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# 1 High-purity cellulose production from birch wood by $\gamma$ -valerolactone/water 2 fractionation and IONCELL-P process

3 Shokoufeh Shokri<sup>a</sup>, Sahab Hedjazi<sup>a\*</sup>, Huy Quang Lê<sup>b</sup>, Ali Abdulkhani<sup>a</sup> and Herbert Sixta<sup>b</sup>

4 This study presents an environmentally friendly process to produce high-purity cellulose (dissolving pulp) from birch wood by combining  $\gamma$ -  
5 valerolactone (GVL)/water fractionation and ionic liquid treatment of pulp, IONCELL-P (IP). A paper grade pulp was produced from optimal GVL  
6 cook with a similar composition to birch kraft pulp and was bleached with ECF sequence before the hemicelluloses were removed using the  
7 IONCELL-P process. The purity of the GVL-IP pulp significantly exceeded that of commercial prehydrolysis kraft (PHK) and prehydrolysis soda-  
8 anthraquinone (PH-Soda-AQ) pulps. IONCELL-P extraction removed more than 90% of the hemicelluloses, resulting in a dissolving pulp with a  
9 purity of 96% and a high molecular mass fraction, 2.3 times higher than that of a conventional PHK pulp. GVL-IP pulps are suitable not only for  
10 regenerated cellulose fibers or films, but also for high-purity, high-viscosity cellulose acetate and ethers, which cannot be produced in an  
11 environmentally friendly way by conventional processes.

12 **Key words:** Organosolv process, Dissolving pulp, Cellulose, GVL.

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## 16 1. Introduction

17  
18 Climate change and the depletion of fossil reserves are major global challenges promoting the adoption of renewable resources to  
19 produce materials, chemicals, fuels, and energy (Shen, Worrell, & Patel, 2010). Amongst the renewable resources, biomass holds  
20 a unique position as the only source of structural polymers (cellulose) and phenolic compounds (lignin) (Sjöström, 1993). Biomass  
21 is processed in the fractionation and conversion facilities called biorefineries to a wide variety of products such as cellulosic fibers  
22 (Ibrahim, Nada, Hagemann, & El Seoud, 1996), platform chemicals (Tuck, Pérez, Horváth, Sheldon, & Poliakov, 2012), electricity  
23 (García-Negrón et al., 2017; Wang, Yang, Stubbs, Li, & He, 2013) and biofuels (Cherubini, 2010; Rabelo, Carrere, Maciel Filho, &  
24 Costa, 2011).

25 However, the production of paper-grade pulp stagnates due to the paper demand decline in the era of digitalization, while on the  
26 other hand, the consumption of high purity cellulose (dissolving pulp) has been growing from 3.3 Mtons in 2007 to 10.2 Mtons in  
27 2019 with further growth forecast in the next five years (Engelhardt, 2020; *FAO year forest products*, 2007)

28 Dissolving pulp is characterized by a high cellulose content (>90%), a low content of hemicelluloses (<6-7%), high brightness  
29 (>90%) and a low macromolecular polydispersity. Dissolving pulp generally serves as a precursor for higher- value products such  
30 as cellulose derivatives and regenerated fibers.

31 Dissolving pulps generally originate from wood (85%) or cotton linters (15%), in which the production of the latter is diminishing  
32 due to the unavailability of land, high production costs (Sixta, 2006), intensive use of water and chemicals, and competition with  
33 agricultural land (Carpenter et al., 2002). Cotton consumption is expected to stagnate at a level of 26-30 Mtons per year, resulting  
34 in a decline in per capita consumption to about 3.1 kg per year. On the other hand, the global textile fibers production is predicted  
35 to grow from 72.5 Mtons in 2010 to 133.5 Mtons in 2030. The specific consumption of cellulosic fiber will increase from the  
36 present 3.7 kg to 5.4 kg per capita in 2030 (Haemmerle, 2011). This “cellulose gap” is the main driving force for the steady growth  
37 of wood-derived regenerated cellulose fibers.

38 Wood-based dissolving pulp is commercially produced by the acid sulfite (AS) and prehydrolysis-kraft (PHK) pulping technologies.  
39 However, both processes encounter several inherent disadvantages. Being the oldest commercial pulping process, AS is  
40 restricted by the low flexibility of raw materials and inefficient chemical recovery (Sixta, 2006). For instance, hemicelluloses-based  
41 sugars are oxidized by hydrogen sulfite anions to the corresponding aldonic acids (Rydholm, 1985), which is irrecoverable by any  
42 commercially relevant technology, thereby reducing the valorization yield of hemicellulose-based monomeric sugars (Sixta et al.,  
43 2013). In addition to the low yield, PHK also underutilizes the hemicelluloses fraction and forms sticky lignin precipitates,  
44 challenging the valorization of the extracted sugar in the prehydrolyzate into valuable products (Leschinsky et al. 2009; Mendes et  
45 al. 2009; Sixta, Schild, and others 2009). Furthermore, both AS and PHK processes employ sulfur-based nucleophiles, posing  
46 environmental risks.

47 Therefore, alternative pulping methods as bases for biorefineries have been extensively investigated. The commercialization of  
48 current organosolv pulping technologies is impeded by their inherent disadvantages. The organosolv processes are restricted by  
49 raw material sensitivity (favoring mostly just hardwood species), poorer strength properties (Sixta, 2006), higher solvent costs and  
50 more energy-intensive chemical recovery, comparing to the Kraft process (Alejandro Rodríguez, Alejandro Rodríguez, Juan  
51 Domínguez-Robles, Juan Domínguez-Robles, & Rosal, 2018). The main concern of organosolv pulping for the future is identifying  
52 solvents with better selectivity towards lignin, which simultaneously allows simple, but efficient recovery.

