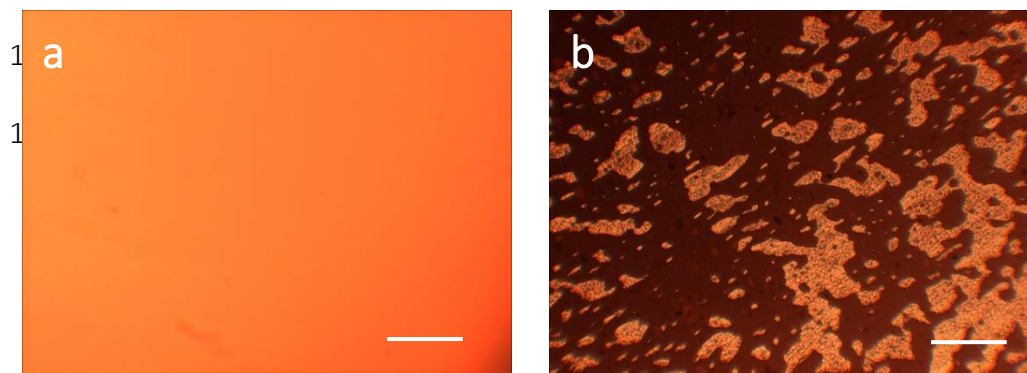


179

180 Figure 2. pH and dissolution efficiency of 0.1 (black), 1 (gray) and 10 (light gray) wt. % kraft

181 lignin dispersed in different acids. Samples marker with "\*" show pH below zero.

182



187

188 Figure 3. Polarized light micrographs of (a) 10 and (b) 20 wt. % kraft lignin dissolved in sulfuric

189 acid, at room temperature. The scale bars represent 1 mm.

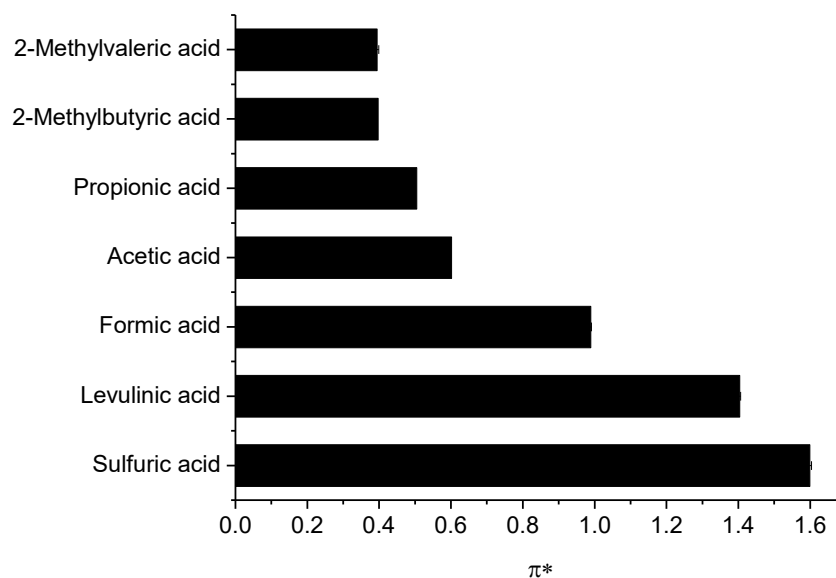
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191 The Kamlet-Taft solvatochromic parameter  $\pi^*$  was estimated for the different acidic solvents

192 (Figure 4). Data suggest that increasing polarizability of the acidic solvents favors lignin

193 dissolution; acids with high polarizability ( $\pi^* > 0.9$ ) were the most effective to dissolve lignin.

194 This trend is opposite to what was verified for the alkaline systems [25]. Furthermore, the  
195 trend observed for carboxylic acids, in which solubility is favored by a higher  $\pi^*$  and a smaller  
196 carbon chain, is similar to alcohols, where it has already been described that  $\pi^*$  of methanol  
197 is higher than that of 2-propanol [26] and the lignin solubility is higher in methanol [27,28].



198

199 Figure 4. Solvatochromic parameter  $\pi^*$  for the different acidic solvent systems.

200

201 A systematic study on the lignin dissolution efficiency with different concentrations of  
202 levulinic acid aqueous solutions was performed, using different initial lignin concentrations  
203 (i.e., 1, 10, 20 and 30 wt. %) and temperatures (i.e., 25, 40 and 60 °C). As it is possible to  
204 observe in Table 1, the temperature rise benefits dissolution in all cases, and this normal  
205 thermal effect has been previously reported for other solvent systems [10,29,30].

206 Lignin dissolution was found complete for water concentrations below 40 wt. % (5.17 M). In  
207 this case, it was possible to dissolve up to 40 wt. % lignin (the same amount using  
208 concentrated levulinic acid). For diluted levulinic acid aqueous solutions, above 40 wt. %

209 water, lignin dissolution was incomplete. A similar behavior has been reported for  $\gamma$ -  
 210 valerolactone aqueous system [10]. It was suggested that, for water contents above 50 wt.  
 211 %, a strong interaction (H-bonding network) between water and  $\gamma$ -valerolactone is  
 212 established decreasing the solvent performance towards lignin. It is reasonable to assume  
 213 that a similar behavior might be occurring with the levulinic acid system. The water effect  
 214 and sensitivity in lignin solubility has been observed in other solvent systems, such as ionic  
 215 liquids (IL); in the IL pyridinium formate, a small amount of water is sufficient to remarkably  
 216 affect the dissolution [29]. The higher the amount of water the lower the solubility of lignin,  
 217 being negligible above 50 % (v/v) of water. In the alkylimidazolium-based IL systems, water  
 218 tolerance is higher and 30 wt. % water in the IL still favors lignin solubility [31].

