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Birch wood pre-hydrolysis vs pulp post-hydrolysis for the production of xylan-based compounds and cellulose for viscose application

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Abstract

Hydrothermal treatments of birch wood and kraft pulp were compared for their ability to extract the xylan and produce viscose-grade pulp. Water post-hydrolysis of kraft pulp produced a high-purity cellulosic pulp with lower viscosity but higher cellulose yield than traditional pre-hydrolysis kraft pulping of wood. Post-hydrolysis of pulp also increased the crystallite dimensions and degree of crystallinity in cellulose, and promoted a higher extent of fibril aggregation. The lower specific surface area in post-hydrolyzed pulps, derived from their larger fibril aggregates, decreased the accessibility of -OH groups. However, this lower accessibility did not seem to decrease the pulp reactivity to derivatizing chemicals. In the aqueous side-stream, the xylose yield was similar in both pre- and post-hydrolysates, although conducting post-hydrolysis of pulp in a flow-through system enabled the recovery of high purity and molar mass (~10 kDa) xylan for high-value applications.

Keywords:

Cellulose, dissolving pulp, hydrothermal treatment, viscose, xylan

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1 1. Introduction

2 In the last decade, the wood pulping industry has experienced a steady increase in the demand of dissolving-grade
3 pulps as the world consumption has increased from 3.3 million tons in 2007 to 6.5 million tons in 2015 (FAO
4 Yearbook 2007, 2015). Dissolving pulps, containing over 90% cellulose and low amounts of impurities, are used
5 in the manufacture of regenerated cellulose fibers, cellulose ethers, and cellulose esters for a wide range of
6 applications, i.e., textiles, films, food, drugs. The high demand for dissolving pulps, mostly driven by the
7 production of viscose fibers for textiles, is partly related to the growing world population and the increasing
8 purchasing power in Asian markets, and thus is expected to continue increasing in the future (Liu, Shi, Cheng, &
9 He, 2016).

10 Dissolving wood pulps are industrially produced by acid sulfite pulping or by pre-hydrolysis kraft (PHK) pulping.
11 Since both of these processes were developed in the first half of last century, new pulping methods that are in line
12 with the requirements of modern pulp mills are currently being investigated. Such requirements include a higher
13 efficiency in the use of raw materials, lower consumption of chemicals and improved recovery cycle, and diverse
14 product portfolio through valorization of side-streams. Examples of recently developed pulping methods to
15 produce dissolving wood pulps are the SO₂-ethanol-water pulping (Iakovlev, You, van Heiningen, & Sixta, 2014),
16 and Organosolv-type fractionation processes that utilize organic solvents like γ -valerolactone (Alonso et al., 2017;
17 Lê, Ma, Borrega, & Sixta, 2016) or methyl isobutyl ketone (Bozell et al., 2011). Alternatively, the upgrade of
18 paper (kraft) pulps into dissolving pulps by selectively removing the hemicellulosic fraction is being investigated.
19 Pulp post-treatments are mainly based on the application of enzymatic hydrolysis and cold caustic extraction
20 (Gehmayr, Schild, & Sixta, 2011; Ibarra, Köpcke, & Ek, 2009), nitren extraction (Janzon, Puls, & Saake, 2006),
21 and ionic liquid extraction (Froschauer et al., 2013; Roselli, Hummel, Monshizadeh, Maloney, & Sixta, 2014).

22 Recently, we have shown that high-purity cellulosic pulp can also be produced by water post-hydrolysis of
23 hardwood kraft pulp (Borrega & Sixta, 2013; Borrega, Concha-Carrasco, Pranovich, & Sixta, 2017), in which the
24 water hydrolytic stage is implemented after pulping, instead of prior to pulping as in a conventional PHK process.
25 Water post-hydrolysis of pulp requires elevated temperatures around 240 °C, but the treatment times are very short
26 (≤ 10 min). One of the main benefits of water post-hydrolysis, compared to other pulp post-treatments reported in
27 the literature, is that water is the only solvent used, and thus complex and costly chemical recovery systems are
28 not required. The pulp quality, in terms of chemical and macromolecular properties, appears to be comparable to
29 that of commercial PHK pulps for viscose application (Borrega et al., 2017). Nonetheless, the most important
30 quality parameter of any dissolving pulp is probably its so-called reactivity.