53 Gamma-valerolactone (GVL) is a green bio-based solvent for biomass conversion and degradation (Alonso, Wettstein, &  
54 Dumesic, 2013; Fitzpatrick, 1996; Galletti, Antonetti, De Luise, & Martinelli, 2012; Horváth, Mehdi, Fábos, Boda, & Mika, 2008)  
55 and a sustainable lignin solvent that offers the possibility of producing biomass-derived fuels (Alonso et al., 2013). In 2014, the  
56 first GVL-based biorefinery concept was proposed, where birch sawdust was fractionated in an aqueous solution of GVL, yielding  
57 a cellulose-rich pulp fraction and a spent liquor from which lignin and hemicelluloses could be isolated and subsequently valorized  
58 (Fang & Sixta, 2015). A one-step, auto-catalyzed GVL/water biorefinery concept was presented in 2016 where the wood  
59 biopolymers were effectively isolated and converted to textile fibers and sulfur-free lignin (Lê, Ma, Borrega, & Sixta, 2016). One  
60 study reported the production of a highly pure cellulose fraction of dissolving pulp grade by GVL/water treatment in the presence  
61 of mineral acid (Alonso et al., 2017). Furthermore, treating birch wood in 50 wt% GVL was reported to yield a paper-grade  
62 unbleached pulp with relatively well-preserved cellulose (Shokri, Hedjazi, Abdulkhani, & Sixta, 2019).

63 Cold caustic extraction (CCE) is the conventional purification method for the production of high-purity dissolving pulp, which is  
64 combined with PHK or AS as post-treatment. However, the performance of CCE is limited by yield losses, polymer degradation  
65 (Gardner PE, 1974; Sixta, 2006), lack of eco-friendly NaOH recovery, inefficient removal of glucomannan from softwood pulps,  
66 and, in particular, the lower pulp reactivity due to the conversion of native cellulose into cellulose-II. Consequently, a novel highly  
67 selective method for the efficient removal and recovery of hemicellulose, even at low hemicellulose content, while preserving the  
68 pulp cellulose-I structure and reactivity is required. The direct extraction/dissolution of hemicellulose would meet the requirements  
69 of a very mild and selective procedure.

70 The addition of a specific amount of an anti-solvent, such as water, to a good cellulose solvent, such as ionic liquids (IL), allows a  
71 controllable molecular mass fractionation that is equally applicable to pure cellulose or hemicellulose-containing pulps. Applying  
72 such principle to hemicellulose-rich paper pulps enables an effective dissolution of the hemicellulose fraction almost without any  
73 loss of material. In other words, the dissolution selectivity of the IL/water system can be tailored by adjusting the water  
74 concentration. The solution properties of the mixture of water and IL can be reasonably estimated with the Kamlet-Taft  
75 parameters (Froschauer et al., 2013). The separation of the hemicellulose from cellulose improves as the difference in molecular  
76 mass between the two fractions increases, which can be facilitated by the reduction of hemicellulose DP, for example, by  
77 enzymatic treatment with xylanases or mannanases. This fractionation method, known as IONCELL-P, abbreviated IP (Roselli,  
78 Hummel, Monshizadeh, Maloney, & Sixta, 2014), presents a simple and selective process for producing a high purity pulp without  
79 yield losses, degradation or transformation of the cellulose-I allomorph.

80 This paper investigates the production of high-quality dissolving pulp from birch wood. A xylan-rich paper pulp was first produced  
81 by GVL-water fractionation and then subjected to hemicellulose removal by the IONCELL-P process in 1-ethyl-  
82 3-methylimidazolium acetate ([EMIM][OAc])-water, while the dissolved xylan was simultaneously recovered as a value-added  
83 product.

## 84 **2. Materials and methods**

85

### 86 *2.1. Materials*

87 Birch wood chips were delivered from the Metsä Group pulp mill in Äänekoski, Finland. The chips were screened according to the  
88 SCAN-CM 40:01 standard and stored in the freezer at -20°C. Screened wood chips, GVL (≥98 wt% purity, Sigma Aldrich) and  
89 demineralized water were used in the GVL pulping experiments.

90 Ultra-pure water (resistivity of 18.2 MΩ.cm, produced by Millipore Synergy UV purification system) and [EMIM][OAc] (>95 wt%  
91 purity, IoLiTec GmbH) were used in all IONCELL-P fractionation experiments and analyses.

### 92 *2.2. GVL fractionation*

93 The small-scaled pulping experiments were performed in 225 mL autoclaves heated in a silicon oil-bath reactor (Haato-tuote,  
94 model 43427) while the larger-scaled pulping was conducted with the optimum fractionation conditions in 2.5 L autoclaves heated  
95 in an air-bath digester (Haato-tuote 16140-538) as described in ESI 1. The pulp produced from GVL cook is called GVL pulp.

### 96 2.3. Pulp Bleaching

97 Selected pulp from the optimum up-scaled experiment was bleached with an ECF (Elemental Chlorine Free) sequence of  
98 OOD<sub>0</sub>E<sub>P</sub>QP. Oxygen delignification was conducted in 2.5 L autoclaves heated in an air-bath digester while the following stages  
99 were performed in plastic bags heated in a water bath. The bleaching conditions are summarized in Table S 2.1.

### 100 2.4. IONCELL-P extraction

101 Hemicellulose extraction by ionic liquid treatment of pulp (IONCELL-P) was performed with 1 g of milled bleached pulp (<0.6 mm  
102 particle size). The pulp was mixed in a test tube at 5% consistency in the [EMIM][OAc] solution containing and 12, 13, 14, 15, 16,  
103 or 17 wt% water. The mixture was incubated at 60°C for 3 hours in a water bath, and the suspension was then filtered. The solid  
104 fraction was washed with the IL solution with the same concentration as in the extraction and subsequently with hot water.

