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# Filament spinning of unbleached birch kraft pulps: Effect of pulping intensity on the processability and the fiber properties

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## Highlights

- Man-made fibres were spun from low refined kraft pulps.
- E-beam as dry, non-chemical treatment was used for DP adjustment of lignocellulose.
- The effect of the chemical compositions on the spinnability is only minor.
- The spinnability is mainly dependent on the molecular integrity of lignocellulose matrix.

**ABSTRACT** Man-made lignocellulosic fibres were successfully prepared from unbleached birch kraft pulps by using the IONCELL-F technology. Pulps with different lignin content were produced by tailored kraft pulping with varying intensity. The degree of polymerization of the pulps was adjusted by acid-catalyzed hydrolysis and electron beam treatment. All substrates were completely soluble in 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]OAc) and the respective solutions were spinnable to yield fibres with good to excellent mechanical properties despite the use of only mildly refined wood pulp. The tensile properties decreased gradually as the lignin concentration in the fibres increased. Changes in the chemical composition also affected the structure and morphology of the fibres. Both the molecular orientation and the crystallinity decreased while the presence of lignin enhanced the water accessibility. The effects of the crystallite size and lignin content on monolayer water adsorption are discussed.

**Keywords:** Lignocellulose, fibres, refining, spinning, ionic liquid.

## 36 1. INTRODUCTION

37 The global demand of textile fibres is gradually increasing in response to the global megatrends  
38 such as population and prosperity growth in combination with sustainability thinking and the  
39 limited increase in the production capacities of cotton. Thus, more man-made cellulosic fibres  
40 (MMCFs) are potentially needed to fill the ‘fibre demand gap’ in the future (Hämmerle, 2011).  
41 Currently, the major markets of MMCFs are dominated by viscose and Lyocell fibres. However,  
42 the viscose fibre process is connected to environmental and safety concerns due to the utilization  
43 of CS<sub>2</sub> for the intermediate derivatization of cellulose into cellulose xanthate (Hermanutz, Meister,  
44 & Uerdingen, 2006). In addition to the mentioned drawbacks of this process, this technology  
45 demands dissolving pulp as feedstock. In the viscose process, the presence of lignin and  
46 hemicellulose will deteriorate the xanthation of the pulp and process filterability drastically. This  
47 results in poor spinnability, if processable at all (Hans Peter Fink et al., 2004; Gübitz, Stebbing,  
48 Johansson, & Saddler, 1998). The Lyocell process is an environmentally friendly process in which  
49 both the cellulose solvent and spent water are fully recovered and circulated. This process allows  
50 for the direct dissolution of cellulose to yield a spin dope that is processed through dry-jet wet  
51 spinning. The spun fibres are clearly stronger than regular viscose fibres. Despite the advantages  
52 of the Lyocell process, the process operates at a relatively high temperature and requires the  
53 addition of stabilizers to prevent dangerous runaway reactions during the dope preparation and  
54 spinning (H P Fink, Weigel, Purz, & Ganster, 2001). From the feedstock point of view, the  
55 NMMO-based Lyocell process can already utilize dissolving pulp, paper grade pulp (with high  
56 hemicellulose content) and even unbleached chemical pulp for fibre production (Rosenau,  
57 Potthast, Sixta, & Kosma, 2001). However, NMMO, as an oxidant, might react with the lignin  
58 present in the raw material to unexpected degradation reaction, especially at high temperatures  
59 between 110 and 130 °C as typically used in the NMMO process. Furthermore, the dissolution of

60 the raw material in NMMO could be more difficult, thus affecting the quality of the dope which  
61 may lead to spinnability problems (Hans Peter Fink et al., 2004).

62 The IONCELL-F process is a recently developed process in which the ionic liquid 1,5-  
63 diazabicyclo [4.3.0]non-5-enium acetate ([DBNH][OAc]) is utilized as a solvent for cellulosic  
64 material and the resulting dope is processed in a dry jet-wet spinning process to form filaments  
65 with high mechanical properties (Hummel et al., 2015; A Michud et al., 2014; Parviainen et al.,  
66 2013; Sixta et al., 2015). The IONCELL-F process, a Lyocell-type fibre process, is considered to  
67 be a green fibre spinning technology. It has been shown that it is largely insensitive to the  
68 composition of lignocellulosic material and tolerates varying amounts of non-cellulosic  
69 components such as lignin and hemicelluloses (Y Ma et al., 2016; Yibo Ma et al., 2015a). Thus, it  
70 is not necessary to source highly refined dissolving pulp for this spinning process.

