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1 Aqueous organic solvent fractionation as means to improve lignin
2 homogeneity and purity

3

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6

7 Abstract

8 Lignin's heterogeneous polymeric structure limit its utilisation in further processing for
9 high-value applications. This paper describes a protocol for kraft lignin precipitation
10 fractionation by water addition from aqueous ethanol, acetone or propyleneglycol
11 monomethyl ether. The solvent-insoluble fractions possessed high molar mass, high
12 polydispersity, high nitrogen and low sulphur content. Also lignin aggregation was
13 observed when acetone was used. The molar mass of the precipitated fractions
14 depended on the amount of water added in the precipitation step. The highly soluble
15 lignin fractions possessed more carboxylic acid groups, higher amount of sulphur and
16 more carbohydrates than other lignin fractions. The presented protocol is simple and
17 easily up-scalable and tunable to fractionate lignin with green solvents when constant
18 quality, high purity or high reactivity are needed.

19 Keywords

20 Kraft lignin; fractionation; molar mass; ethanol; acetone; propyleneglycol monomethyl
21 ether

22 1. Introduction

23 Lignin is the second most abundant natural polymer after cellulose and it composes of
24 ca. 20-30% of wood and most other lignocellulosic biomasses (Boerjan et al., 2003;

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25 Ragauskas et al., 2014). Lignin is considered as the most promising aromatic raw
26 material to replace petrochemical-based feedstocks (Ragauskas et al., 2014). Currently,
27 worldwide chemical wood pulping industry produces ca. 70 Mt of lignin which is
28 mostly incinerated to generate energy. Novel technological solutions provide means to
29 recover part of lignin from the existing process streams without impeding the energy or
30 chemical balances of the mills (Tomani, 2010). In addition to pulping industry also
31 lignocellulosic ethanol production is expected to produce another 62 million tons of
32 lignin as side streams by 2022 (Ragauskas et al., 2014) These volumes illustrate the
33 high availability of technical lignins, and it is expected that lignin will become a
34 commercially relevant feedstock for a range of materials (Gellerstedt, 2015; Ragauskas
35 et al., 2014).

36 Lignin is composed mostly of three types of phenyl propane units, i.e. p-hydroxyphenyl
37 (H), guaiacyl (G) and syringyl (S) units, which differ by the number of methoxyl groups
38 attached on the aromatic ring. H units have no methoxyl groups, G units possess one
39 methoxyl group and S units possess two methoxyl groups attached on the aromatic ring.
40 The relative content of these units depend mostly of plant species, as softwood lignin is
41 composed mostly of G and some H units, hardwood lignin contains both G and S units
42 and minor amount of H units and herbaceous lignins contain all three units in
43 remarkable quantities (Vanholme et al., 2010). The phenyl propane units in lignin are
44 interlinked via different, mostly ether, linkages (Boerjan et al., 2003). There is
45 significant variation in lignin interunit linkages within trees and even cell wall layers
46 (Vanholme et al., 2010) which indicates that lignin is inherently heterogeneous
47 polymer. Furthermore, in chemical pulping processes the heterogeneity is increased due
48 to incomplete impregnation of the chemicals in the feedstock. The heterogeneity is a
49 challenge when lignin is used in material applications where constant molecular size,

50 functionality and reactivity are required (Chatterjee and Saito, 2015; Gellerstedt, 2015;
51 Norberg et al., 2013; Teng et al., 2013).

52 Ultrafiltration (Brodin et al., 2009; Norgren, Magnus, 2000; Sevastyanova et al., 2014;
53 Toledano et al., 2010; Toledano et al., 2010), solvent fractionation (Boeriu et al., 2014;
54 Cui et al., 2014; Duval et al., 2015; Li and McDonald, 2014; Lovell and Hibbert, 1941;
55 Mörck et al., 1986; Ni, Y., Hu, 1995; Ropponen et al., 2011; Sadeghifar and
56 Argyropoulos, 2016) and their combinations (Helander et al., 2013) are potential
57 techniques to decrease the heterogeneity of lignin isolates. Ultrafiltration provides an
58 efficient method to control the molar mass distribution of lignin by the selection of
59 membranes with suitable cut-offs (Brodin et al., 2009; Sevastyanova et al., 2014;
60 Toledano et al., 2010). A major advantage of this method is that the technology can be
61 applied directly to cooking liquor at pulp mill without a need to adjust pH or
62 temperature (Sevastyanova et al., 2014). On the other hand, the poor solubility of some
63 lignins (e.g. hydrolysis lignin from ethanol production plant), fouling of the membranes
64 and expensive instrumentation are major limitations for ultrafiltration.

65 Solvent fractionation is based on partial solubility of polymers into solvents. Several
66 solvent fractionation methods have been developed to produce polymer fractions with
67 narrow distribution of molar mass, branching or chemical composition (Francuskiewicz,
68 1994). Solvent fractionation of lignin can be performed either by selective dissolution of
69 solid lignin or selective precipitation of dissolved lignin. In the pioneering work by
70 Lovell and Hibbert (1941), lignin was first dissolved in methanol followed by
71 fractionation using two immiscible solvents, carbon tetrachloride and chloroform. Later,
72 Mörck et al. (1986) developed a sequential fractionation process using dichloromethane
73 (DCM), isopropanol, methanol and methanol-DCM mixture to extract lignin fractions.