105 The washed solid fraction was then air-dried. The filtrate was combined with the washing liquids, thus inducing the precipitation of  
106 hemicelluloses. The suspension was centrifuged for 15 minutes at the speed of 4500 rpm. The precipitate was washed with hot  
107 water and then freeze-dried.

### 108 2.5. Wood, pulp and hand sheet characterization

109 Wood extractive content was determined by acetone extraction according to SCAN-CM 49:03 standard. Pulp intrinsic viscosity ( $\eta$ )  
110 and kappa number ( $\kappa$ ) were analyzed according to SCAN-CM 15:88 and SCAN-C 1:00 standards, respectively (ESI 1).

111 The carbohydrates and lignin content of the birch wood and pulps were determined according to the two-step hydrolysis method  
112 described in NREL/TP-510-42618 standard. The molecular mass distribution of unbleached, bleached, and IONCELL-P-treated  
113 pulp was measured by gel permeation chromatography (GPC) (ESI 3).

114 Kamlet-Taft (KT) parameters ( $\alpha$ ,  $\beta$ ,  $\pi^*$ ) of the ionic liquids were determined from the absorption peaks of the three dyes. The KT  
115 parameters were calculated with published equations (Doherty, Mora-Pale, Foley, Linhardt, & Dordick, 2010)(ESI 4)

116 The functional chemical groups and chemical interactions of the bleached and IONCELL-P-treated pulp were investigated by  
117 Fourier transform infrared spectroscopy (FTIR). The crystallinity was determined by infrared (IR) crystallinity ratios as proposed in  
118 the literatures (Carrillo, Colom, Sunol, & Saurina, 2004; Corgié, Smith, & Walker, 2011)(ESI 5).

119 Morphological properties of bleached and IONCELL-P-treated pulp were examined by Scanning Electron Spectroscopy (SEM)  
120 using a Zeiss Sigma VP scanning electron microscope (ESI 6).

121 The specific surface areas (SSA) of the freeze-dried bleached and IONCELL-P-treated pulps were measured by nitrogen sorption  
122 apparatus Tristar II (Micromeritics), and the data was analyzed using Tristar 3020 (Micromeritics) (ESI 7).

123 The GVL pulp and kraft pulp were refined to Schopper Riegler (SR) freeness of 31° and 40°, from which the hand sheets were  
124 made according to the ISO 5269-1 standard. The density and thickness, bulk and basic weight, internal bonds, tear, tensile,  
125 brightness and opacity characterizations of the hand sheets were determined according to ISO 534, ISO 536, TAPPI UM-403,  
126 ISO 1974, ISO1924-2 and ISO 2470 standards, respectively (ESI 8).

## 127 3. Results and discussion

### 128 3.1. GVL fractionation of birch wood for paper-grade pulp production

129 Table 1 summarizes the properties of the pulps obtained from the experiments. The reaction time threshold for a reject-free  
130 pulping was about 120 – 150 minutes. In contrast to a 50 wt% GVL concentration in the cooking liquor which was optimal for a  
131 single-staged cook for dissolving pulp production, we chose a GVL concentration of 75 wt% to produce hemicellulose-rich pulp,  
132 based on our previous experience (Fang & Sixta, 2015; Lê et al., 2016; Shokri et al., 2019) that a higher GVL concentration in the  
133 cooking liquor better preserved the hemicellulose by limiting the extent of carbohydrate hydrolysis without compromising the

delignification. As expected, the obtained pulps meet the specification for paper-grade pulp, particularly with a higher hemicellulose content, ca. 12 – 15 % on wood for reject-free cooks in comparison to ca. 8 – 11 % on wood in our preliminary study using 50 wt% GVL (Shokri et al., 2019). Higher hemicellulose preservation should improve its valorization rate via the IONCELL-P treatment. The pulp yield is comparable to that of a kraft pulp with a corresponding kappa number (Buzala et al., 2019). The optimum conditions were selected based on the lowest residual lignin content, expressed as the minimum pulp kappa number, and the least degraded cellulose fraction, expressed as the maximum pulp intrinsic viscosity (Sixta, 2006). A decrease in the degree of polymerization of cellulose is the result of acidic cleavage of glycosidic bonds in the cellulose chains under severe cooking conditions. The cellulose fraction was well preserved with relatively low yield loss (< 3% on wood, Table 1 and Figure 1a). At all L: W applied, the cellulose content remained approximately stable while the intrinsic viscosity stayed sufficiently high (> 1000 mL/g, Figure 1 b). A higher temperature (180°C vs 170°C) enabled a sufficient delignification in the uncatalyzed pulping experiments, which agrees with our previous work (Fang & Sixta, 2015). Highest delignification of about 85.8% was observed at the reaction times of 210 and 240 minutes and at a constant L:W ratio of 8. It was reported significant hemicellulose removal in the H<sub>2</sub>SO<sub>4</sub>- catalyzed pulping experiment with high GVL concentration, yielding a high-purity dissolving pulp (Alonso et al., 2017). In this study, 57.8% hemicellulose removal was achieved. A regression model was used to evaluate the effect of the L:W and the cooking time on kappa number and viscosity (ESI 1).

The optimized conditions for producing paper-grade pulp by GVL/water fractionation were selected as: 75 wt% GVL in an aqueous solution, a cooking temperature of 180°C for a duration of 210 minutes with a L:W ratio of 8 (entry 8/210 of Table 1). Under these conditions, hemicellulose removal and delignification were 57.8% and 85.5%, respectively. The residual lignin content of GVL pulp (6.3 % on pulp) was higher than that of a birch kraft pulp (3.1 % on pulp) and the screened pulp yield was

**Table 1.** Properties of the unbleached pulps obtained from GVL/water fractionation of birch wood chips in 75 wt% GVL solution at 180°C, for 90-240 min with L:W = 4-8 L/kg in the oil-bath digester. The wood component is calculated by multiplying the corresponding pulp component with the screened yield (%odp: percent on oven-dried pulp; %odw: percent on oven-dried wood).