71 In previous studies (Le, Ma, Borrega, & Sixta, 2016; Y Ma et al., 2016), we have demonstrated  
72 the possibility to spin unbleached organosolv pulps, waste fine paper and pre-treated waste  
73 cardboard in IL solution and the spun fibres showed good to excellent properties. However,  
74 untreated waste cardboard (made from mainly low-refined semi-chemical pulp), which contains a  
75 large lignin content, cannot be dissolved in the IL completely. The spinning dope resulting from  
76 the untreated waste cardboard behaves like a gel, which can only be spun with low draw ratio and  
77 the fibre properties were unacceptably low for commercial and technical applications. Jiang et  
78 al.(Jiang, Sun, Hao, & Chen, 2011) and Sun et al.(Sun et al., 2011) have also reported the  
79 possibility of spinning fibres from lignocellulosics using IL as a solvent. However, due to the  
80 presence of lignin and hemicellulose, the spun fibres showed rather low mechanical properties, not  
81 suitable for commercial use. To confirm the negative effect of native lignin on the solubility and  
82 spinnability, polymer blends of cellulose and lignin with different ratio were subjected to

83 dissolution and fibre spinning (Yibo Ma et al., 2015a). Different to the native lignocellulosic  
84 material, the polymer blends with up to 50% lignin can be readily dissolved in IL and the fibres  
85 produced from the IL – polymer dope show good mechanical properties. Presumably, lignin  
86 molecules embedded in the cell wall architecture are associated with polysaccharides, mainly  
87 hemicellulose, forming lignin-carbohydrate complexes (LCCs), which hamper the complete  
88 dissolution of the native lignocellulosics in IL and leads to a gel-like solution, respectively (Hauru  
89 et al., 2013; Sun et al., 2009).

90 The main objectives of the study at hand are to investigate the spinnability of unbleached,  
91 hemicellulose-rich kraft pulps from birch wood. The primary goal is to identify the critical content  
92 of native lignin at which the pulp cannot be dissolved efficiently in an IL solvent and thus, results  
93 in poor spinnability. The findings from this research work provide valuable information on the  
94 necessary minimum refining degree for the dry-jet wet spinning of lignocellulosic material.

95

## 96 **2. Experimental Section**

### 97 **2.1 Kraft cooking**

98 Birchwood (*Betula pendula*) chips were provided by Metla, Finland. The dissolving grade birch  
99 prehydrolyzed kraft (PHK) pulp (Enocell Pulp) was kindly supplied by Stora Enso, Finland. The  
100 birchwood chips were screened according to standard SCAN-N 2:88 prior to kraft cooking. The  
101 cooking was executed in 2 L autoclaves attached in a rotary air bath digester. The cooking  
102 conditions are list in Table S1. Pulp samples were taken at H-factor (Sixta, 2006) 25, 50, 200, 500,  
103 800, 1000 and 1200. These samples will be referred to as H25, H50 etc. After kraft cooking, the  
104 black liquor was removed and the pulps were washed. The kraft pulps H1200, H1000, H800 and  
105 H500 were subjected to screening with a Mänttä flat screen using a screen plate with a slot width

106 of 0.35 mm. The screening rejects were collected from the screen plate and dried in an oven at 105  
107 °C for the determination of the rejects content. Due to the low degree of refining, the pulps H200,  
108 H50 and H25 could not be defibrillated manually. Thus, a disc refiner was utilized for pulp  
109 defibration. These samples were not screened due to the large amount of oversize fibers.

## 110 **2.2 Degree of polymerization (DP) adjustments**

111 The DP of the refined material was adjusted using two methods: acid-catalyzed hydrolysis and  
112 electron beam (E-beam) irradiation treatment. The acid-catalyzed hydrolysis was done in the same  
113 autoclave as was used for the kraft cooking. 5 samples, derived from H1200, H1000, H800, H500  
114 and H200, were selected for the acid-catalyzed hydrolysis. The hydrolysis was accomplished for  
115 2 hours at 130 °C with an acid concentration of 6 g/l. The samples were then washed and air-dried  
116 for further use.

117 Birch PHK, birch H50 and birch H25 pulps were irradiated at LEONI Studer AG, Switzerland,  
118 with a 10 MeV Rhodotron TT300 accelerator built by IBA for DP adjustment. Prior to E-beam  
119 treatment, pulp sheets (thickness is 0.15 mm for each sheet) were prepared using a laboratory sheet  
120 former. For establishing a dosage-DP relationship, the E-beam dosages were varied from 5 to 30  
121 kGy for the different pulps. The large batch treatment for H25 and H50 pulps was performed at an  
122 E-beam dosage of 20 kGy.

## 123 **2.3 Pulp dissolution**

124 [DBNH][OAc] was first melted at 70 °C, then blended with the air-dried pulp (ground with a  
125 Willey mill with 1 mm mesh sieves), stirred for 1.5 h at 80 °C with 10 rpm at reduced pressure  
126 (50–200 mbar) using a vertical kneader system. The polymer concentration of the dope was  
127 adjusted to 13 or 15 wt% according to the intrinsic viscosity of the pulps. The solutions were  
128 filtered through a hydraulic press filter device (metal filter mesh with 5 µm absolute fineness, Gebr.

129 Kufferath AG, Germany) at 2 MPa and 80 °C to remove undissolved substrate, which would lead  
130 to unstable spinning. The prepared dope was finally shaped into the dimensions of the spinning  
131 cylinder and solidified upon cooling overnight to ensure filling without inclusion of air bubbles.