74 Similar strategies have been implemented over the years and the methods are based on
75 organic solvents such as DCM, isopropanol, methanol, ethanol, acetone, diethyl ether,
76 dioxane, tetrahydrofuran, butanone and hexane as pure solvents or as mixtures.
77 (Arshanitsa et al., 2013; Dodd et al., 2015; Duval et al., 2015; Jiang et al., 2017; Li and
78 McDonald, 2014; Ni, Y., Hu, 1995; Passoni et al., 2016; Ropponen et al., 2011)
79 However, most of these solvents are classified as problematic or even hazardous (Prat et
80 al., 2016) and therefore cannot be considered as green or safe options in lignin
81 fractionation.

82 A fractional precipitation fractionation scheme for lignin was first proposed by Cui et
83 al. (2014) who dissolved kraft lignin in acetone and then added hexane gradually to
84 precipitate lignin fractions from the solution. Mixing two miscible solvents allowed the
85 flexible manipulation of the yield and molecular composition of each lignin fraction and
86 hence provided an attractive approach for lignin fractionation. A similar approach was
87 applied by Sadeghifar et al (2017), who dissolved organosolv lignin into aqueous
88 acetone followed by controlled lignin precipitation fractionation with water addition.

89 In this paper, we demonstrate a solvent fractionation method to separate kraft lignin in
90 homogeneous fractions using aqueous solutions of ethanol, acetone or propyleneglycol
91 monomethyl ether (PGME). The lignin precipitation fractionation was performed by
92 first dissolving lignin in aqueous solvent followed by addition of water to controlled
93 precipitation of lignin. The chemical structures of the produced lignin fractions were
94 characterised to assess the performance of the process. This fractional precipitation
95 procedure provides an easily controllable process to manipulate the yield and structural
96 composition of produced lignin fractions without the use of harmful or hazardous
97 solvents or expensive instrumentation.

98 2. Materials and Methods

99

100 2.1. Kraft lignin and its characterization

101 Dry softwood kraft lignin (dry matter 95%) was an industrial kraft lignin precipitated
102 from softwood black liquor and kindly gifted by Metsä Fibre. Klason lignin content was
103 determined gravimetrically after acid hydrolysis of the sample (Allsopp and Misra,
104 1940), and the hydrolysate was analysed to determine the acid soluble lignin using UV
105 spectroscopy (Goldschmid, 1971) and carbohydrates using HPAEC-PAD (Tenkanen
106 and Siika-aho, 2000).

107 Elemental analysis (C, H, N and S) was determined from 20-30 mg of ground and dried
108 (105°C for overnight) using FLASH 2000 series elemental analyzer.

109 UV absorption coefficient for the unfractionated kraft lignin was determined by
110 dissolving 13.5 mg of lignin (o.d.) in 1000 ml NaOH solution (0.1M) at room
111 temperature. The absorbance at 280 nm (0.350 ± 0.020) designates the absorptivity value
112 of $25.9 \text{ l} \cdot \text{g}^{-1} \cdot \text{cm}^{-1}$, which was applied to determine the concentration of dissolved lignin.

113 The molar mass distribution was defined by dissolving lignin in 0.1M NaOH solution at
114 room temperature followed by size exclusion chromatography using UV detection at
115 280 nm (Baumberger et al., 2007). The molar mass calculations were performed based
116 on external calibration of the method using polystyrene sulphonate standards.

117 The number of hydroxyl groups were determined with ^{31}P NMR spectroscopy by using
118 the procedure by Granata and Argyropoulos (Granata and Argyropoulos, 1995) using a
119 Bruker 500 MHz spectrometer. 1024 scans with pulse delay of 5 s, 90° pulse, line
120 broadening of 2 and default baseline correction were used in spectral collection. The
121 quantification limits applied were 150-145 ppm for aliphatic OH groups, 145-140.5

122 ppm for 3 and 5-substituted phenolic OH groups, 140.5-138.5 ppm for guaiacylic OH
123 groups, 138.5-137 ppm for p-hydroxyphenyl groups and 136-134 ppm for carboxylic
124 acid groups.

125 2.2. Solvent fractionation of lignin

126 Lignin fractionation followed the scheme in Fig. 1: 10 g (o.d.) of kraft lignin was mixed
127 with 100 ml of aqueous ethanol (80 % by volume), acetone (60% by volume) or PGME
128 (60% by volume) solution. The dispersion was mixed in an Erlenmeyer flask under
129 magnetic stirring for 20 minutes at room temperature. The solution was centrifuged for
130 20 minutes and the supernatant was recovered. The insoluble lignin fraction was washed
131 twice with aqueous solvent of same concentration, dried (in vacuum at 40°C for 16-72
132 hours) and weighed.