219

220 Table 1. Dissolution efficiency (%) of kraft lignin in levulinic acid aqueous solutions. Effect of  
 221 levulinic acid and lignin concentrations at different temperatures.

Levulinic acid (M)	Kraft lignin (wt. %)	Temperature (°C)		
		25	40	60
0.86	1	10.93 ± 0.07	12.0 ± 0.2	16.5 ± 0.2
	10	3.28 ± 0.04	3.68 ± 0.02	4.6 ± 0.5
	20	2.16 ± 0.02	2.33 ± 0.04	2.56 ± 0.01
	30	1.75 ± 0.00	1.79 ± 0.01	2.06 ± 0.01
1.72	1	23.6 ± 0.9	24.8 ± 0.2	30.9 ± 0.8
	10	7.84 ± 0.09	8.4 ± 0.1	8.5 ± 0.1

	20	$5.30 \pm 0.05$	$5.4 \pm 0.2$	$6.0 \pm 0.1$
	30	$3.94 \pm 0.00$	$3.96 \pm 0.04$	$4.14 \pm 0.03$
2.58	1	$41.70 \pm 0.03$	$42.9 \pm 0.1$	$48.5 \pm 0.9$
	10	$16.0 \pm 0.3$	$17.9 \pm 0.3$	$21.49 \pm 0.04$
	20	$10.86 \pm 0.05$	$11.6 \pm 0.2$	$11.6 \pm 0.2$
	30	$7.4 \pm 0.4$	$9.9 \pm 0.2$	$10.58 \pm 0.01$
3.44	1	$71.0 \pm 0.7$	$79 \pm 1$	$90.11 \pm 0.01$
	10	$31 \pm 1$	$36.5 \pm 0.4$	$40.2 \pm 0.1$
	20	$23.2 \pm 0.4$	$24.1 \pm 0.1$	$28.2 \pm 0.8$
	30	$15.8 \pm 0.2$	$17.8 \pm 0.5$	$18.3 \pm 0.1$
4.31	1	$99 \pm 4$	100	100
	10	$61.4 \pm 0.4$	$67 \pm 3$	$78.9 \pm 0.9$
	20	$63 \pm 2$	$61.4 \pm 0.3$	$75.2 \pm 0.5$
	30	$44 \pm 2$	$49 \pm 3$	$65 \pm 3$
5.17	1	100	100	100
	10	100	100	100
	20	100	100	100
	30	100	100	100

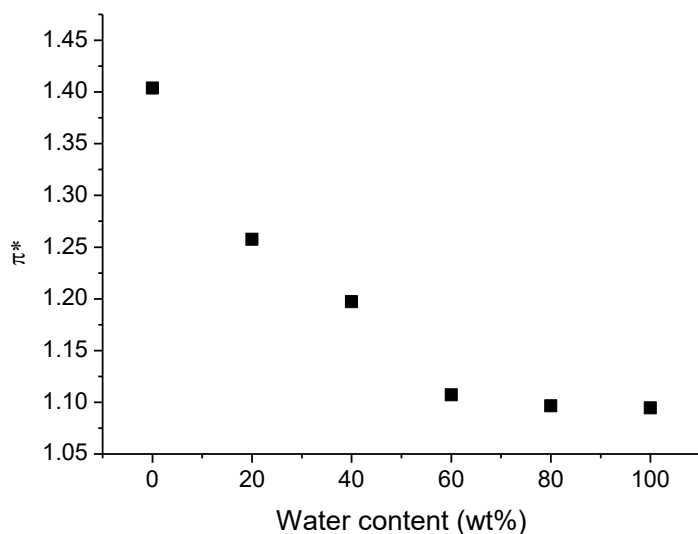
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223

224 The water content effect on the solvatochromic parameter  $\pi^*$  was also evaluated (Figure 5).

225 Overall, this parameter was found to decrease with increasing water content. Above 60 wt.

226 % of water (4.31 M levulinic acid), the  $\pi^*$  approaches the  $\pi^*$  value of pure water. As we have  
227 previously observed, this also coincides with the point where the dissolution efficiency is  
228 seriously compromised.



229

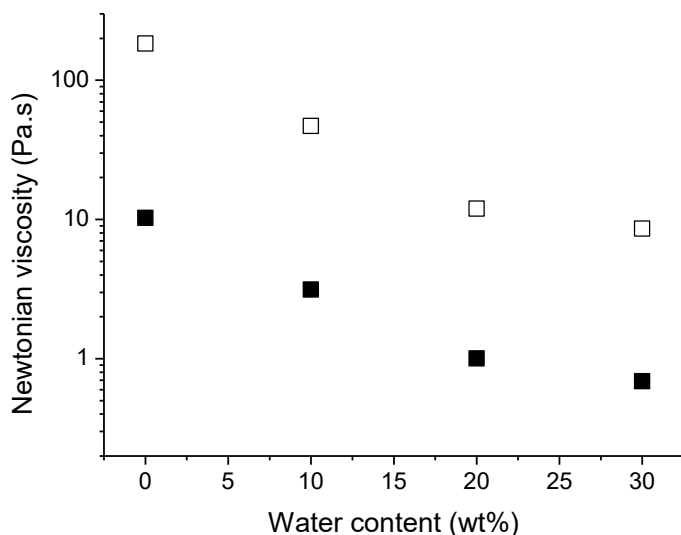
230 Figure 5. Solvatochromic parameter  $\pi^*$  of levulinic acid aqueous solutions with different  
231 water contents.