31 Pulp reactivity refers to the tendency of the pulp to react with derivatising chemicals under certain reaction
32 conditions. The pulp reactivity is a function of its chemical, molecular and fibrillar features, and thus cannot be
33 defined by a single parameter (Sixta, 2006). In practice, however, the chemical reactivity of pulp is typically
34 estimated with indirect methods that determine its solubility in a specific solvent system. In the viscose industry,
35 the most reliable indicator to assess the pulp reactivity is the filterability value of the cellulose xanthate as
36 determined by the Treiber test, which mimics all the steps applied in the actual conversion of pulp into viscose
37 dope. This method is not only complex and time-consuming, but also needs special equipment and relatively large
38 amounts of pulp material, making the analyses difficult in laboratory scale. Therefore, the Fock test, a simplified
39 method that quantifies the amount of cellulose dissolved (or regenerated) in a solution containing sodium

40 hydroxide (NaOH) and carbon disulfide (CS₂), is commonly used to provide a measure of the pulp reactivity in
41 viscose conversion (Christoffersson, Sjoström, Edlund, Lindgren, & Dolk, 2002; Engström, Ek, & Henriksson,
42 2006; Miao et al., 2014). Since the reactivity is related to the accessibility of functional groups in the pulp,
43 predominantly hydroxyl groups (-OH), it may also be estimated from several molecular and structural features
44 (Gehmayr et al., 2011; Wollboldt, Zuckerstätter, Weber, Larsson, & Sixta, 2010). In this article, we will discuss
45 the pulp reactivity based on its solubility behavior in chemical solvent systems.

46 In recent years, the transformation of traditional pulp mills into advanced biorefineries, having a wider product
47 portfolio than simply paper- or dissolving-grade pulp, has attracted a lot of attention. Modern pulp mills
48 (biorefineries) are regarded as one of the cornerstones for the development of biobased economies. Within this
49 context, water post-hydrolysis of pulp is of interest because, if applied in a flow-through system, the extracted
50 hemicelluloses may be recovered from the aqueous hydrolysate in high yield and relatively high molar mass,
51 depending on the flow rate (Borrega & Sixta, 2013; Borrega, Concha-Carrasco, Pranovich, & Sixta, 2017).
52 Hemicelluloses are valuable sugars that can be utilized in a wide range of chemical and material applications
53 (Deutschmann & Dekker, 2012; Hansen & Plackett, 2008). It should be mentioned that the extraction and recovery
54 of hemicelluloses for their subsequent valorization can also be realized by water pre-hydrolysis of wood. However,
55 the presence of other chemical compounds originating from lignin and extractives in the wood pre-hydrolysates
56 tends to complicate the recovery of hemicelluloses using membrane separation techniques (Koivula et al., 2011).
57 Owing to the more homogenous composition of pulp, compared to wood, the recovery of the hemicelluloses from
58 post- hydrolysates may be accomplished rather easily by membrane ultrafiltration.

59 In this study, we have compared the performance of pre- and post-hydrolysis processes to produce viscose-grade
60 pulp on the one hand, and xylan-based sugars on the other hand. Water pre-hydrolysis experiments of birch wood
61 under different intensities were first conducted prior to kraft pulping. After pulping, the unbleached pulps were
62 subjected to post-hydrolysis experiments to further decrease the xylan content, and selected pulps with potential
63 to be used in viscose production were then bleached. The chemical, molecular, and supramolecular properties of
64 the bleached pulps were thoroughly characterized and related to the accessibility and reactivity of the pulps.
65 Finally, the recovery of sugars from the aqueous hydrolysates as well their chemical and molecular characteristics
66 were determined. Based on the results, the advantages and disadvantages of water pre- and post-hydrolysis
67 processes are here presented.

68 **2. Experimental**

69 *2.1. Wood material*

70 Birch (*Betula spp.*) wood chips were delivered by a pulp mill in Finland. Upon delivery, the chips were screened
71 according to the SCAN-CM 40:01 method and stored in the freezer until further use. The identified chemical
72 composition of the wood was 38.4% glucose, 20.8% xylose, 1.6% mannose, 0.6% galactose, 0.4% rhamnose,
73 0.3% arabinose, 20.7% acid insoluble (Klason) lignin and 4.8 % acid soluble lignin (ASL).