133 A predefined volume of supernatant from the first fractionation stage was placed in
134 Erlenmeyer flask followed by water addition to reach the desired solvent concentration
135 (70% for ethanol and 50% for acetone or PGME). This solution was mixed for 20
136 minutes to allow lignin to precipitate followed by centrifugation and recovering the
137 supernatant. The precipitate was washed twice with aqueous solvent, dried (40°C
138 vacuum) and weighed. Again, a predefined volume of supernatant was replaced in
139 Erlenmeyer flask followed by water addition to precipitate a new fraction of lignin.
140 These steps were repeated until solvent concentration of 50% was reached. At this stage
141 the lignin concentration was so low that the precipitation fractionation was not practical
142 to continue further. A new fractionation sequence was started by mixing 10 g of lignin
143 with aqueous solvent (50% by volume) and repeating the fractionation as explained
144 above. This way, the solvent volumes and lignin concentrations remained at practical

145 level until solvent concentration of 10%. The last lignin fraction was recovered from
146 this solution by evaporating the solvent under vacuum at 40°C.

147 3. Results and discussion

148

149 3.1. Mass balances of lignin fractionation

150 The principle of precipitation fractionation is to dissolve the polymer in a solvent
151 followed by addition of nonsolvent to precipitate fractions with narrow molar mass
152 distribution (Francuskiewicz, 1994). Since lignin has high solubility in aqueous ethanol,
153 acetone and PGME (Jääskeläinen et al., 2016), these three organic solvents were
154 selected as fractionation media and water was applied as nonsolvent. The fractionation
155 was initiated by first dissolving lignin as completely as possible but still close to the
156 tipping point where small increase in water content results in significant precipitation of
157 lignin. As was defined by the solubility tests earlier (Jääskeläinen et al., 2016), the
158 optimal solvent concentration was 80% for ethanol and 60 % for acetone and PGME for
159 this softwood kraft lignin, whereas lignin solubility in pure ethanol or acetone were
160 lower. For PGME, a nearly quantitative dissolution was observed at water content of 0-
161 40% (Jääskeläinen et al., 2016) indicating that this solvent provides a potential
162 alternative to dissolve technical lignins with limited solubility in ethanol or acetone.

163 The insoluble lignin fraction composed of 32%, 16% and 0.8% of total lignin in ethanol
164 (80%), acetone (60%) and PGME (60%) processes, respectively, as is illustrated Fig. 2.

165 Addition of water, i.e. decreasing the solvent concentration, resulted in lignin
166 precipitation and thus lignin fractionation. In the ethanol-based process, relatively low
167 amount of lignin was precipitated in each step, whereas in acetone or PGME-based
168 processes the yield of two first precipitated fractions covered 24-37% of total lignin

169 each. This indicates that acetone and PGME-based processes were more sensitive to
170 solvent concentration than ethanol-based process.

171 At solvent concentrations of ca. 20% lignin precipitation levelled off as further addition
172 of water resulted in only negligible precipitation of lignin. Therefore, the last fractions
173 were recovered by evaporating the aqueous solvent and the yield of these fractions were
174 9-13% on original lignin.

175 3.2. Molar mass

176 The solvent fractionation separated lignin into fractions mostly based on the molar
177 mass, as illustrated in Fig.3. In ethanol and acetone-based fractionations, the insoluble
178 fraction possessed significantly higher molar mass and polydispersity than the
179 unfractionated lignin. However, in the PGME-based process, the insoluble fraction
180 possessed nearly the same molar mass as the unfractionated lignin. However, this
181 fraction possessed only less than 1% of the total unfractionated lignin.

182 The acetone-insoluble (60% ins) fraction possessed unexpectedly high molar mass and
183 very high polydispersity (Fig. 3. and Table 1). Similar observation was not made in
184 aqueous acetone fractionation for other types of technical lignins (Sadeghifar et al.,
185 2017). It is likely that in this sample, lignin was aggregated since aggregation is known
186 to take place in lignin solutions (Mantler et al., 1984). The formed lignin aggregates did
187 not disaggregate when lignin was dissolved in 0.1M sodium hydroxide solution at room
188 temperature for molar mass determination. However, heating lignin at 80°C in dilute
189 alkaline conditions decreased the molar mass (Supplement information, S1), which
190 supports the theory for aggregate formation in acetone-containing solution and their
191 partial disruption under alkaline conditions. This result agrees with the knowledge that

192 the dissociation takes place in alkaline solutions at low concentrations but only very
193 slowly (Mantler et al., 1984). Interestingly, no aggregation was observed in other
194 fractionation processes, but only in the acetone-based fractionations. The mechanism of
195 the lignin aggregation is proposed to be π - π stacking (Deng et al., 2011; Mantler et al.,
196 1984) and was also recently observed in pure acetone fractionation (Sadeghifar and
197 Argyropoulos, 2016). In organic media, alkali lignin forms a sandwich-type head-to-tail
198 stacking (J-aggregates) and these aggregates are reversible and can be disaggregated
199 e.g. by addition of iodine which forms lignin-iodine charge-transfer complexes that
200 cannot form novel π - π stacks (Deng et al., 2011). In addition, the disaggregation takes
201 place slowly in alkaline solutions at low lignin concentrations (Mantler et al., 1984). In
202 practice, the formation of aggregates affects lignin utilisation due to lowered solubility
203 and reactivity and in most applications has a negative impact on lignin utilisation.