### 132 **2.3 Spinning trials**

133 Multi-filaments were spun with a customized laboratory piston spinning system (Fourné  
134 Polymertechnik, Germany). The solidified spinning dope was heated to 70 °C in the spinning  
135 cylinder to form a highly viscous, air-bubble-free spinning dope. The molten solution was then  
136 extruded through a 36-hole spinneret with a capillary diameter of 100 µm and a length to diameter  
137 ratio (L/D) of 0.2. After the generated filaments had passed an air gap of 10 mm, they were  
138 coagulated in a water bath (10 to 15 °C) in which they were guided by Teflon rollers to the godet  
139 couple. The extrusion velocity ( $V_e$ ) was set to 1.6 ml/min (5.66 m/min), while the take-up velocity  
140 ( $V_t$ ) of the godet was varied from 5 to 85 m/min to reach the maximum draw ratio ( $DR= V_t/V_e$ ) at  
141 which stable spinning was ensured. The fibres were washed off-line in hot water (60 °C) and air-  
142 dried. The analytical methods of the raw materials, spinning dopes and spun fibres including were  
143 carried out according to Yibo Ma et al. (2015b) and were presented in ESI section 1.

## 144 **3. Results and Discussion**

### 145 **3.1 Pulp properties**

146 To obtain pulps with different lignin content, seven birch wood kraft pulps (from H-factor 1200  
147 to 25) were produced by means of a conventional kraft cooking method. As expected (and shown  
148 in Table S1), the pulp yield before screening decreases as the H-factor increases. Pulp screening  
149 was not possible for low refined pulps H25, H50, H200 due to incomplete defibration. Therefore,  
150 the yield after screening could not be determined. The intrinsic viscosity of the different pulp  
151 samples was almost at the same level. A significant reduction in viscosity was observed for H25

152 and 50. This is likely an artifact resulting from the low refining which prevents the dissolution of  
 153 high molecular weight fractions of pulp in CED.

154 Birch wood kraft pulps from H200 to H1200 were subjected to acid catalyzed hydrolysis in order  
 155 to reduce the intrinsic viscosity (optimal range 420 to 450 ml/g), which has been identified earlier  
 156 as optimum viscosity level to yield spinnable solutions. Table 1 lists the intrinsic viscosity ( $\eta_0$ ) of  
 157 the pulps before and after the hydrolysis. The viscosity of the pulps was efficiently reduced by  
 158 acid catalyzed hydrolysis, albeit to a slightly lower level than initially aimed at. Concomitantly,  
 159 low molecular weight hemicelluloses were also degraded to such an extent that they became  
 160 soluble in the reaction liquor (Mosier et al., 2005). These phenomena were reflected by the MMD  
 161 as shown in Figure S1. Untreated pulps revealed a bimodal MMD (representing low-molecular  
 162 weight hemicellulose and high-molecular weight cellulose). However, as expected, after acidic  
 163 hydrolysis and further conversion to regenerated fibers (through dissolution in IL and regeneration  
 164 during the spinning process) the low molar mass peaks almost disappeared, leaving a cellulose  
 165 peak with a subtle shoulder at relatively low molar mass.

166

167 **Table 1.** Intrinsic viscosity and chemical compositions of the original and DP adjusted kraft  
 168 pulps and their spun fibres.

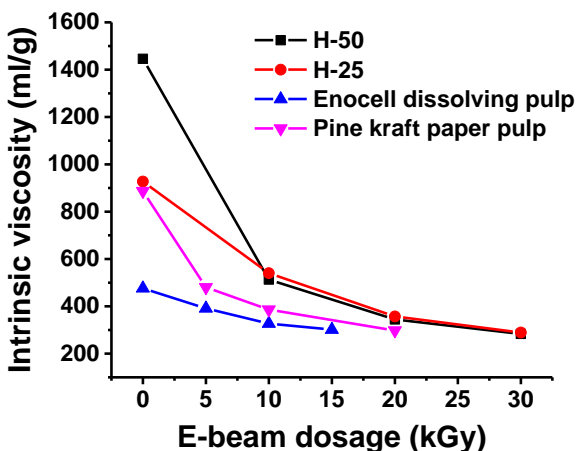
Samples	Original kraft pulp				DP adjusted pulps				Fibres		
	Cellulose	Hemicellulose	Lignin	$\eta_0$ ml/g	Cellulose	Hemicellulose	Lignin	$\eta_0$ ml/g	Cellulose	Hemicellulose	Lignin
H25	53.7	22.4	23.9	-	-	-	-	-	55.8	20.2	24.0
H50	56.4	21.8	21.8	-	-	-	-	-	57.9	21.7	20.4
H200	63.6	21.9	14.5	1795	75.1	9.8	15.1	361	75.2	6.1	18.7
H500	68.9	22.5	8.6	1591	83.6	7.9	8.5	390	85.9	5.2	8.9
H800	71.2	23.0	5.8	1626	84.6	10.4	5.0	367	88.5	6.9	4.6
H1000	72.0	22.6	5.4	1656	85.0	10.2	4.8	403	88.1	8.0	3.9
H1200	72.7	22.2	5.1	1599	85.9	9.8	4.3	351	87.8	7.2	5.0

169



170 The chemical composition of the initial kraft pulps, the DP adjusted pulps, and the spun fibres  
171 are summarized in Table 1. The hemicellulose content of acid hydrolyzed pulps is notably lower  
172 than in the kraft pulps. Furthermore, there is a slight decrease in the lignin content. The reduction  
173 in the hemicellulose and lignin contents result in a rise in the relative cellulose concentration of  
174 the pulp, which facilitates the subsequent fiber spinning.