232

### 233 3.2. Rheology

234 Using a levulinic acid aqueous binary system has several obvious advantages. Not only the  
235 solvent system becomes inexpensive and more environmentally friendly, but the viscosity  
236 significantly decreases benefiting its manipulation. Remarkably, by adding water, it is  
237 possible to decrease the viscosity by, ca. one order of magnitude without seriously  
238 compromising the dissolution efficiency of levulinic acid (Figure 6). The lower solution  
239 viscosity has benefits in some applications, such as in the production of lignin-based  
240 polyurethane foams, where the high viscosity of commercial lignins is a serious issue [32] or

241 in development of lignin-based composite materials, where the typical high viscosity limits,  
242 for instance, the potential of grafting [33].



243

244 Figure 6. Newtonian viscosity of solutions with 30 (full symbols) and 40 (empty symbols) wt.  
245 % kraft lignin dissolved in levulinic acid with different water concentrations. Note that in all  
246 cases lignin dissolution is complete.

247

### 248 3.3. Lignin characterization after solubilization in levulinic and formic acids

249 After full dissolution in levulinic acid, lignin was precipitated and recovered by adding excess  
250 water. The regenerated material was lyophilized and characterized using FTIR, TGA and SEM.  
251 For comparison, the same procedure was performed with formic acid which, in the same  
252 conditions, has a similar dissolution performance to levulinic acid (see Figure 2 for details).

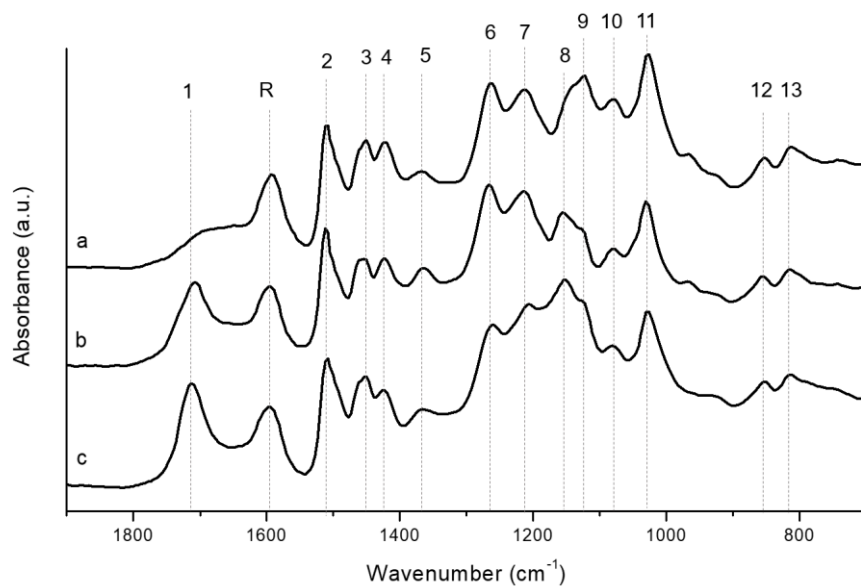
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#### 254 3.3.1. Fourier transform infrared spectroscopy

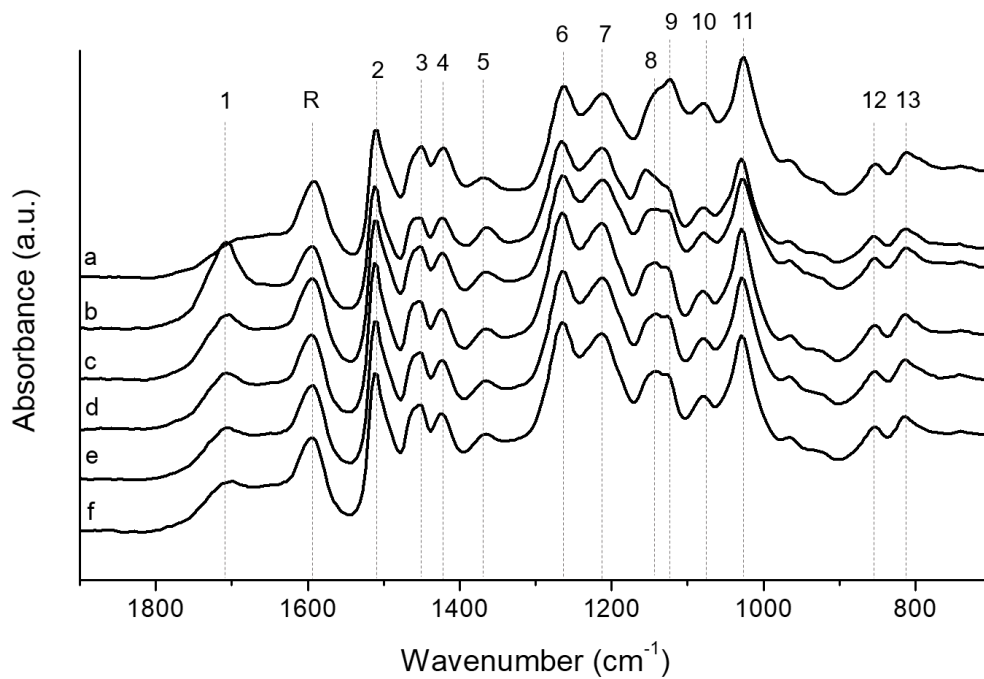
255 The FTIR spectra of the initial and regenerated lignins, after dissolution in levulinic and formic  
256 acids, are shown in Figure 7 and 8. The ratio of absorbances  $A_x/A_{1600}$ , where  $A_x$  represents  
257 each band identified and numbered in Figures 7 and 8, allows a comparative assessment of  
258 the effect of type of acids and concentration on the lignin structure [38,39]. This analysis was  
259 performed for all observed vibrational modes, and the data is summarized in tables S1 and  
260 S2. The reference band (R) can be attributed to aromatic skeletal vibrations plus the C=O  
261 stretch [34]. The most significant difference in spectra is the appearance of a well-defined  
262 band at  $1705 - 1712 \text{ cm}^{-1}$  (#1). This band is assigned to the C=O stretching in unconjugated  
263 ketone, carbonyl and in ester groups [34]. In electrochemical applications, the increase  
264 content of carbonyl groups is an advantage for enhanced protonic and electrical  
265 conductivities in active materials [35]. Its relative intensity is higher using formic acid than  
266 when using levulinic acid in the dissolution process. For the diluted levulinic acid, the lower  
267 the acid concentration, the less intense the band is (Figure 9). The band #2, at  $1510 - 1512$   
268  $\text{cm}^{-1}$ , is assigned to the aromatic skeleton vibration [34]. The absence of a significant  
269 decrease in the relative intensity of this band suggests that the dissolution and regeneration  
270 processes do not affect significantly the integrity of the aromatic rings [36]. The decrease of  
271 the relative absorbance in the bands #3 (i.e., C-H bending of the methyl or methylene groups  
272 [37]) and #4 (i.e., aromatic skeletal vibration combined with the C-H asymmetric deformation  
273 of the methyl groups [34]) for all regenerated lignins, suggests the possible hydrolysis of the  
274 methoxy groups during the dissolution or regeneration process [36]. In addition, the  
275 intensity decreases of the C-O deformation in primary (#11) and secondary (#10) alcohols,  
276 suggests a degradation of the aliphatic chain of the phenyl propane units for all regenerated