204 The average molar mass was the lower the lower was the solvent concentration in the
205 precipitation step (Table 1). In general, the precipitated lignin possessed lower
206 polydispersity than the unfractionated lignin or the insoluble lignin fraction. Therefore
207 this protocol provides a method to produce a lignin fraction with desired molar mass
208 and low polydispersity by tuning the solvent concentration in the precipitation step. In
209 the last fractionation steps, the soluble lignin had weight average molar mass of ca.
210 1500 g/mol, which corresponds to lignin with ca. 8 monomeric units. However, this
211 degree of polymerisation is indicative only, since the size exclusion chromatography
212 was calibrated using polystyrene sulphonates and does not correlate exactly with the
213 molar mass of lignin in this range (Baumberger et al., 2007).

214 3.3. Elemental composition of lignin fractions

215 Elemental compositions of the lignin samples reflect their chemical compositions. The
216 carbon contents of the insoluble fractions from the first and last stages were lower than
217 that of unfractionated lignin, whereas the selected middle fractions possessed higher
218 proportions of carbon (Table 2). This result indicates that carbohydrates, which have
219 much lower carbon content than lignin, are enriched in both high and low molar mass
220 fractions. According to literature (Duval et al., 2015) the lignin fractions with high
221 molar mass contain more carbohydrates than the unfractionated lignin. These
222 carbohydrates were proposed to be covalently linked with lignin (Duval et al., 2015).
223 The high content of carbohydrates in the low molar mass fractions were confirmed by
224 lignin compositional analysis (Table 3).

225 Sulphur accumulated in the low molar mass fractions (Table 2). This result is consistent
226 with other fractionation studies, which have illustrated that the sulphur content in the
227 low molar mass lignin fraction is much higher than in the high molar mass fractions
228 (Dodd et al., 2015; Sevastyanova et al., 2014).

229 Nitrogen was present in the initial lignin in only minute content, which is a typical level
230 for kraft lignin (Tomani, 2010). Nitrogen originates most likely from the wood cell
231 proteins. Interestingly, most of nitrogen retained in the insoluble fraction which is
232 logical due to large polymeric size and low solubility of proteins.

233 3.4. Chemical composition of lignin fractions

234 Klason and acid-soluble lignin content is the most common method to define the total
235 lignin content in a sample. The unfractionated kraft lignin revealed Klason lignin and
236 acid-soluble lignin contents of 92.3% and 2.5%, respectively, which are typical values

237 for kraft lignin which is precipitated from black liquor using CO₂ followed by acid wash
238 (Brodin et al., 2009; Sevastyanova et al., 2014; Tomani, 2010).

239 The Klason lignin contents of the low molar mass fractions (10% sol) were only 57-
240 67% on lignin (Table 3) which are very low when compared to typical values published
241 for kraft lignin in literature (> 90 %) (Brodin et al., 2009; Duval et al., 2015; Fang et al.,
242 2015; Helander et al., 2013; Li and McDonald, 2014; Sevastyanova et al., 2014). These
243 lignins contained also extremely high proportions of acid-soluble lignin (16-21%)
244 which are much higher than any corresponding values found in literature for kraft
245 lignin. The highest acid-soluble lignin content reported for kraft lignin was 9.6%, and
246 this was a kraft lignin fraction obtained by ethyl acetate extraction (Duval et al., 2015).
247 Otherwise, typical kraft lignin fractions contain only 2-6% of acid soluble lignin.
248 (Brodin et al., 2009; Fang et al., 2015; Helander et al., 2013; Li and McDonald, 2014;
249 Sevastyanova et al., 2014)

250 The carbohydrate content of the unfractionated lignin was 1.1% which is a typical value
251 for kraft lignin, although at the low side of the ordinary range (Tomani, 2010). The most
252 soluble lignin contained surprisingly high amount of carbohydrates indicating the
253 accumulation of carbohydrates in this fraction (Table 3). This result was unexpected,
254 since it has been published by several authors (Duval et al., 2015; Mörck et al., 1986;
255 Ropponen et al., 2011), that in other fractionation processes the carbohydrates are
256 accumulated in the high molar mass lignin fraction.

257 The carbohydrate compositions in Table 4 reveal that the highly soluble lignin was
258 enriched in galactose which is the most common carbohydrate covalently bound to
259 softwood kraft lignin (Hortling et al., 2001).

260 3.5. Functional groups

261 The number of hydroxyl groups in aliphatic, phenolic and carboxylic acid moieties was
262 determined using ^{31}P NMR spectroscopy after derivatising the hydroxyl groups in the
263 lignin samples with phosphorus-containing reagent. The NMR spectral shifts allow the
264 differentiation of hydroxyl groups, namely aliphatic and aromatic hydroxyl groups and
265 carboxylic acid groups (Granata and Argyropoulos, 1995) (Fig. 4). In addition, the
266 different substitution pattern of the aromatic moieties (syringyl and condensed
267 guaiacylic units, guaiacylic units and p-hydroxyphenyl units) are separated and they can
268 all be quantified based on their chemical shifts (Granata and Argyropoulos, 1995).
269 However, the poor solubility of selected kraft lignin fractions in DMSO restricted the
270 analysis of the acetone (60%) and PGME (60%) insoluble fractions.