175 Birchwood kraft pulps H25, H50 were subjected to electron beam irradiation treatment. Electron  
176 beam irradiation is an environmental friendly pre-treatment technology for lignocellulosic biomass,  
177 that reduces the molecular weight and crystallinity by breaking chemical bonds in cellulose,  
178 hemicellulose and lignin (Khan, Labrie, & McKeown, 1986; Kristiani, Effendi, Styarini, Aulia, &  
179 Sudiyani, 2016; Lee et al., 2014). Prior to the main trials, several E-beam dosages had been  
180 screened in order to find the optimal radiation dosage for the DP adjustment. Pre-hydrolyzed birch  
181 kraft pulp and pine kraft paper pulp were selected as model pulps that were treated together with  
182 H25 and H50 by E-beam dosages from 5 to 30 kGy. E-beam treatment – especially at such low  
183 irradiation intensity – was expected to not alter the chemical compositions of the pulps (Imamura,  
184 Murakami, & Ueno, 1972; Kassim et al., 2016; Kristiani et al., 2016). Figure 1 presents the  
185 intrinsic viscosity of the original and the E-beam treated kraft pulps as a function of the irradiation  
186 dosages. A pronounced decrease in intrinsic viscosity (DP) was visible already at 10 kGy. The  
187 viscosity then tended to decrease gradually upon progressive increase of the E-beam dosage. This  
188 finding confirmed that E-beam irradiation is a suitable method to reduce the polymer-DP through  
189 chain scission (Imamura et al., 1972).



190  
191

192 **Figure 1.** The intrinsic viscosity of E-beam treated H25 and H50 samples and a reference birch  
193 PHK pulp.

194 To assess the effects of E-beam treatment on the carbohydrates in more detail, the molecular  
195 weight distribution of the E-beam treated pulps was analyzed (Figure S2). Typically, a bimodal  
196 molecular weight distribution was obtained for all the measured samples. The results of GPC  
197 measurements clearly demonstrated that the high molecular weight domains shifted to lower molar  
198 mass, while the molecular weight of the short-chain fraction remained unchanged. This is in  
199 agreement with the intrinsic viscosity measurement where the intrinsic viscosity decreases as E-  
200 beam dosage increases.

201

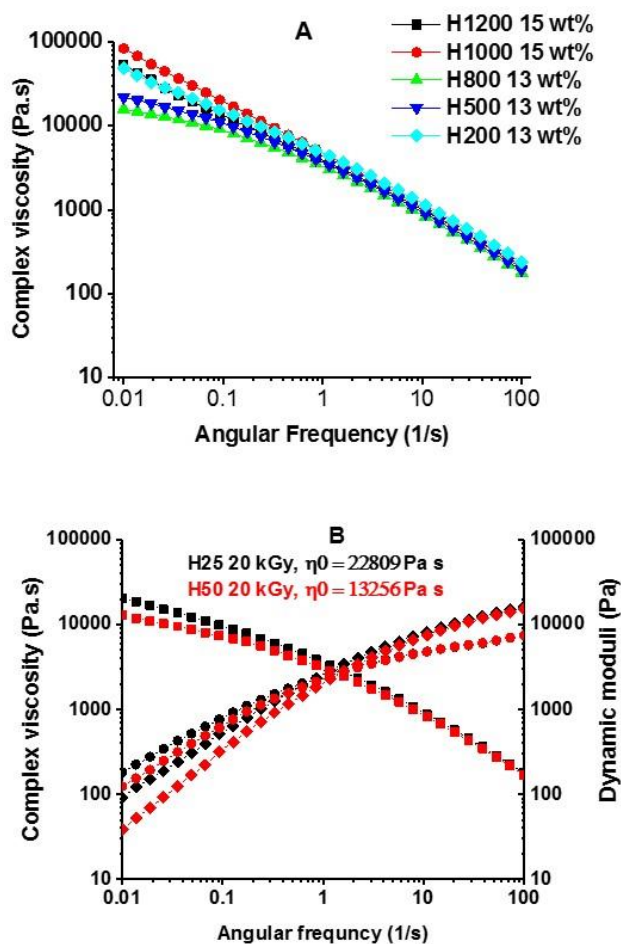
### 202 **3.2 Dissolution and dope properties**

203 Spinning dopes were prepared in [DBNH]OAc with the acid hydrolyzed kraft pulp from H1200  
204 to H200 and E-beam treated (20 kGy) kraft pulps H25 and H50. The rheological properties of the  
205 dopes were determined via oscillatory shear measurements yielding the complex viscosity and  
206 dynamic moduli as a function of the angular frequency. The crossover point of the dynamic moduli

207 and the zero shear viscosity were calculated using the Cross model and assuming the validity of  
208 the Cox-Merz rule (Hummel et al., 2015). In previous studies (Sixta et al., 2015), it was found that  
209 stable spinning is possible if the zero shear viscosity of the spin dope is around 30 000 Pa.s and  
210 the crossover modulus ranges between 3000 and 5000 Pa at a crossover frequency of around  $1 \text{ s}^{-1}$ .  
211 Several subsequent studies (Asaadi et al., 2016; Yibo Ma et al., 2015a; A Michud et al., 2014;  
212 Anne Michud, Tantt, et al., 2016) have confirmed these requirements for successful fibre spinning.  
213 However, a successful fibre spinning was observed when attempting to spin a spinning dope from  
214 an unbleached pulp, of which the rheology was outside the optimal spinning window (Y Ma et al.,  
215 2016).