277 lignins. This reaction also contributes for the enhancement of the relative intensity of the  
278 C=O band [36]. Differences between levulinic and formic acid are observed regarding the  
279 cleavage of ether bonds. Using levulinic acid, an increase of the vibrational band assigned to  
280 the phenolic hydroxyl groups occurs[29] (#5) while a decrease of the intensity of the ether-  
281 O bands [29] (#9), is observed. Such decrease is most likely related to the cleavage of these  
282 linkages, mainly  $\beta$ -O-4, the most abundant linkage in lignin and one of the most easily cleaved  
283 bonds [40]. Using formic acid, an opposite effect was observed.  
284

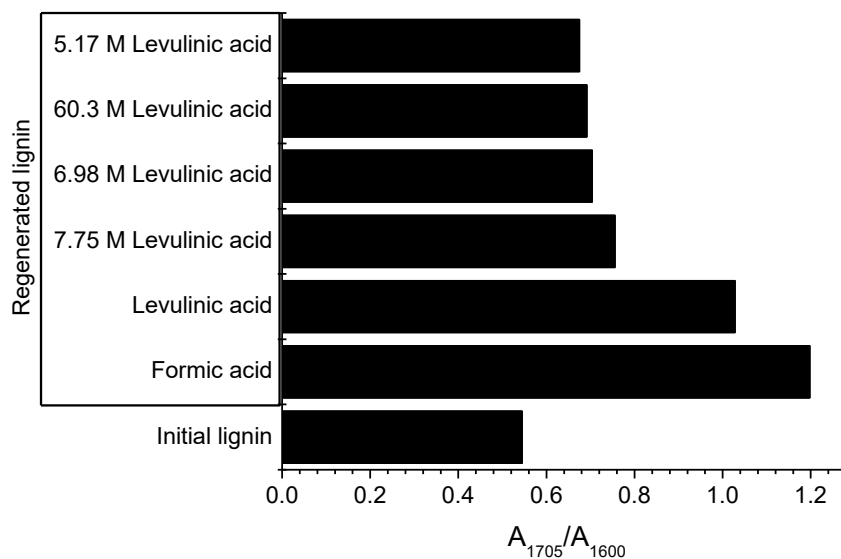


285  
286 Figure 7. Normalized FTIR spectra of: (a) initial lignin and recovered lignin after dissolution in  
287 (b) levulinic acid and (c) formic acid. The vibration mode assignment and semiquantitative  
288 analysis is performed in Table S1 and discussed in the text.  
289



290

291 Figure 8. Normalized FTIR spectra of: (a) initial lignin; recovered lignin after dissolution in (b)  
292 concentrated levulinic acid and levulinic acid aqueous solutions of (c) 7.75 M, (d) 6.89 M, (e)  
293 6.03 M, and (f) 5.17 M. The vibration mode assignment and semiquantitative analysis is  
294 performed in Table S2 and discussed in the text.



295

296 Figure 92. Semi-quantitative analysis ( $A_{1705}/A_{1600}$ ) of initial and regenerated lignins.

297

### 298 3.3.2. Thermogravimetric analysis

299 The thermal decomposition of native and regenerated lignins was performed and compared

300 in Figure 10. From the analysis of thermograms and corresponding DTGs, it can be observed

301 that some weight loss occurs at temperatures between 80-150 °C, corresponding to the

302 evaporation of physically adsorbed water [41]. In the raw lignin and regenerated material

303 after the dissolution in levulinic acid, this step occurs until 100 °C. In the case of the lignin

304 regenerated after being dissolved in formic acid, this step is verified until 150 °C, most likely

305 due to the volatilization of low molecular weight compounds in addition to the removal of

306 water [29]. The main degradation step occurs at a maximum temperature,  $T_m$ , corresponding