Sample <sup>a</sup>	Screened Yield [%]	Rejects [%]	Spent liquor pH	Pulp component [%odp]			Wood component [%odw]			κ	η [mL/g]
				Cell <sup>b</sup>	Hemi <sup>c</sup>	lignin	Cell <sup>b</sup>	Hemi <sup>c</sup>	lignin		
Wood	-	-	-	-	-	-	40.2	31.3	23.3	-	-
Ref. <sup>d</sup>	-	-	-	69.9	29.3	0.8	-	-	-	-	-
4/90	29.8	39.2 <sup>e</sup>	3.66	57.8	26.2	16.0	17.2	7.8	4.7	84.3	-
4/120	56.8	8.4 <sup>e</sup>	3.66	58.6	25.5	13.7	34.1	14.8	7.8	71.5	1047
4/150	59.2	0.3 <sup>e</sup>	3.61	63.9	24.4	11.6	37.8	14.5	6.8	64.4	1085
4/180	60.3	0.0	3.60	63.9	25.4	10.6	38.5	15.3	6.4	53.1	1120
4/210	56.7	0.0	3.52	66.7	23.3	9.9	37.8	13.2	5.6	53.0	1090
4/240	53.9	0.0	3.50	68.8	24.5	6.6	37.1	13.2	3.5	38.0	1072
6/90	23.6	45.1 <sup>e</sup>	3.81	60.2	25.3	14.4	14.2	5.9	3.4	74.6	-
6/120	51.1	12.1 <sup>e</sup>	3.70	62.2	24.5	13.2	31.7	12.5	6.7	76.9	1056
6/150	59.0	2.2 <sup>e</sup>	3.74	64.0	24.2	11.7	37.7	14.3	6.9	59.7	1170
6/180	57.2	0.0	3.67	66.6	23.9	9.3	38.4	11.3	5.0	52.7	1150
6/210	57.0	0.0	3.61	68.7	23.8	7.4	39.2	13.6	4.2	37.6	1129
6/240	54.2	0.0	3.57	70.4	22.4	7.1	38.1	12.1	3.8	35.4	1091
8/90	34.0	23.3	3.77	60.4	25.8	13.6	20.6	8.8	4.6	72.5	1023
8/120	52.0	0.0	3.75	63.2	25.1	11.5	32.8	13.1	6.0	64.0	1117
8/150	58.2	0.0	3.76	65.9	24.7	9.3	38.4	14.4	5.4	50.0	1172
8/180	54.6	0.0	3.69	67.7	24.3	7.8	37.0	13.3	4.3	39.0	1197
8/210	53.4	0.0	3.63	68.9	24.7	6.3	36.8	13.2	3.3	29.8	1194
8/240	53.5	0.0	3.63	69.9	23.8	6.2	37.4	12.7	3.3	29.2	1137

<sup>a</sup> The sample is named as "solvent : wood ratio/fractionation time (in minutes)"; <sup>b</sup> Cellulose; <sup>c</sup> Hemicelluloses; <sup>d</sup> Reference pulp: ECF-bleached birch kraft pulp. <sup>e</sup> Higher L:W should facilitate the mass transfer of cooking chemical, resulting in lower rejects. These unexpected results in rejects could be due to the non-uniform mixing of the cooking liquor during experiments.

159 comparable to that of an unbleached kraft pulp. Due to the hydrolysis reaction under mild acidic conditions, the intrinsic viscosity  
 160 of unbleached GVL paper-grade pulp (1194 mL/g) was slightly less than that of a unbleached birch kraft pulp (1445 mL/g), but still  
 161 adequate for a standard ECF bleaching sequence (Borrega & Sixta, 2013)  
 162

163  
 164 **3.2. Pulp bleaching and characterization**

165 There were variations in the chemical composition between the pulp produced on a small scale (Table 1) and the pulp produced  
 166 on a larger scale (Table S 2.2) under the same optimized conditions.

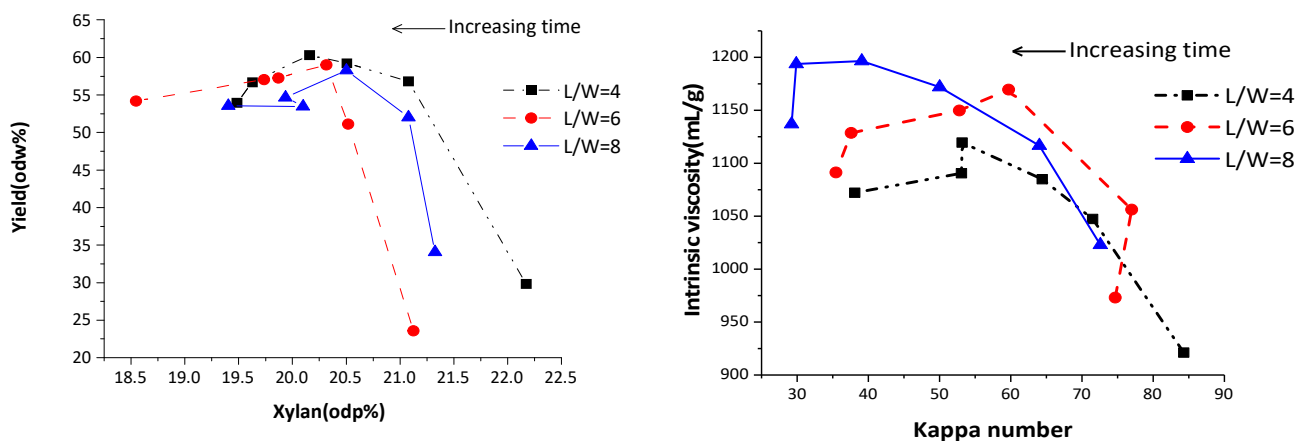
167 Oxygen delignification was the preferred method for cooking extension due to the high lignin selectivity, reflected in relatively low  
 168 yield loss and significant reduction in kappa number. Residual lignin content of pulp was removed by 38% after the first oxygen  
 169 delignification, 55% after the second one and >95% after the whole bleaching sequence, accompanied by only a marginal  
 170 reduction of intrinsic viscosity in the selected bleaching sequence was marginal, which confirms the preservation of the cellulose  
 171 fraction during bleaching (Table S 2.2). The viscosity reduction for birch kraft bleaching is significantly higher. Commercial fully  
 172 bleached birch kraft pulps have a viscosity of 808 mL/g (Roselli et al., 2016) and thus experience massive DP degradation of  
 173 cellulose during typical ECF bleaching, which is attributed to the resistance of hexenuronic acid (HexA), responsible for a high  
 174 share of kappa number in kraft hardwood pulps, during O-stage. HexA is only degraded under acidic oxidative conditions such as  
 175 those found in a chlorine dioxide stage of the ozone (Sixta, 2006). The bleachability of GVL pulps is therefore significantly better  
 176 than that of kraft pulps, mainly due to the absence of HexA in the unbleached pulp and the higher reactivity of the residual lignin.  
 177 As a result, a significantly higher unbleached lignin content can be accepted after GVL water fractionation than is the case with  
 178 conventional kraft pulp.