216 Since the molar mass distribution and the DP of the raw material are crucial for the viscoelastic  
217 properties of the spinning dope, the selection of the polymer concentration (or spinning  
218 temperatures) has to be adjusted in order to meet the above-mentioned dope properties (Anne  
219 Michud, Hummel, & Sixta, 2015, 2016). Because of the low intrinsic viscosity of the resulting  
220 acid hydrolyzed kraft pulps, H1200 and H1000, a 15 wt% concentration of these pulps in  
221 [DBNH]OAc was prepared to adjust the required viscoelastic properties and thus to ensure their  
222 spinnability. Contrary to our expectation, these two dopes exhibited a high complex viscosity  
223 without a Newtonian plateau within the measured angular frequency range (gel-like power-law  
224 dependency). To reduce the dope viscosity, spinning dopes from H800, H500 and H200 were  
225 prepared with a polymer concentration of 13 wt%. However, only two of them, the H800 and  
226 H500-derived dopes, revealed the expected complex viscosity typical for spinnable solutions  
227 (Figure 2A). The zero shear viscosity of the spinning dopes from H200 to H1200 is listed in Table  
228 S2. At a low H-factor of H200, the respective dope showed a strong gel-character even at 13 wt%  
229 polymer concentration and despite a low pulp intrinsic pulp viscosity. This was attributed to a

230 lignin with a relatively high content of 15%, which is presumably bond to hemicellulose and/or  
 231 cellulose to form lignin-carbohydrate complexes (LCC). Thus, it can be hypothesized that residual  
 232 lignin embedded in the cell wall architecture acts as a crosslinker between the carbohydrate  
 233 polymer chains, which tend to form extended aggregates in solution exhibiting a gel behavior of  
 234 the resulting dope.



235  
 236 **Figure 2.** A) Complex viscosity of the spinning dopes from H200 to H1200 at the spinning  
 237 temperatures. B) Complex viscosity and dynamic moduli of E-beam treated kraft pulps H25 and  
 238 H50 at 70 °C. ■: Complex viscosity. ◆: Storage modulus. ●: Loss modulus.

239

240 The E-beam treated birch kraft pulps (20 kGy, H25 and H50) were dissolved in [DBNH]OAc at  
241 a polymer concentration of 13 wt%. Figure 2B illustrates the viscoelastic properties of the E-beam  
242 treated pulps. Unlike a solution from H200, these two dopes did not show any gel behavior  
243 regardless of the high lignin content. This could be explained by the efficient cleavage of the  
244 cellulose and lignin chains as well as the LCC bonds by the electron beam irradiation (Bak, 2014).  
245 Direct comparison of the viscoelastic properties of the dopes prepared from H25 and H50, revealed  
246 a more pronounced solution state for the H50. At high angular frequency complex viscosity and  
247 dynamic moduli of the two dopes were almost perfectly superimposed. At low angular frequency  
248 the complex viscosity of the H50 dope started to enter the Newtonian plateau whereas the complex  
249 viscosity of the H25 dope continues to raise. As a result, the zero shear viscosity of H25 dope was  
250 higher than that from the H50 dope.

251

### 252 **3.3 Dope spinnability and tensile properties of the spun fibres**

253 The spinning performance depends on several factors of which most are connected to the dope  
254 rheology. The polymer solution must exhibit the right fluidity to be extruded through the spinneret  
255 orifices. Further, a dry-jet wet spinning process demands the stretch of the filaments in the air gap.  
256 Hence, the filaments must have a certain visco-elasticity to withstand the draw without rupture.  
257 We have thus defined spinnability in terms of accessible draw ratios:  $DR < 2$  non-spinnable, 2–8  
258 poor, 8–14 good,  $> 14$  excellent spinnability. All dopes showed good to excellent spinnability. In  
259 the case of acid hydrolyzed kraft pulps, only H1200 showed a relative low spinnability (reflected  
260 by the low draw ratio of 8.8). Considering the high cellulose content in H1200, a better spinning  
261 performance was expected. Possibly, the high dope viscosity and the relatively high spinning  
262 temperature may have limited the spinnability. The solution prepared from the H800 pulp showed  
263 the highest spinnability with a maximum draw ratio of 17.7. Surprisingly, the dopes from H200,

264 H50 and H25, which contained large amounts of lignin and hemicellulose, were still spinnable and  
 265 showed good spinnability (15.9 for H200 and 9.7 for both H25 and 50). Table 2 summarizes the  
 266 mechanical properties of the spun fibres. The fibre tenacity is closely linked with the cellulose  
 267 microfibril orientation in the fibre (H P Fink et al., 2001; Kong & Eichhorn, 2005). A high draw  
 268 ratio results in fibres with more pronounced lateral orientation of the polymer chain, therefore,  
 269 yields fibres with improved tenacity. Due to the low spinnability, the fibre spun from H1200 dope  
 270 had the lowest conditioned (32.9 cN/tex) and wet tenacity (19.9 cN/tex) among the fibres from  
 271 acid hydrolyzed kraft pulps, while the H800 fibre showed the highest conditioned tenacity of 40.2  
 272 cN/tex and wet tenacity of 29.3 cN/tex due to the excellent spinnability of the dope. The lignin and  
 273 hemicellulose content do not only affect the spinnability, but also influence the mechanical  
 274 properties of the spun fibres through their relatively low DP and their inability to orient themselves  
 275 along the molecular axis. Because the lignin contents in H200, H50 and H25 pulps are significantly  
 276 higher as compared to the other pulps, the mechanical properties of the resulting fibres were  
 277 notably reduced. Especially, the fibres spun from the H50 and H25 pulps reveal a conditioned  
 278 tenacity of only 24.4 and 23.0 cN/tex, which may be explained by a very low cellulose content of  
 279 56% and 58%, respectively (Table 2).