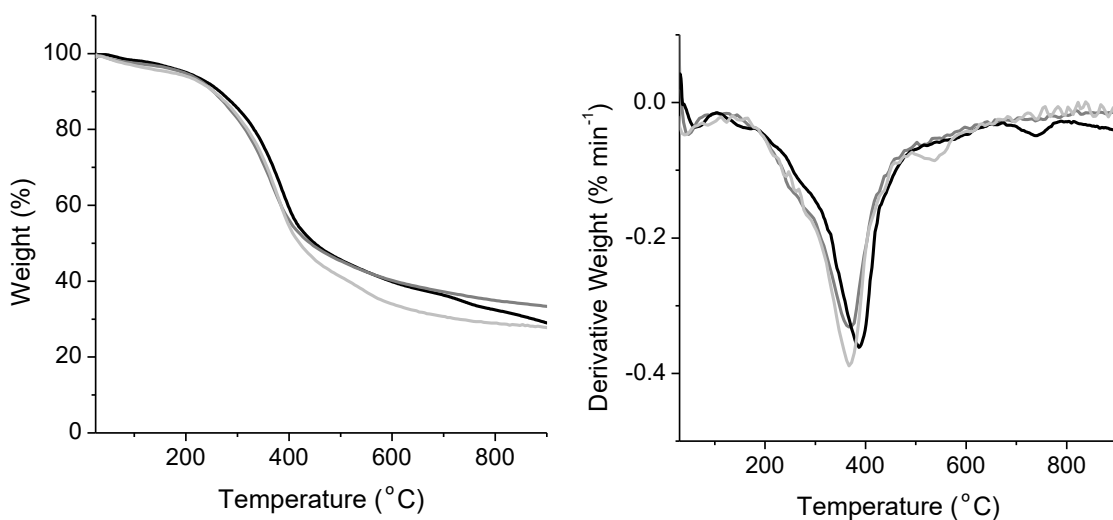
307 to the maximum rate of degradation, 383 °C for the initial lignin. However, for the

308 regenerated lignin previously dissolved in formic and levulinic acids, the  $T_m$  decreases to 377

309 and 367 °C, respectively. These values are in agreement with those reported in literature,

310 where most lignins present their maximum weight loss rate between 300 and 400 °C [41].  
311 Nevertheless, , these results also suggest that lignin becomes less structured upon  
312 regeneration. This effect is more pronounced when using levulinic acid, due to the cleavage  
313 of the ether linkages discussed in the FTIR analysis. After heating to 900 °C, the regenerated  
314 material obtained after dissolution in formic and levulinic acids, have a portion unvolatilized  
315 equivalent to ca. 28 and 33 wt. %, respectively. Since in the initial kraft lignin, ca. 29 wt. %  
316 remains unvolatilized, this suggests that some condensed aromatic structures may be  
317 formed during the dissolution and regeneration processes[43].

318



319

320 Figure 10. TGA (left) and the correspondent DTG (right) of the regenerated material obtained  
321 from the dissolution of 40 wt. % kraft lignin in formic (light gray line) and levulinic acid (gray  
322 line). The initial raw kraft lignin is represented with a black line.

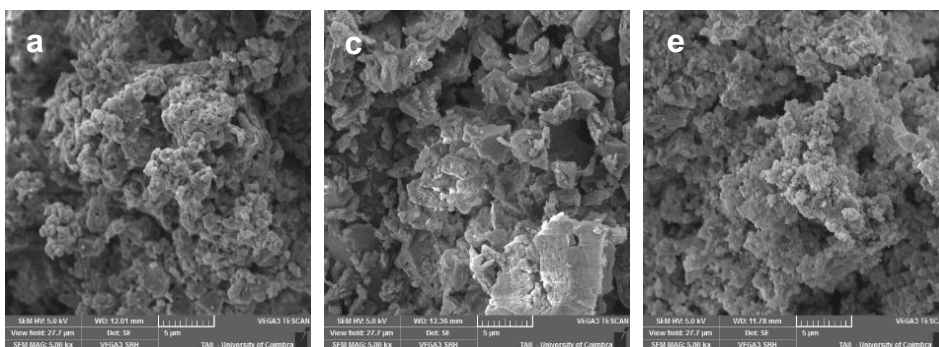
323

324 **3.3.3. Scanning electron microscopy**

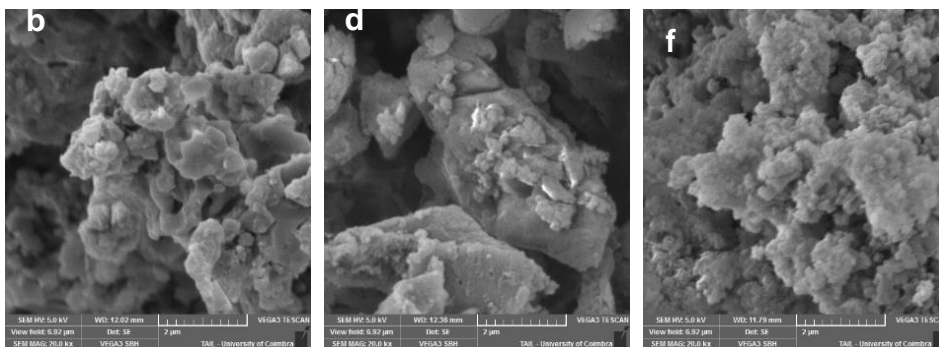
325 The dissolution and regeneration effects on the morphology and microstructure of the  
326 regenerated materials were analyzed by SEM and compared to the initial raw kraft lignin  
327 (Figure 11). The initial lignin sample presents particles with different shapes and sizes, which  
328 are typical for this type of lignin [44]. Their average size is in accordance with previous works,  
329 ca. 1-2  $\mu\text{m}$  [45]. On the other hand, the regenerated lignins present some differences; lignin  
330 dissolved in formic acid (Figures 11c and 11d) have a more heterogeneous structure, with  
331 larger and very smaller particles, in comparison to the initial lignin. On the other hand, when  
332 dissolved in levulinic acid (Figures 11e and 11f) the structure is more homogeneous, but the  
333 particles are smaller when compared to raw lignin. Most likely, this morphological effect is  
334 due to higher degree of depolymerization, as suggested by the FTIR and TG analysis.

335

336



337



338 Figure 11. SEM images at different magnifications of a, b) initial raw lignin; c, d) lignin  
339 regenerated after dissolution in formic acid; and e, f) lignin regenerated after dissolution in  
340 levulinic acid. Magnification x 5,000 and 20,000.