179 The total bleaching yield losses were 11.2 %odp (6.0 %odw), which is relatively low considering the very high residual lignin  
 180 content and comparable or better than birch kraft pulp bleaching with significantly lower initial lignin content. Of the total losses of  
 181 wood constituents, 72% are from lignin removal and 28% was from the loss of carbohydrates.

182 The mechanical properties of the GVL/water hand sheets were comparable with the kraft paper while consuming only about 50%  
 183 of the refining energy to achieve similar degree of freeness. Details on the refining results are summarized in Table S 8.1 (ESI 8).

184 **3.3. Kamlet-Taft parameters**

185 [EMIM][OAc] retains good cellulose dissolving power even up to a water content of 12 wt%, as shown in Table S 4.1 and Figure  
 186 S 4.1. Between 12 and 14 wt% water, cellulose is partially dissolved while hemicelluloses are completely dissolved. At a water  
 187 content of 13 wt%, as in the case of the BL-I-P-13% treatment, the  $\beta$  was 0.90 and  $(\beta-\alpha)$  was 0.39 (Table S 4.1). Under these  
 188 conditions, 32.8% of the dissolved fraction was cellulose, while at a water content of 14 wt% water, about 27.3 % cellulose was



189 **Figure 1.** Selectivity of GVL pulping of birch wood chips in oil-bath reactor at 180°C, in 75 wt% GVL, with L:W = 4 – 8 for 120 –  
 190 240 minutes (a) pulp yield vs. residual xylan (b) intrinsic viscosity vs. kappa number.  
 191

192

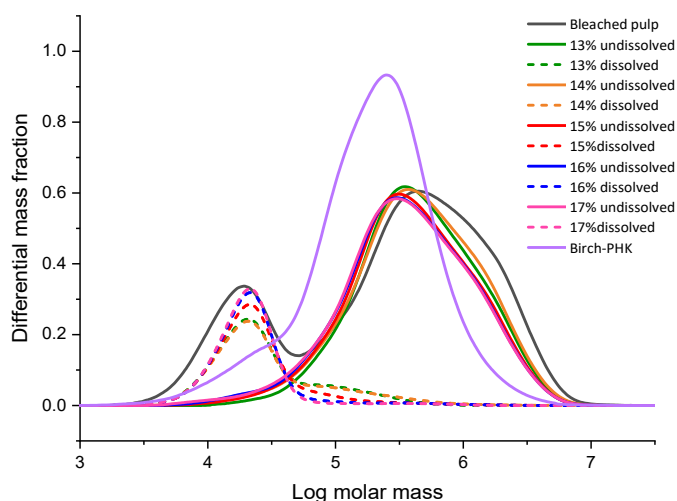
193 dissolved (Table 2). The selective dissolution window for hemicelluloses from birch pulp exists when [EMIM][OAc] contained 15-  
194 17 wt% water (Figure S4.1).

### 195 3.4. IONCELL-P extraction of bleached GVL pulp

196 Figure 2 and Table S 3.1 summarize the molecular mass distribution and macromolecular properties of the IONCELL-P treated  
197 bleached GVL pulps (undissolved fractions) and those of the isolated hemicelluloses (dissolved fractions). The short-chain  
198 hemicelluloses were clearly detectable in the pretreated pulp as a peak at log (molar mass) of ca. 4.5 (Figure 2). The IONCELL-P  
199 treatment effectively separated the hemicellulose fraction, yielding a less degraded pulp with lower polydispersity and higher  
200 cellulose purity than a commercial PHK birch pulp (Figure 2 and Table 2).

201 IONCELL-P extraction with an ionic liquid ([EMIM][OAc]) solution containing 12 wt% water resulted in highly viscous and  
202 unfilterable suspensions. In the experiments with 13 – 16 wt% water, the IONCELL-P extracted pulp was of high purity (>96%  
203 cellulose content). The significant increase in the intrinsic viscosity of the pulp (from 1056 to ca. 1200 – 1300 mL/g) indicated a  
204 good preservation of the cellulose fraction and successful removal of the low molecular mass hemicellulose fraction.  
205 [EMIM][OAc]/water solutions containing 13 – 16 wt% water effectively extracted hemicellulose from the bleached GVL birch pulp,  
206 as demonstrated in Table 2. The low molecular mass fraction (DP<100) decreased significantly after IONCELL-P treatment (Table  
207 S 3.1), while the high molecular mass fraction (DP>2000) was relatively well-preserved.