271 The ^{31}P NMR spectra of the lignin fractions from ethanol, acetone and PGME-based
272 fractionations are shown in Fig. 4. It can be seen that the spectra from ethanol and
273 PGME-based processes additional narrow bands occurred at 146-147 and 145-146 ppm,
274 respectively, which are not present in other samples. These bands correspond to the
275 shifts of phosphorylated alcohol groups in ethanol (146.3 ppm (Pu et al., 2011)) and
276 PGME and therefore it is obvious that they originate from residual solvent present in the
277 fractionated lignin despite of sample drying at 40°C vacuum oven for at least 16 hours.
278 The thermal desorption test of the lignin fractions (Kalliola et al., 2012) revealed, that
279 the residual solvent was trapped in the lignin and was not removed even by heating the
280 sample to 150°C (Supplement information S2).

281 The solvent was not covalently linked, since the solvent-originating free hydroxyl group
282 could be observed in the ^{31}P NMR spectra, which would not be present if the alcohol

283 would be etherified in lignin. Therefore it is likely that the solvent was adsorbed to
284 lignin with physical interactions that restricted its evaporation during heating.

285 The residual ethanol and PGME contents in the samples were quantified by integrating
286 these solvent bands in the ^{31}P NMR spectra (Table 5). The residual solvent content
287 varied between 1.3 and 5.0% for ethanol and 7.2 and 7.8% for PGME-based samples.
288 The higher PGME content compared to ethanol could be explained by its higher boiling
289 point, but otherwise no clear trend in solvent concentrations as function of the
290 fractionation process could be assessed. The content of residual acetone in the samples
291 from the acetone-based processes cannot be measured by this ^{31}P NMR spectroscopic
292 method due to the lack of hydroxyl groups in acetone.

293 The aliphatic hydroxyl groups in the lignin samples originate either from free hydroxyl
294 groups in the side chain of the phenylpropane units or any residual carbohydrates in the
295 sample. No clear trends in the content of aliphatic hydroxyl groups could be observed
296 (Table 5), except that in the low molar mass fractions (10% sol) the number of aliphatic
297 hydroxyl groups was high. This agrees with the high content of carbohydrates in these
298 samples. On the other hand, this result does not agree with other fractionation studies, in
299 which low molar mass lignin fractions have been found to possess less aliphatic
300 hydroxyl groups than lignin with higher molar mass (Cui et al., 2014; Sadeghifar et al.,
301 2017) .

302 The phenolic hydroxyl groups in lignin can be classified based on the aromatic
303 substitution of the phenolic units. The amount of syringyl units is low by nature in
304 softwood lignin and therefore the spectral range that corresponds to 3,5-disubstituted
305 units originate mostly from condensed phenolic units. The value for kraft lignin (1.20
306 mmol/g) is at the same range that has been published for residual kraft lignin earlier

307 (Jääskeläinen et al., 2003). In the ethanol-based fractionation these units were highest in
308 the insoluble residue and lowest in the most water-soluble fraction. Surprisingly, this
309 trend could not be observed for acetone or PGME fractionations.

310 Guaiacyl-type of phenols are the most prominent phenolic unit in softwood lignin. The
311 content of free phenolic guaiacyl units increased steadily as the fractionation proceeded
312 (Table 5). The most soluble lignin fractions contained significantly higher amount of
313 guaiacylic phenols than other lignin fractions. This result is logical as the molar mass of
314 lignin in these samples was also remarkably lower. When lignin is depolymerised by the
315 cleavage of β -aryl ether linkage, the most common interunit linkage in lignin, the molar
316 mass is reduced and a novel phenolic hydroxyl group is introduced. Hence, the lower
317 the molar mass, the higher the number of phenolic hydroxyl groups. This correlation is
318 also visualised graphically in Fig. 5 which summarises the relation between the weight
319 average molar mass and the number of guaiacylic hydroxyl groups in lignin. This
320 correlation is similar as has been observed with other lignin fractionation processes (Cui
321 et al., 2014).

322 The number of carboxylic acid structures was the highest in the last fractions which also
323 supports the high solubility of these fractions aqueous systems with high water content.
324 The result is consistent with the solvent process by Cui et al. (2014) who also illustrated
325 that the low-molar mass fractions contain a high number of phenolic hydroxyl groups
326 and carboxylic acid moieties. On the other hand, this result is clearly different than has
327 been obtained by ultrafiltration, where the content of carboxylic acid groups was not
328 affected by fractionation, i.e. the amount of carboxylic acid groups was nearly constant
329 in each lignin fractions regardless of the molar mass (Sevastyanova et al., 2014).

330 4. Conclusions

331 The proposed lignin precipitation fractionation scheme is based on the use of safe green
332 solvents. The aqueous solvent protocol allows the fractionation of wet lignin, which is
333 typical when lignin is recovered from an industrial source. In addition, the chemical
334 recovery and recycling of one organic solvent simple when compared to fractionation
335 processes that utilise several organic solvents. The gradient mixing of the solvents
336 enables an easy tuning of the process and the number of precipitation steps can be freely
337 selected depending on the purity, molar mass and solubility requirements set for the
338 final lignin product. The paper describes a selection of three different solvents which all
339 produced lignin fractions with similar properties.