341

#### 342 **4. Conclusions**

343 This work reports, for the first time, the use of levulinic acid as a sustainable solvent of  
344 superior performance for lignin dissolution. In addition to the benefits of using an  
345 environmentally friendly solvent when compared to the harmful systems commonly used,  
346 levulinic acid is still quite efficient upon water dilution up to a concentration of ca. 5.17 M.  
347 Lignin dissolution seems to correlate well with solvent polarizability. The addition of water  
348 greatly reduces the viscosity of the solution, which might facilitate large-scale processing,  
349 such as mixing, pumping or extrusion from containers, and also makes the solvent  
350 inexpensive. The lignins dissolved in levulinic can be regenerated by the addition of excess  
351 water. These regenerated materials have different contents of functional groups, being the  
352 most important difference found in the C=O content. Besides that, the FTIR analysis suggests  
353 the occurrence of partial methoxy groups hydrolysis, degradation of aliphatic chain of  
354 phenylpropane and cleavage of ether bonds. Nevertheless, these changes do not result in  
355 significant differences in terms of thermal stability and morphological characteristics, when  
356 compared to the initial raw material or lignin dissolved in formic acid. Overall, this work  
357 characterizes a novel and ecofriendly aqueous-based solvent for lignin, which might be very  
358 interesting for its processing at the industrial level, creating opportunities for the  
359 development of new applications for lignin that have not been exploited so far due to its

360 difficult dissolution. Additionally, this work also sheds light on the mechanisms involved in  
361 lignin dissolution highlighting the role of solvent polarizability.

362

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### 370 **References**

- 371 [1] Y. Pu, N. Jiang, A.J. Ragauskas, Ionic liquid as a green solvent for lignin, *J. Wood Chem.*  
372 *Technol.* (2007). doi:10.1080/02773810701282330.
- 373 [2] D. Kai, M.J. Tan, P.L. Chee, Y.K. Chua, Y.L. Yap, X.J. Loh, Towards lignin-based functional  
374 materials in a sustainable world, *Green Chem.* 18 (2016) 1175–1200.  
375 doi:10.1039/c5gc02616d.
- 376 [3] M. Norgren, H. Edlund, Lignin: Recent advances and emerging applications, *Curr. Opin.*  
377 *Colloid Interface Sci.* (2014). doi:10.1016/j.cocis.2014.08.004.
- 378 [4] M. Norgren, B. Lindström, Dissociation of phenolic groups in kraft lignin at elevated  
379 temperatures, *Holzforschung.* (2000). doi:10.1515/HF.2000.088.
- 380 [5] M. Norgren, H. Edlund, L. Wågberg, B. Lindström, G. Annergren, Aggregation of kraft  
381 lignin derivatives under conditions relevant to the process, part I: Phase behaviour,

- 382 Colloids Surfaces A Physicochem. Eng. Asp. (2001). doi:10.1016/S0927-  
383 7757(01)00753-1.
- 384 [6] M. Norgren, H. Edlund, L. Wågberg, Aggregation of lignin derivatives under alkaline  
385 conditions. Kinetics and aggregate structure, Langmuir. (2002).  
386 doi:10.1021/la011627d.
- 387 [7] M. Norgren, B. Lindström, Physico-chemical characterization of a fractionated kraft  
388 lignin, Holzforschung. (2000). doi:10.1515/HF.2000.089.
- 389 [8] M. Norgren, H. Edlund, Stabilisation of kraft lignin solutions by surfactant additions,  
390 Colloids Surfaces A Physicochem. Eng. Asp. (2001). doi:10.1016/S0927-  
391 7757(01)00806-8.
- 392 [9] M. Norgren, H. Edlund, Ion specific differences in salt induced precipitation of kraft  
393 lignin, Nord. Pulp Pap. Res. J. (2003). doi:10.3183/npprj-2003-18-04-p400-403.
- 394 [10] Z. Xue, X. Zhao, R.C. Sun, T. Mu, Biomass-derived  $\gamma$ -valerolactone-based solvent  
395 systems for highly efficient dissolution of various lignins: Dissolution behavior and  
396 mechanism study, ACS Sustain. Chem. Eng. (2016).  
397 doi:10.1021/acssuschemeng.6b00639.
- 398 [11] X.R. Shen, D.Z. Xia, Y.X. Xiang, J.G. Gao,  $\gamma$ -valerolactone (GVL) as a bio-based green  
399 solvent and ligand for iron-mediated AGET ATRP, E-Polymers. (2019).  
400 doi:10.1515/epoly-2019-0033.
- 401 [12] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Gamma-valerolactone, a sustainable  
402 platform molecule derived from lignocellulosic biomass, Green Chem. (2013).  
403 doi:10.1039/c3gc37065h.