208 The cellulose peak from the experiment with 13 wt% water was slightly more pronounced, while the amount of short-chain  
209 fraction was lower (Figure 2), which was consistent with the lower PDI compared to the pulps from the other experiments (Table S 3.1).  
210 This also explains that the decreasing amount of water in the ionic liquid improves the ability of the IL/water mixture to solubilize  
211 biopolymers, which increases the extraction efficiency. As shown in Figure 2, the molar mass distribution of cellulose was  
212 effectively separated from that of the hemicellulose fraction in the experiments with 13 wt% water. Removal of the hemicellulose  
213 at 13 wt% water content was accompanied by the dissolution of low DP cellulose, resulting in a significant loss of yield with no  
214 apparent improvement in purity. A higher extent of purification can only be achieved after an extra enzymatic treatment, e.g.  
215 xylanase, which further degrades the hemicellulose fraction and significantly reduces the overlap in the molecular mass  
216 distribution of hemicelluloses and cellulose, thus improving the separation of the two carbohydrate fractions (Stepan, Michud,  
217 Hellstén, Hummel, & Sixta, 2016). The loss of cellulose yield when extracted with 13 or 14 wt% water in [EMIM][OAc] was  
218 confirmed by analyzing the chemical composition of the isolated hemicellulose fractions (Table 2). With 17 wt% water in the IL  
219 solution, the hemicellulose dissolution capacity of the IL/water mixture started to decrease. The sum of cellulose and  
220 hemicellulose yields is lower than expected (Table 2), which could be explained by the hemicellulose leaching loss during



221

222 **Figure 2.** Molecular mass distribution of the initial bleached paper-grade GVL birch pulp, IONCELL-P-treated bleached GVL birch  
223 pulps (undissolved fraction) and the isolated hemicelluloses (dissolved fraction), in comparison with birch-PHK pulp. IONCELL-P  
224 extraction was conducted in [EMIM][OAc] containing 13 – 17 wt% water, at 60°C, with 5% consistency, for 3 hours.

225 washing. ESI 9 presents similar IONCELL-P treatment of unbleached GVL birch pulps. However, the best purity was achieved at  
226 lower water content due to a less degraded cellulose fraction.

227 The effect of IONCELL-P extraction on GVL pulp was comparable to that on a kraft pulp. One study reported the IONCELL-P  
228 extraction of birch kraft pulp at the same temperature, time, and consistency, identifying the best selectivity of xylan removal in the  
229 range of 17.5-20 wt% water in [EMIM][OAc]. Consistent with our study, the amount of dissolved xylan increased with water  
230 content below 15 wt%, at the expense of cellulose yield. The cellulose loss in the precipitated hemicellulose fraction was  
231 considerably higher when extracted with an IL solution containing 13 wt% water compared to 14 wt% water (Froschauer et al.,  
232 2013). Besides, another study reported the successful employment of another IL, 1,5-diazabicyclo[4.3.0]non-5-ene acetate  
233 [DBNH][OAc], to produce dissolving pulp from birch kraft pulp under similar conditions (Stepan et al., 2016). IONCELL-P  
234 fractionation at 5% consistency with 15% water and 85% [DBNH][OAc] at 60°C for 180 min yield a pulp with 7.5% residual xylan.  
235 The introduction of a xylanase treatment prior to IONCELL-P extraction could further reduce the xylan content to 5.2%. Lower  
236 pulp consistency of 2% a further decrease of the xylan content to 6.5% in the pulp could be achieved after IONCELL-P  
237 fractionation, due to the lower density of the suspension, thus facilitating the diffusion processes. After three stages of xylanase  
238 pretreatment, IONCELL-P extraction, and acid treatment, respectively, with the same consistency, the xylan decreased to 4.4%  
239 (Stepan et al., 2016). The amount of residual xylan in the bleached GVL was less than 3% after a single step of IONCELL-P  
240 extraction in [EMIM][OAc].

241 **Table 2.** Chemical composition of the pulp obtained from the IONCELL-P extraction of bleached GVL birch pulp. IONCELL-P  
242 extraction was conducted in [EMIM][OAc] containing 12 – 17 wt% water, at 60°C, with 5% consistency, for 3 hours. (%odp:  
243 percent on oven-dried pulp).

Sample <sup>a</sup>	IONCELL-P extracted pulp (undissolved fraction)						Precipitated hemicelluloses (dissolved fraction)				
	PDI	viscosity [mL/g]	Yield [%]	Cell <sup>c</sup> [%odp]	Xyl <sup>d</sup> [%odp]	Glm <sup>e</sup> [%odp]	Hemi. rem. <sup>f</sup> [%]	Yield [%]	Cell <sup>c</sup> [%odp]	Xyl <sup>d</sup> [%odp]	Glm <sup>e</sup> [%odp]
GVL	13.7	1056	100	76.4	18.7	3.5	-	-	-	-	-
GVL-IP-12%							Un-filterable				
GVL-IP-13%	3.0	1216	65.9	96.7	2.4	0.8	85.7	22.5	32.8	56.4	10.7
GVL-IP-14%	3.8	1197	68.4	96.6	2.4	0.9	85.2	18.3	27.3	63.2	9.4
GVL-IP-15%	3.4	1266	72.8	96.5	2.1	1.2	85.2	16.1	b	b	b
GVL-IP-16%	3.7	1331	72.7	96.5	2.2	1.2	84.8	15.6	b	b	b
GVL-IP-17%	3.9	1258	75.6	95.9	2.8	1.2	82.1	13.7	b	b	b

244 <sup>a</sup> GVL = Bleached GVL birch pulp produced from the optimized up-scaled experiment, IP = IONCELL-P, number: water content of  
245 [EMIM][OAc] solution; <sup>b</sup> Not available; <sup>c</sup> Cellulose; <sup>d</sup> Arabinoglucorono xylan; <sup>e</sup> Galactoglucomanan; <sup>f</sup> Hemicelluloses removal.  
246  
247

248  
249 **Table 3.** Comparison of the prehydrolysis-kraft (PHK), prehydrolysis-soda-anthraquinone (PH-Soda-AQ), GVL - IONCELL-P (IP)  
250 pulp produced from birch wood.