280

281 **Table 2.** Tensile properties of the spun fibres from H1200 to H200 dopes.

282

283

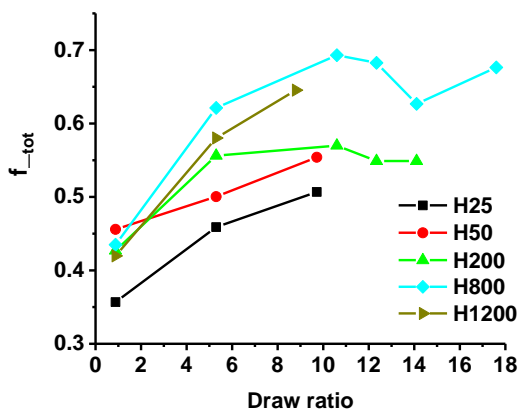
Samples	Draw ratio	Titer (dtex)	Dry elongation (%)	Dry tenacity (cN/tex)	Wet elongation (%)	Wet tenacity (cN/tex)
H25	9.7	2.02	8.1	23.0	7.7	11.1
H50	9.7	2.14	7.4	24.4	7.0	13.7
H200	15.9	1.71	7.6	32.1	8.8	20.1
H500	12.4	1.78	9.0	38.1	9.2	26.1
H800	17.7	1.43	7.7	40.2	9.7	29.3
H1000	15.9	1.58	8.0	37.3	8.6	24.9
H1200	8.8	2.74	9.2	32.9	9.4	19.9
Lyocell	-	1.3	9.5	34.3	-	-

284

### 285 **3.4 Structural properties of fibres**

286 As stated above, the tensile properties of the fibre are directly connected to the cellulose  
287 orientation. The total orientation of cellulose molecules in a fiber matrix can be assessed by means  
288 of birefringence measurement. In agreement with the previous studies (Asaadi et al., 2016; Yibo  
289 Ma et al., 2015a), the degree of orientation of the fibers increased significantly at low draw ratio  
290 and tends to level-off when exceeding a draw ratio of 5. A slight drop in the orientation might  
291 occur at higher draw ratio due to relaxation of the cellulose molecules, which is caused by the  
292 slippage of cellulose chains and the breakage of the intermolecular hydrogen bonds among the  
293 cellulose molecules (Asaadi et al., 2016; Kong & Eichhorn, 2005). Figure 3 shows that the total  
294 degree of orientation was affected by both the lignin concentration and the spinnability,  
295 characterized by the draw ratio during spinning. Surprisingly, H1200 fibres that could be produced  
296 only at relatively low draw ratio showed an overall lower orientation than pulps with a similar  
297 composition. In the case of H200, H50 and H25 fibres, having a significantly higher lignin content,  
298 the total orientation was notably reduced. The presence of lignin disturbs the highly ordered  
299 structure formed by cellulose chains and, thus, reduces the total orientation of the fiber (Kong &  
300 Eichhorn, 2005). The development of the degree of orientation is consistent with the tensile  
301 properties of the fibres. A reduction of total orientation caused a decrease of the fibre tenacity.

302



303  
 304 **Figure 3.** Degree of total orientation  $f_{tot}$  of the fibres at selected draw ratios.

305 The crystallinity and the crystallite size of fibres listed in Table 3 were assessed by XRD  
 306 measurement. The XRD spectra of selected samples are shown in Figure S3. The crystallinity of  
 307 the fibres increases upon progressive cooking intensity of pulp production, with the fibre spun  
 308 from the H1200 pulp having the largest crystallinity of 50%. The increase in the lignin content of  
 309 the fibres spun from kraft pulps prepared with gradually decreased cooking intensity (from H-  
 310 factor 200 to H-factor 25) results in a crystallinity drop to 43% and 40% in relation to the total  
 311 sample, respectively. The crystallite dimensions were assessed in 110, 1-10 and 020 direction and  
 312 extrapolated by using the Scherrer equation (Leppänen et al., 2011). The crystallite width  
 313 measured in 110 direction (perpendicular to the cellulose crystal plane) follows the trend of the  
 314 degree of crystallinity. By contrast, there is no distinct difference observed in the crystalline width  
 315 in 1-10 direction. However, it has to be noted that the fit quality of the 110 and 1-10 crystallite  
 316 width suffered from the overlap of the respective peaks. Furthermore, it has been shown that the  
 317 signals from 110 and 1-10 may include crystal aggregations or less ordered cellulose chains on the  
 318 surface which result in erroneous values for the crystallite width (Cheng et al., 2011; Maurer, Sax,  
 319 & Ribitsch, 2013). In general, the crystallite width estimated in 020 direction (sharp peak from 22  
 320 to 25° with high intensity in the XRD diffractograms) is more reliable. However, no distinct