- 404 [13] E. Melro, L. Alves, F.E. Antunes, B. Medronho, A brief overview on lignin dissolution, J.  
405 Mol. Liq. 265 (2018). doi:10.1016/j.molliq.2018.06.021.
- 406 [14] H. Singh, N. Iyengar, R. Yadav, A. Raj, A.K. Sinha, Facile conversion of levulinic acid to  
407  $\gamma$ -valerolactone using a high surface area magnetically separable Ni/NiO catalyst,  
408 Sustain. Energy Fuels. (2018). doi:10.1039/c8se00274f.
- 409 [15] L. Lomba, B. Giner, I. Bandrés, C. Lafuente, M.R. Pino, Physicochemical properties of  
410 green solvents derived from biomass, Green Chem. (2011). doi:10.1039/c0gc00853b.
- 411 [16] D.W. Rackemann, W.O. Doherty, The conversion of lignocellulosics to levulinic acid,  
412 Biofuels, Bioprod. Biorefining. (2011). doi:10.1002/bbb.267.
- 413 [17] C. CHANG, X. MA, P. CEN, Kinetics of Levulinic Acid Formation from Glucose  
414 Decomposition at High Temperature, Chinese J. Chem. Eng. (2006).  
415 doi:10.1016/s1004-9541(06)60139-0.
- 416 [18] D. Datta, M.E. Marti, D. Pal, S. Kumar, Equilibrium study on the extraction of levulinic  
417 acid from aqueous solution with aliquat 336 dissolved in different diluents: Solvent's  
418 polarity effect and column design, J. Chem. Eng. Data. (2017).  
419 doi:10.1021/acs.jced.6b00164.
- 420 [19] C. Chang, P. Cen, X. Ma, Levulinic acid production from wheat straw, Bioresour.  
421 Technol. (2007). doi:10.1016/j.biortech.2006.03.031.
- 422 [20] M.J. Kamlet, J.L. Abboud, R.W. Taft, The Solvatochromic Comparison Method. 6. The  
423  $\pi^*$  Scale of Solvent Polarities<sup>1</sup>, J. Am. Chem. Soc. (1977). doi:10.1021/ja00460a031.
- 424 [21] D. González-Arjona, G. López-Pérez, M.M. Domínguez, A.G. González,  
425 Solvatochromism: A Comprehensive Project for the Final Year Undergraduate

- 426 Chemistry Laboratory, *J. Lab. Chem. Educ.* (2016). doi:10.5923/j.jlce.20160403.01.
- 427 [22] A. Duval, F. Vilaplana, C. Crestini, M. Lawoko, Solvent screening for the fractionation  
428 of industrial kraft lignin, *Holzforschung*. 70 (2016) 11–20. doi:10.1515/hf-2014-0346.
- 429 [23] T.H. Eberlein, *Essentials of Organic Chemistry: For Students of Pharmacy, Medicinal*  
430 *Chemistry, and Biological Chemistry* (Paul M. Dewick), *J. Chem. Educ.* (2008).  
431 doi:10.1021/ed085p204.
- 432 [24] A.A. Sibirny, *Biotechnology of yeasts and filamentous fungi*, 2017. doi:10.1007/978-3-  
433 319-58829-2.
- 434 [25] E. Melro, A. Filipe, D. Sousa, A.J.M. Valente, A. Romano, F.E. Antunes, B. Medronho,  
435 Dissolution of kraft lignin in alkaline solutions, *Int. J. Biol. Macromol.* (2020).  
436 doi:10.1016/j.ijbiomac.2020.01.153.
- 437 [26] W.J. Cheong, P.W. Carr, Kamlet-Taft  $\pi^*$  Polarizability/Dipolarity of Mixtures of Water  
438 with Various Organic Solvents, *Anal. Chem.* (1988). doi:10.1021/ac00159a018.
- 439 [27] J. Sameni, S. Krigstin, M. Sain, Solubility of Lignin and Acetylated Lignin in Organic  
440 Solvents, *BioResources*. (2017). doi:10.15376/biores.12.1.1548-1565.
- 441 [28] J. Sun, T. Dutta, R. Parthasarathi, K.H. Kim, N. Tolic, R.K. Chu, N.G. Isern, J.R. Cort, B.A.  
442 Simmons, S. Singh, Rapid room temperature solubilization and depolymerization of  
443 polymeric lignin at high loadings, *Green Chem.* (2016). doi:10.1039/c6gc02258h.
- 444 [29] T. Rashid, C.F. Kait, I. Regupathi, T. Murugesan, Dissolution of kraft lignin using Protic  
445 Ionic Liquids and characterization, *Ind. Crops Prod.* (2016).  
446 doi:10.1016/j.indcrop.2016.02.017.
- 447 [30] D. Glas, C. Van Doorslaer, D. Depuydt, F. Liebner, T. Rosenau, K. Binnemans, D.E. De

- 448 Vos, Lignin solubility in non-imidazolium ionic liquids, *J. Chem. Technol. Biotechnol.*  
449 (2015). doi:10.1002/jctb.4492.
- 450 [31] Y. Wang, L. Wei, K. Li, Y. Ma, N. Ma, S. Ding, L. Wang, D. Zhao, B. Yan, W. Wan, Q.  
451 Zhang, X. Wang, J. Wang, H. Li, Lignin dissolution in dialkylimidazolium-based ionic  
452 liquid-water mixtures, *Bioresour. Technol.* (2014).  
453 doi:10.1016/j.biortech.2014.08.020.
- 454 [32] J. Bernardini, P. Cinelli, I. Anguillesi, M.B. Coltelli, A. Lazzeri, Flexible polyurethane  
455 foams green production employing lignin or oxypropylated lignin, *Eur. Polym. J.* 64  
456 (2015) 147–156. doi:10.1016/j.eurpolymj.2014.11.039.
- 457 [33] W. Thielemans, E. Can, S.S. Morye, R.P. Wool, Novel applications of lignin in composite  
458 materials, *J. Appl. Polym. Sci.* (2002). doi:10.1002/app.2247.
- 459 [34] O. Faix, Classification of Lignins from Different Botanical Origins by FT-IR Spectroscopy,  
460 *Holzforschung.* (1991). doi:10.1515/hfsg.1991.45.s1.21.
- 461 [35] Ł. Klapiszewski, T.J. Szalaty, B. Kurc, M. Stanis, B. Zawadzki, A. Skrzypczak, T.  
462 Jesionowski, Development of Acidic Imidazolium Ionic Liquids for Activation of Kraft  
463 Lignin by Controlled Oxidation: Comprehensive Evaluation and Practical Utility,  
464 *Chempluschem.* (2018). doi:10.1002/cplu.201800123.
- 465 [36] A.A.M.A. Nada, M.A. Yousef, K.A. Shaffei, A.M. Salah, Infrared spectroscopy of some  
466 treated lignins, *Polym. Degrad. Stab.* (1998). doi:10.1016/S0141-3910(97)00273-5.
- 467 [37] S. Sathawong, W. Sridach, K.A. Techato, Lignin: Isolation and preparing the lignin  
468 based hydrogel, *J. Environ. Chem. Eng.* (2018). doi:10.1016/j.jece.2018.05.008.
- 469 [38] A. Tawansi, A. El-Khodary, M.M. Abdelnaby, A study of the physical properties of FeCl<sub>3</sub>

470 filled PVA, *Curr. Appl. Phys.* (2005). doi:10.1016/j.cap.2004.06.026.