Sample	$\eta$ [mL/g]	Cellulose	Hemicellulose	Mn <sup>a</sup> [kDa]	Mw <sup>b</sup> [kDa]	PDI <sup>c</sup>	DP<100 <sup>d</sup>	DP>2000 <sup>e</sup>
PHK <sup>f</sup>	468	92.3	6.8	75.4	328.4	4.4	4.2	28.9
PH-Soda-AQ <sup>g</sup>	507	94.2	5.8	76.9	352	4.6	4.0	33.0
GVL-IP-14% <sup>h</sup>	1197	96.6	3.3	197.2	755.5	3.8	0.79	60.4

251 <sup>a</sup> The number average molecular mass; <sup>b</sup> The weight average molecular mass; <sup>c</sup> Poly dispersity index; <sup>d</sup> The fraction with degree  
252 of polymerization lower than 100; <sup>e</sup> The fraction with degree of polymerization higher than 2000; <sup>f</sup> Commercial PHK birch pulp; <sup>g</sup>  
253 Birch pulp produced from prehydrolysis at 170°C for 100 min (effective time), soda-anthraquinone cook at 150°C, H-factor 350,  
254 and O-A-D0-EP-P bleaching (Testova et al., 2014); <sup>h</sup> birch pulp produced from GVL cook (optimized up-scaled experiment),  
255 OOD<sub>0</sub>EPQP bleaching, and IONCELL-P treatment in [EMIM][OAc] containing 14 wt% water at 60°C with 5% consistency for 3  
256 hours.  
257



258 The chemical composition and macromolecular properties of IONCELL-P treated bleached birch GVL pulp approached that of an  
259 acetate-grade dissolving pulp and far exceeded the quality of common dissolving pulp such as prehydrolysis kraft or  
260 prehydrolysis-soda-anthraquinone pulps (Table 3).

### 261 262 3.5. Fiber morphology analysis by SEM and physical gas sorption

263 The microscopic structure and fiber surface morphology of the bleached GVL pulp (produced from the optimized up-scaled  
264 experiment) and the corresponding IONCELL-P treated pulp were examined by SEM. The IONCELL-P treatment resulted in  
265 thinner fibers, as fiber diameter was 15.51  $\mu\text{m}$  in the bleached pulp and 9.15  $\mu\text{m}$  in the IONCELL-P treated pulp, although,  
266 IONCELL-P was mild and did not drastically change the fiber structure (Figure 3). Morphological change of the pulp was further  
267 investigated by BET surface area determination.

268 All experiments exhibited type II isotherms and a mesoporous texture (84-110  $\text{\AA}$ ) and revealed no significant increase in SSA  
269 (ESI 7). A slight increase in SSA can be attributed mainly to the removal of hemicelluloses and the associated increased porosity.  
270 The SSA of all analyzed fibers (Figure 4), was about 1 - 1.5  $\text{m}^2/\text{g}$ , which is consistent with that of birch kraft pulp (Hellström,  
271 Heijnesson-Hultén, Paulsson, Håkansson, & Germgård, 2014).

272 The total crystalline index and lateral order index of the pulp samples (Table S5.1) were almost identical, suggesting that the  
273 crystallinity and orientation of the cellulosic fibers remained unchanged after IONCELL-P extraction, which confirms that  
274 IONCELL-P treatment did not affect the intra molecular H-bonds and the three-dimensional network of cellulosic fibers (ESI 5).

## 275 4. Conclusions

276 GVL pulping, an environmentally friendly organosolv fractionation concept was investigated for the production of birch wood  
277 paper- grade pulp, which was then purified by an IONCELL-P treatment to high-purity pulp. The GVL content was selected at  
278 75wt% to reduce the hydrolytic activities upon carbohydrate and produce a paper-grade hemicellulose-rich pulp which was then  
279 further fractionated to dissolving pulp and hemicellulose. Under optimum pulping conditions of 75 wt% GVL in the pulping solution,  
280 180°C cooking temperature with a reaction time of 210 minutes and an L:W ratio of 8, a pulp with a cellulose content of 69% and  
281 a hemicellulose content of 24.7% was obtained from birch wood at a high pulp viscosity of 1194  $\text{mL/g}$ , in good comparability with  
282 a kraft pulp. In addition, mechanical properties of hand sheets made from GVL pulp were similar to kraft pulp while the refining  
283 energy consumption was significantly lower. The GVL fractionation at such proposed conditions is, therefore, an interesting  
284 alternative to conventional paper-pulp manufacturing process, with high potential for industrial implementation.

285 The pulp produced under optimal conditions was delignified in a sequential two-stage oxygen treatment and bleached with an  
286 ECF sequence to 86% ISO-brightness. Subsequently, the GVL pulp was subjected to IONCELL-P treatment to produce a  
287 dissolving pulp with significantly higher purity than PHK and PH-Soda-AQ pulp produced from the same raw material and at the  
288 same time significantly higher molecular mass, measured as pulp viscosity of 1197  $\text{mL/g}$  compared to 476 in PHK and 507  $\text{mL/g}$   
289 in PH soda AQ pulp, respectively.