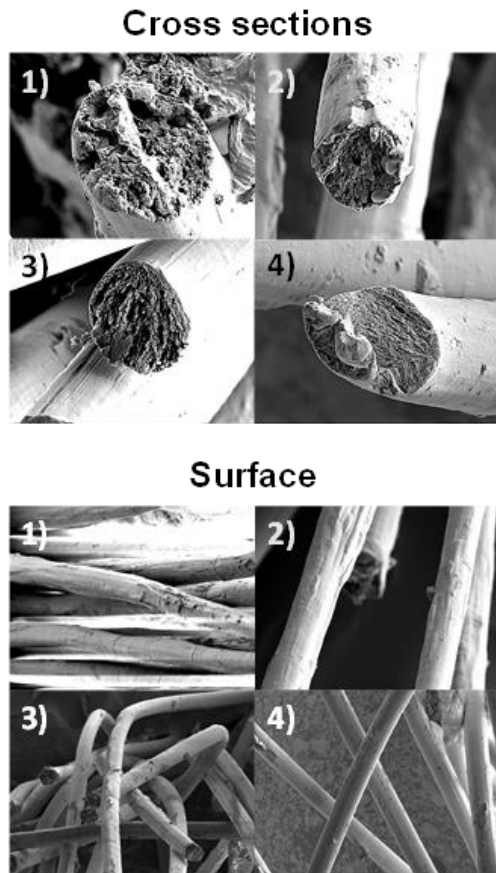
321 correlation between the 020 crystallite width and the lignin content (i.e. pretreatment intensity)  
 322 was observed.

323  
 324 **Table 3.** Crystallinity and crystallite width analyzed by XRD from the H1200, H800, H200, H50  
 325 and H25 fibres at the highest draw ratio.

Samples	Draw ratio	Crystallinity index (%)	Crystallite width (nm)		
			110	1 $\bar{1}$ 0	020
H25	9.7	40±3	2.6±0.15	3.2±0.3	5.7±0.3
H50	9.7	40±3	2.9±0.15	3.2±0.3	6.0±0.3
H200	15.9	43±3	3.4±0.15	2.9±0.3	5.6±0.3
H800	17.7	48±3	3.8±0.15	2.9±0.3	5.8±0.3
H1200	8.8	50±3	3.8±0.15	3.1±0.3	5.5±0.3

333  
 334 Scanning electron microscopy images of the fibres (surfaces and cross sections) were recorded  
 335 in order to examine their structural alterations along their compositional changes (Figure 4). Indeed,  
 336 SEM images reveal a significant effect of the pretreatment intensity on the structure of the fibre.  
 337 When the fibres contained a higher amount of lignin (H25 and H200), the microfibrils became less  
 338 orientated and voids were clearly visible in the SEM images of the cross section. Consequently,  
 339 the fibres become more ductile which leads to a loose structure. When the cellulose content  
 340 increased (H800 and H1200), the orientation of the cellulose microfibrils became more  
 341 pronounced and the fibre surfaces appeared smooth.

342

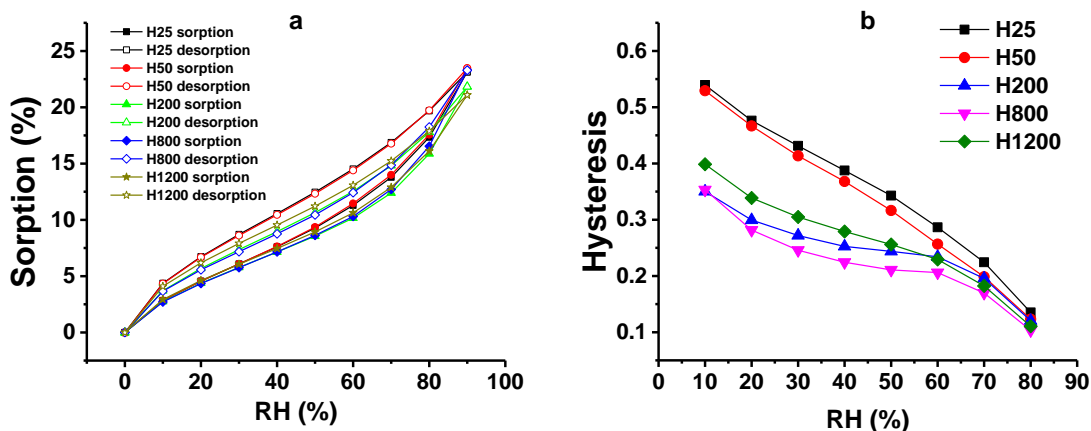


343

344 **Figure 4.** SEM images of fibres cross sections (top) and surface (bottom); 1) H25, 2) H200, 3)  
 345 H800 and 4) H1200.