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479

Figure captions

Fig. 1. Schematic description of the aqueous ethanol solvent fractionation. The same principle was applied for aqueous acetone and aqueous PGME fractionations, except that lignin was dissolved directly in 60% solvent concentration.

Fig. 2. Yield of solid (insoluble or precipitated) lignin fraction from ethanol, acetone and PGME processes. * denotes the lignin recovered from the solution after solvent evaporation.

Fig. 3. Molar mass distributions of precipitated lignin fractions. The green curve denotes the molar mass distribution of the unfractionated kraft lignin.

Fig. 4. ^{31}P -NMR spectra of initial kraft lignin, and lignin fractionated with ethanol, acetone and PGME. The asterisks denote the residual solvent observed in the aliphatic range of the spectra.

Fig. 5. Correlation between the molar mass and the number of guaiacylic hydroxyl groups in the unfractionated lignin and in lignins fractionated with aqueous ethanol, acetone and PGME.

Table 1. Number average and weight average molar mass and polydispersities of lignins from different fractionation steps.

	M_n (g/mol)	M_w (g/mol)	PDI
Kraft lignin	2100	4100	1.98
Ethanol			
80% ins	3000	7600	2.54
70% prec	3600	5300	1.48
60% prec	3000	4300	1.41
50% prec	2400	3300	1.38
40% prec	2000	2800	1.40
30% prec	1700	2200	1.33
20% prec	1500	2000	1.32
10% prec	1500	2000	1.34
10% sol	1100	1500	1.36
Acetone			
60% ins	3400 ^a	18900 ^a	5.62 ^a
50% prec	3000	6000	1.97
40% prec	2300	3500	1.55
30% prec	1800	2700	1.46
20% prec	1600	2300	1.41
10% prec	1500	2100	1.40
10% sol	1100	1600	1.44
PGME			
60% ins	1900	4300	2.24
50% prec	2900	6700	2.31
40% prec	2400	3900	1.66
30% prec	2000	2800	1.45
20% prec	1700	2400	1.42
10% prec	1600	2200	1.40
10% sol	1200	1700	1.43

^a aggregation of lignin

Table 2. Carbon, hydrogen, nitrogen and sulphur composition of selected lignin fractions.

	Carbon, %	Hydrogen, %	Nitrogen, %	Sulphur, %
Kraft lignin	65.0	5.7	0.12	1.62
Ethanol				
80% ins	64.3	5.7	0.15	1.48
50% prec	68.1	5.9	0.14	1.63
10% sol	58.9	6.2	0.08	2.88
Acetone				
60% ins	56.0	6.1	0.33	0.74
50% prec	66.4	5.8	0.14	1.45
10% sol	63.9	6.0	0.12	1.59
PGME				
60% ins	59.7	6.1	0.43	1.10
50% prec	65.9	5.9	0.12	1.35
10% sol	59.1	5.9	0.09	2.75

Table 3. Klason lignin, acid-soluble lignin and carbohydrate content of the most soluble lignin fractions.

	Klason lignin, %	Acid soluble lignin, %	Carbohydrates, %
Kraft lignin	92.3	2.5	1.1
Ethanol 10% sol	57.0	20.5	5.7
Acetone 10% sol	64.4	16.9	6.1
PGME 10% sol	67.1	15.6	5.3

Table 4. Carbohydrate content (% on lignin fraction) and composition (% on total carbohydrates, in parenthesis) in unfractionated kraft lignin and in selected lignin fractions. Ara = arabinose, Gal = galactose, Glu = glucose, Xyl = xylose, Man = mannose.

	Ara, %	Gal, %	Glu, %	Xyl, %	Man, %
Kraft lignin	0.2 (18%)	0.3 (27%)	0.1 (9%)	0.3 (27%)	<0.1 (9%)
Ethanol 10% sol	1.00 (18%)	2.42 (42%)	0.25 (4%)	1.64 (29%)	0.15 (3%)
Acetone 10% sol	0.99 (16%)	2.89 (47%)	0.26 (4%)	1.60 (26%)	0.16 (3%)
PGME 10% sol	0.86 (16%)	2.55 (48%)	0.21 (4%)	1.39 (26%)	0.12 (2%)

Table 5. Number of aliphatic and phenolic hydroxyl groups and carboxylic acids in selected lignin fractions. Cond PhOH = free phenols in condensed syringyl units; G-PhOH = free phenols in guaiacylic structures and p-PhOH = free phenols in *para*-hydroxyphenyl structures and COOH = carboxylic acids.