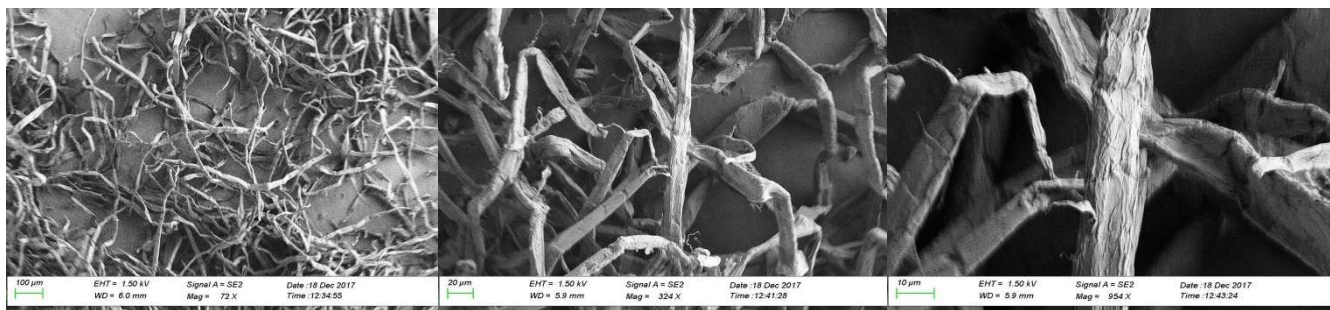
290 Optimal hemicellulose extraction efficiency was achieved by using [EMIM][OAc] containing 14 to 16 wt% water. Under these  
291 conditions, more than 90% of the xylan can be separated with minimal cellulose yield loss or structural change. By applying the  
292 concept of net basicity, ( $\beta$ - $\alpha$ ) vs  $\beta$ , the range of selective hemicelluloses separation can be well selected for each system. The  
293 hemicelluloses could be recovered in high purity from the extraction filtrate.

294 As expected and confirmed by various analytical methods, the IONCELL-P treatment was a mild treatment that yielded the  
295 resulting pulp with insignificant changes in structure and morphology according to the SEM images, with the crystallinity and  
296 orientation of the cellulose fibers remaining approximately constant, confirming that the intramolecular hydrogen bonds of the  
297 cellulose fibers and the three-dimensional structure of the fibers remained approximately intact. In addition, this treatment makes  
298 the fibers a little flexible with a small increase in specific surface area due to the removal of hemicelluloses from the matrix.

299 With the developed GVL-IP pulp, it was possible to achieve high pulp purity with unchanged intrinsic viscosity, which is a  
300 prerequisite for the production of acetate and ether pulps of the highest quality, which cannot be achieved by any conventional  
301 methods without sustaining significant yield loss (high pre-hydrolysis intensity) or structure-altering treatments (such as cold  
302 caustic extraction, which leads to partial conversion to cellulose II and to the formation of alkali-induced carbohydrate degradation  
303 products). Besides, the recycling of two organic solvents (GVL and [EMIM][OAc]) are of utmost importance for the scaling-up of

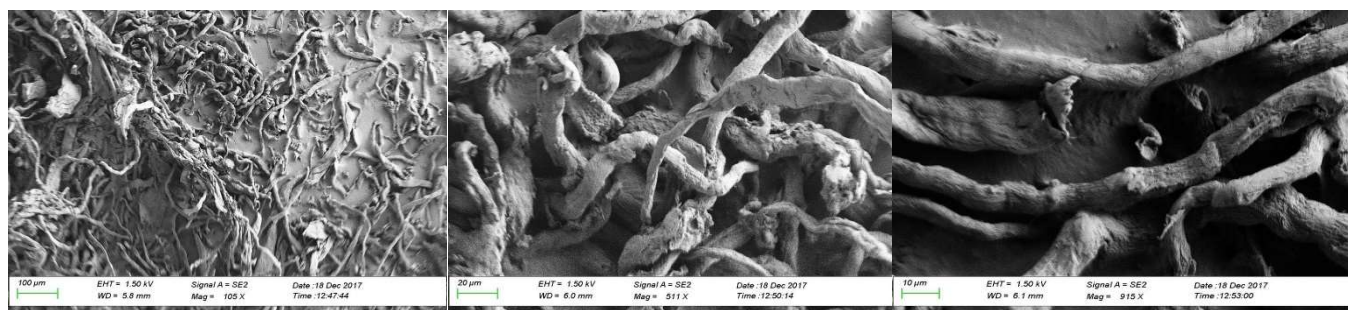
304 the GVL-IP process. This issue has been extensively and intensively researched on, resulting in reasonable resolution for a close-  
 305 loop operation for these two solvents (Elsayed, 2021; Lê, 2018).

306 a.  
 307



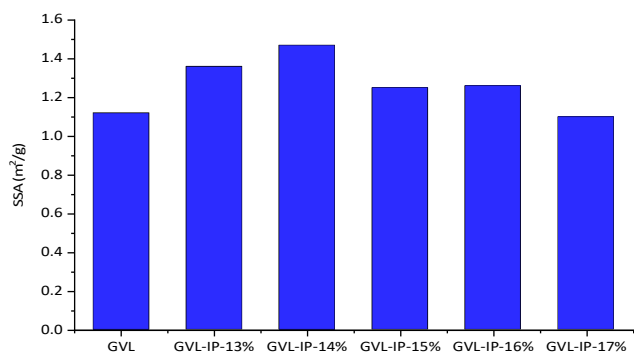
100 μm magnification                      20 μm magnification                      10 μm magnification

310 b.



100 μm magnification                      20 μm magnification                      10 μm magnification

313 **Figure 3.** SEM images of (a) the paper-graded bleached GVL birch pulp and (b) the corresponding IONCELL-P extracted pulp.



314  
 315 **Figure 4.** Specific surface area of bleached and IONCELL-P extracted GVL birch pulp. GVL = Bleached GVL birch pulp produced  
 316 from the optimized up-scaled experiment, IP = IONCELL-P, number: water content of [EMIM][OAc] solution.

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### 323 **Supplementary data**

324 Supplementary material related to this article can be found, in the online version, at doi:

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