346 Dynamic vapour sorption (DVS) studies were conducted to gain further insight into the  
 347 relationship between the structural and chemical characteristics of the fibers. Water sorption  
 348 behavior of regenerated cellulosic fibres depends on several factors, e.g. morphology, crystallinity,  
 349 degree of orientation and the chemical compositions (Bingham, 1964; Kreze & Malej, 2003;  
 350 Okubayashi, Griesser, & Bechtold, 2004, 2005b, 2005a; Siroka, Noisternig, Griesser, & Bechtold,  
 351 2008; Stana-Kleinschek, Ribitsch, Kreže, Sfiligoj-Smole, & Peršin, 2003). It has been shown that  
 352 Lyocell type fibres absorb a little bit less moisture compared to viscose fibres due to their higher  
 353 degree of orientation (which is closely related to crystallinity) and more compact structure.

354 However, when lignin as a hydrophobic component is present in the fibres it may hamper the  
 355 moisture absorption as was observed earlier (Yibo Ma et al., 2015a). Figure 5 illustrates the  
 356 equilibrium moisture sorption and desorption isotherms of tested fibres (a) and shows their  
 357 hysteresis (b).  
 358



359 **Figure 5.** Equilibrium moisture isotherms of spun fibres (a) and the hystereses of the sorption and  
 360 desorption isotherms from H25, H50, H200, H800 and H1200 fibres (b).

361  
 362 Comparing with the previous studies on the DVS of man-made cellulose fibres (Okubayashi et  
 363 al., 2004, 2005a, 2005b), a similar moisture sorption and desorption development was found with  
 364 the fibres spun from kraft pulp/ionic liquid dopes, which is typical for cellulosic materials.  
 365 Contrary to our expectation, lignin did not act as a moisture repellent in these fibres. However, it  
 366 contributed more to the loss of the fibre orientation together with hemicellulose. Thus, a clear  
 367 effect of the degree of orientation on the wetting of the fibres was noted. Moreover, the role of the  
 368 cellulose crystallite size (derived from the 020 reflection) on the monolayer (ML) hydration has  
 369 been investigated based on the theory proposed by Driemeier (Driemeier & Bragatto, 2013) using  
 370 the Hailwood-Horrobin (HH) model (Hailwood & Horrobin, 1946; Skaar, 1988) with lignin-free

371 cellulose I samples. However, no clear relationship between ML water sorption and reciprocal  
372 crystallite width could be identified, because of the presence of lignin and different crystal  
373 structure in our spun fibres (see ESI section 4, Table S2). Lignin, hemicellulose and the degree of  
374 orientation seem to be more dominant factors.

375  
376 To further exhibit the influence of the chemical composition/total orientation of the spun fibres  
377 on the water sorption/desorption (presented as ML water sorption, desorption and their hysteresis),  
378 multiple regression analysis was carried out with lignin content, hemicellulose content and total  
379 orientation as predictor variables. The multiple regression equations are listed in the ESI, section  
380 4. In this work, the three predictor variables are collinear, from which it is possible to express e.g.  
381 the total orientation as a linear combination of the other two variables. Thus, there is no need to  
382 estimate the responses of the ML water sorption/desorption for any arbitrary combination of the  
383 predictor variables. In this scenario, the total orientation could be used as third predictor and  
384 restricted to an interval centered around the value obtained by linearly fitting the total orientation  
385 to the other predictors. The responses of ML water sorption/desorption are visualized (shown as  
386 contour plots in Figure S3-5), in which lignin and hemicellulose are predictors at different levels  
387 of aberration of the total variables. The interpretation of the visualization almost proved that the  
388 wetting behavior is largely dependent on the chemical composition and the total orientation of the  
389 fibre. According to Figure S3, the ML sorption slightly decreases with the hemicellulose content  
390 and increases with the lignin content as well as with the total orientation. Figure S4 allows for a  
391 similar interpretation on ML desorption, but with the exception that increasing hemicellulose  
392 content causes a slight raise on the ML water desorption. Eventually, Figure S5 reveals that  
393 increasing the hemicellulose and lignin content simultaneously increases the hysteresis, whereas  
394 the increasing total orientation once again has a decreasing effect. However, it has to be stressed

395 that the five data points are not enough for a compelling regression analysis in three variables.  
396 Hence, the regression is rather a means of comprehensively visualizing the observed responses at  
397 different values of the predictor variables.

398  
399

#### 400 **4. CONCLUSION**

401 1,5-diazabicyclo[4.3.0]non-5-enium acetate is a promising biopolymer solvent for the  
402 production of high quality fibres, not only from costly dissolving pulps but also from low-refined  
403 unbleached pulps. In this study, our objective to find a limit in the lignin content was not achieved;  
404 even at the highest lignin content the pulp was still spinnable. The fibres showed good to excellent  
405 mechanical properties. The spinnability was primarily dependent on the macromolecular integrity  
406 of the carbohydrate matrix but not as much on its composition. Contrary to our previous study, the  
407 lignin present in the fibre did not render the fibre hydrophobic. However, it reduced the total  
408 orientation of the fibre, which leads to a more pronounced wetting of the fibre.

409 Most importantly, E-beam irradiation was identified as an environmentally friendly alternative  
410 for DP adjustment and production of fibres from unbleached birch kraft pulp with varying amount  
411 of lignin and hemicellulose. Contrary to the DP adjustment with an acid treatment, E-beam  
412 irradiation does not yield any material losses. This increases the overall process economy and  
413 environmental sustainability of the Ioncell-F technology. For further work, a milder pre-treatment  
414 in combination with E-beam irradiation (which cleaves the LCC bonds) is still necessary to  
415 investigate the spinning limitation.

416

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