	Solvent %	Aliph OH mmol/g	Tot PhOH mmol/g	Cond PhOH, mmol/g	G-PhOH, mmol/g	<i>p</i> -PhOH, mmol/g	COOH, mmol/g
Kraft lignin	-	1.17	2.76	1.20	1.39	0.17	0.28
Ethanol							
80% ins	3.8	1.85	3.43	1.69	1.49	0.25	0.33
70% prec	1.8	1.50	2.75	1.36	1.24	0.16	0.20
60% prec	1.7	1.40	2.53	1.20	1.16	0.17	0.23
50% prec	1.3	1.29	2.82	1.26	1.40	0.17	0.29
40% prec	1.6	1.37	3.01	1.26	1.56	0.18	0.37
30% prec	5.0	2.09	2.94	1.08	1.70	0.16s	0.40
10% sol	1.6	2.22	4.05	1.05	2.72	0.28	0.71
Acetone							
60% ins	is	is	is	is	is	is	is
50% prec	-	1.28	2.62	1.24	1.21	0.17	0.26
40% prec	-	1.13	2.94	1.30	1.46	0.18	0.32
30% prec	-	1.06	2.87	1.17	1.53	0.18	0.33
10% sol	-	2.25	4.04	1.21	2.52	0.32	0.63
PGME							
60% ins	is	is	is	is	is	is	is
50% prec	7.3	1.97	2.33	1.10	1.09	0.13	0.20
40% prec	7.2	1.86	2.63	1.18	1.30	0.15	0.24
30% prec	7.8	1.88	2.74	1.14	1.41	0.18	0.29
10% sol	4.0	1.89	3.95	1.21	2.43	0.31	0.56

Figure 1

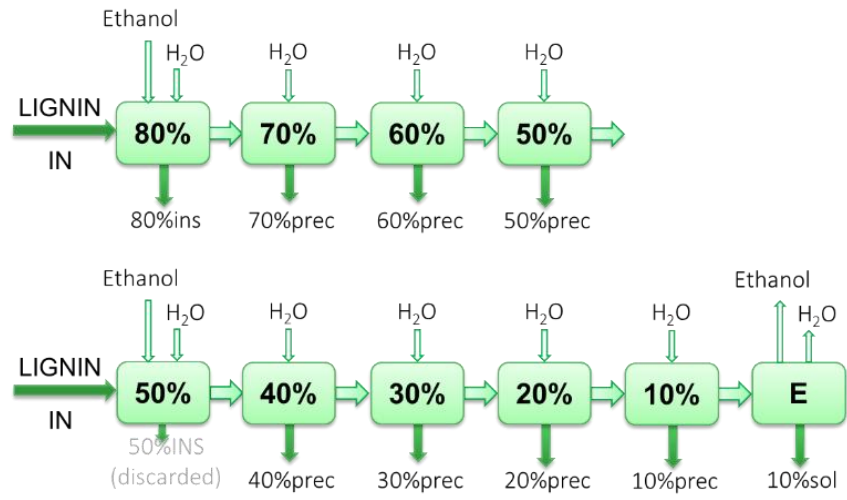


Fig. 1.

Figure 2

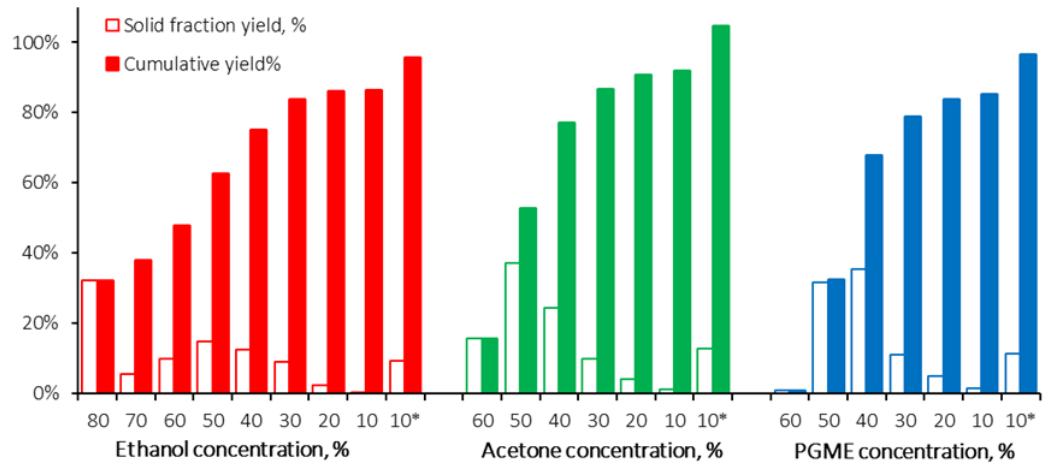


Fig 2.