471 [39] A. Papancea, A.J.M. Valente, S. Patachia, Diffusion and sorption studies of dyes  
472 through PVA cryogel membranes, *J. Appl. Polym. Sci.* (2010). doi:10.1002/app.30983.

473 [40] P.K. Mishra, A. Ekielski, The self-assembly of lignin and its application in nanoparticle  
474 synthesis: A short review, *Nanomaterials.* (2019). doi:10.3390/nano9020243.

475 [41] H. Yoshida, R. Mörck, K.P. Kringstad, H. Hatakeyama, Fractionation of kraft lignin by  
476 successive extraction with organic solvents: II. Thermal properties of kraft lignin  
477 fractions, *Holzforschung.* 41 (1987) 171–176. doi:10.1515/hfsg.1987.41.3.171.

478 [42] R.C. Sun, J. Tomkinson, G. Lloyd Jones, Fractional characterization of ash-AQ lignin by  
479 successive extraction with organic solvents from oil palm EFB fibre, *Polym. Degrad.*  
480 *Stab.* (2000). doi:10.1016/S0141-3910(99)00174-3.

481 [43] A. Tejado, C. Peña, J. Labidi, J.M. Echeverria, I. Mondragon, Physico-chemical  
482 characterization of lignins from different sources for use in phenol-formaldehyde resin  
483 synthesis, *Bioresour. Technol.* (2007). doi:10.1016/j.biortech.2006.05.042.

484 [44] M. Wysokowski, Ł. Klapiszewski, D. Moszyński, P. Bartczak, T. Szatkowski, I. Majchrzak,  
485 K. Siwińska-Stefańska, V. V. Bazhenov, T. Jesionowski, Modification of chitin with kraft  
486 lignin and development of new biosorbents for removal of cadmium(II) and nickel(II)  
487 ions, *Mar. Drugs.* (2014). doi:10.3390/md12042245.

488 [45] Q. Yan, J. Li, J. Zhang, Z. Cai, Thermal decomposition of Kraft Lignin under Gas  
489 atmospheres of argon, hydrogen, and carbon dioxide, *Polymers (Basel).* (2018).  
490 doi:10.3390/polym10070729.

491

492

## Supporting information

493

494 **Table S1**

495 FTIR semiquantitative analysis of initial lignin and regenerated lignins obtained after

496 dissolution in levulinic and formic acid.

Nº	Kraft Lignin		Regenerated lignin			
			Levulinic acid		Formic acid	
	Band	Ax/A1600	Band	Ax/A1600	Band	Ax/A1600
1	Shoulder		1709	1.0284	1712	1.1980
R	1593	1.0000	1593	1.0000	1595	1.000
2	1510	1.4000	1512	1.4102	1510	1.4117
3	1450	1.2761	1453	1.1936	1450	1.2597
4	1423	1.2598	1423	1.1964	1423	1.1419
5	1369	1.0246	1365	1.1297	1365	0.9763
6	1261	1.7415	1265	1.7145	1257	1.6971
7	1211	1.6863	1211	1.6682	1207	1.8733
8	1142	1.7063	1153	1.5187	1153	2.0852
9	1122	1.8015	1126	1.4058	1126	1.9083
10	1080	1.6115	1080	1.2648	1080	1.5233
11	1026	1.9720	1029	1.5989	1026	1.8130
12	852	1.1367	856	1.0691	852	1.2165
13	814	1.2230	814	1.1197	814	1.2725

497

498 **Table S2**

499 FTIR semiquantitative analysis of regenerated lignins previously dissolved in levulinic acid  
 500 aqueous solutions of different concentrations.

Nº	Concentration of aqueous levulinic acid solutions							
	7.75 M		6.98 M		6.03 M		5.17 M	
	Band	Ax/A1600	Band	Ax/A1600	Band	Ax/A1600	Band	Ax/A1600
1	1705	0.7560	1705	0.7039	1705	0.6920	1705	0.6752
R	1593	1.0000	1593	1.0000	1593	1.0000	1593	1.0000
2	1512	1.3896	1512	1.5545	1512	1.4660	1512	1.4776
3	1454	1.2140	1454	1.2633	1454	1.2369	1454	1.2427
4	1423	1.1710	1423	1.2022	1423	1.1834	1423	1.1771
5	1365	1.0415	1365	1.0477	1365	1.0338	1365	1.0251
6	1265	1.69808	1265	1.9444	1265	1.8308	1265	1.8519
7	1212	1.6611	1212	1.8605	1212	1.7822	1212	1.7659
8	1142	1.4671	1142	1.5618	1142	1.5233	1142	1.4932
9	1126	1.4557	1126	1.5240	1126	1.5059	1126	1.4682
10	1080	1.3050	1080	1.3409	1080	1.3432	1080	1.3061
11	1030	1.6658	1030	1.8235	1030	1.7837	1030	1.7562
12	852	1.1362	852	1.0803	852	1.1014	852	1.0806
13	814	1.2062	814	1.1594	814	1.1882	814	1.1594

501

502