Figure 3

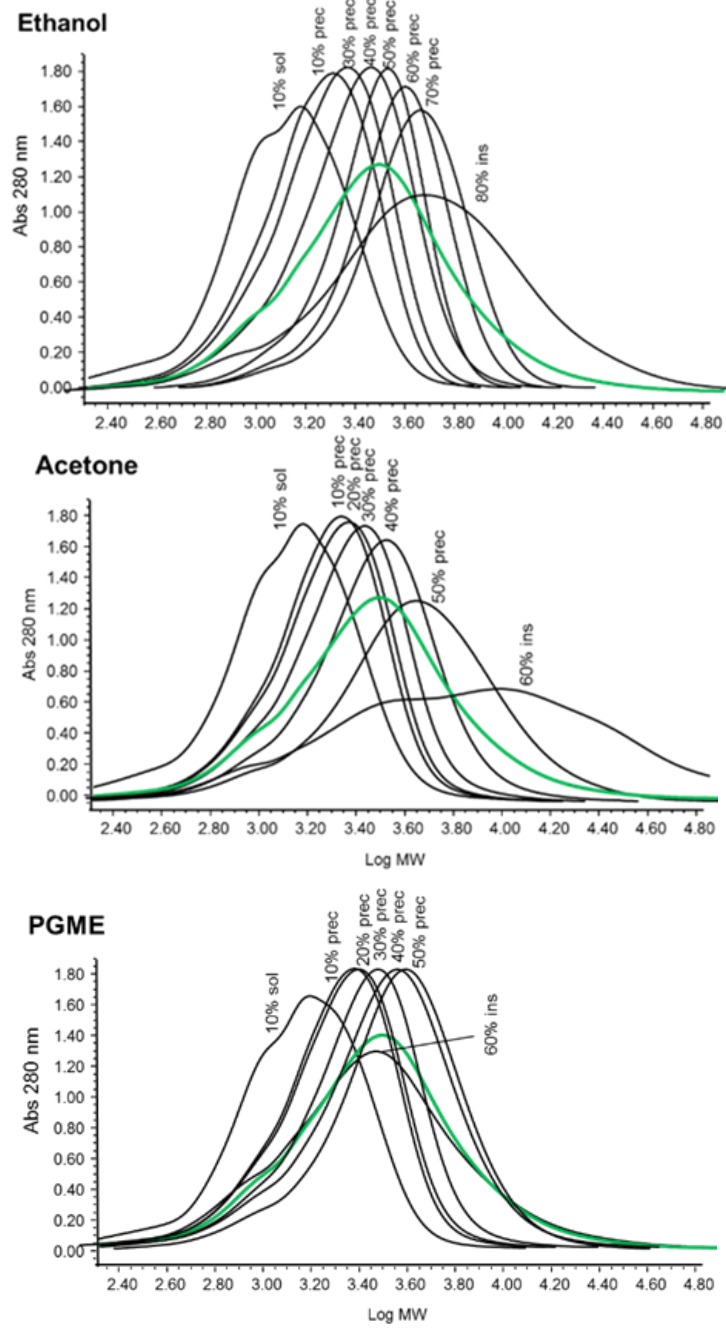


Fig. 3

Figure 4

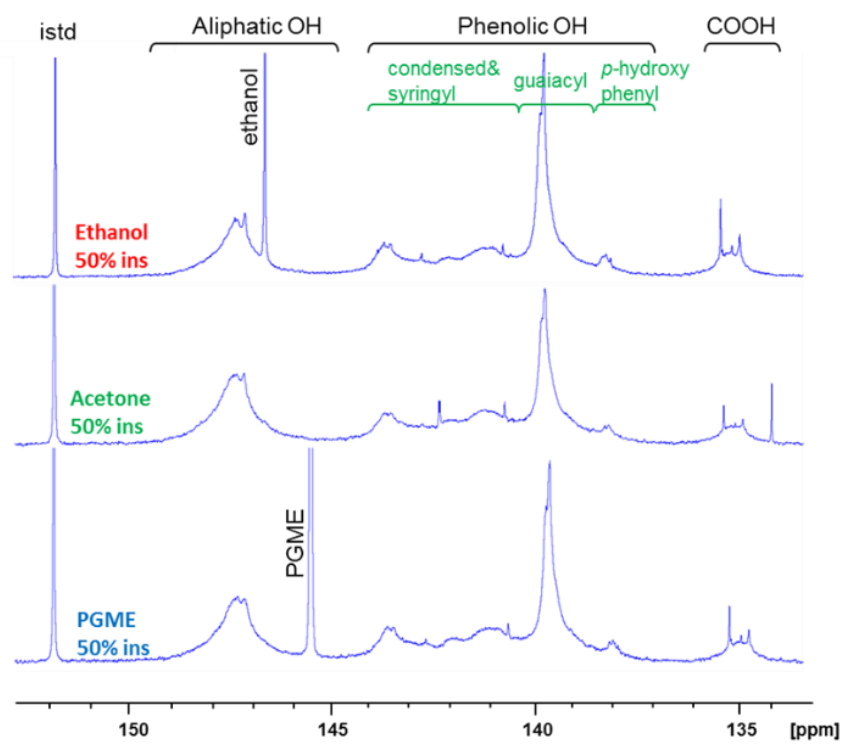


Fig 4.

Figure 5

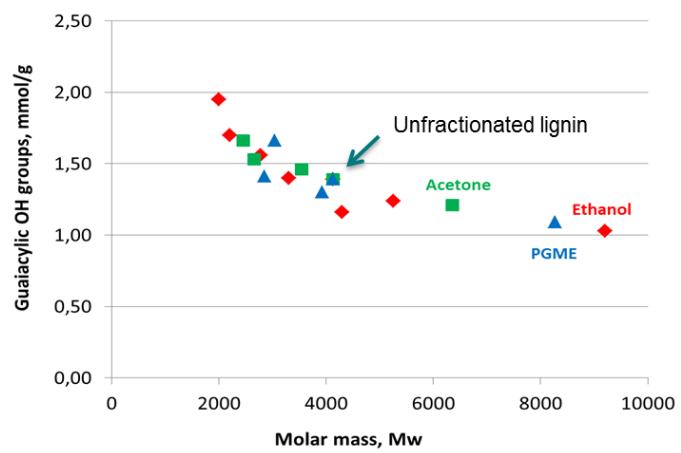


Fig 5