74 *2.2. Production of pulps*

75 A series of pulps were produced by water pre-hydrolysis, kraft pulping, and water post-hydrolysis. Pre-hydrolysis
76 of birch wood chips was conducted in 2.5 L autoclaves in a rotating air-bath digester (Haato Oy, Finland), at a
77 liquid-to-wood ratio of 4:1 L/kg. The temperature in the autoclaves was raised to 170 °C and kept constant until

78 a predetermined P-factor (170, 550, or 1000) was reached. The P-factor is an intensity factor that combines the
79 effects of temperature and time into a single variable, using an Arrhenius-type equation with an activation energy
80 of 125.6 kJ mol⁻¹, corresponding to the removal of easily degradable xylan (Sixta, 2006). Once the P-factor was
81 reached, the autoclaves were submerged in a cold water-bath to quench further reactions. The aqueous hydrolysate
82 and pre-hydrolyzed chips were separated by filtration and stored for subsequent experiments and analyses. About
83 8-10 grams (o.d.) of chips from each pre-hydrolysis experiment, roughly corresponding to 5% of the initial mass
84 of wood charged into the autoclave, were oven-dried, thoroughly washed, and oven-dried again to determine the
85 wood yields after washing.

86 Kraft pulping of raw and pre-hydrolyzed wood chips (without washing) was conducted in the air-bath digester at
87 a liquid-to-wood ratio of 4:1 L/kg. White liquor was prepared from concentrated solutions of NaOH and Na₂S in
88 deionized water. The effective alkali (EA) charge was 19% on initial oven-dry (o.d.) wood, and the sulphidity was
89 30%. The temperature in the autoclaves was raised to 155 °C and kept constant until a predetermined H-factor
90 (200, 400, 650, or 1000) was reached. Similar to the P-factor, the H-factor is an intensity factor that combines the
91 effects of pulping temperature and time into a single variable (Vroom, 1957). The H-factor was selected in order
92 to reach a kappa number of about 16 in the unbleached pulp. The pulping was ended by submerging the autoclaves
93 in a cold water-bath, and after cooling, the pulp was recovered by filtration, thoroughly washed, and screened in
94 a table-top plate screener (0.35 mm mesh). The amount of rejects was less than 0.5% on dry pulp.

95 Water post-hydrolysis of unbleached kraft and PHK pulps was conducted in a 190 mL flow-through percolation
96 reactor (Unipress Equipment, Poland). About 15 g (o.d.) of pulp were placed in the reactor, equipped with a high-
97 pressure pump, preheater and electric heaters, heat exchanger, and back-pressure regulator (BPR). Water at room
98 temperature was initially pumped through the reactor to wet the pulp and to set the BPR to the operating pressure.
99 The preheater was then turned on, and once the water reached the desired setup temperature, the hot water was
100 circulated into the reactor. The aqueous hydrolysate exiting the reactor was immediately cooled by the heat
101 exchanger and collected in a sampling container. After a predetermined amount of time, the pump was stopped
102 and the pulp was washed (and cooled) by circulating cold tap water through the reactor. The treatment temperature
103 was 240 °C, treatment times ranged from 3 to 15 min, and the flow rate was 400 mL/min.

104 Selected pulps were bleached following a D₀-Ep-P sequence. The bleaching conditions were: D₀: temperature 50
105 °C, 60 min, kappa factor 0.25; Ep: temperature 70 °C, 60 min, 1.5% NaOH, 0.5% H₂O₂; P: temperature 70 °C,
106 120 min, 0.6% NaOH, 0.5% H₂O₂, 0.5 kg of Mg per ton of o.d. pulp. The pulp consistency was 10% in all
107 bleaching stages, and the bleaching was performed in plastic bags heated by steam in a water-bath. Bleaching
108 yields were not be determined.

109 *2.3. Chemical composition*

110 The carbohydrates and lignin composition in wood and pulp was determined after a two-stage acid hydrolysis,
111 according to the analytical method NREL/TP-510-42618 issued by the US National Renewable Laboratory
112 (NREL). Neutral monosaccharides were determined by high-performance anion exchange chromatography with
113 pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 (Sunnyvale CA, USA) system, equipped
114 with a CarboPacTM PA-20 (3.0 X 150 mm) analytical column. Milli-Q water was the eluent used, with a flow rate
115 of 0.4 mL/min at 30 °C temperature. Based on the amount of neutral monosaccharides, the cellulose, xylan and
116 glucomannan fractions in the lignocellulosic material were calculated with the Janson's formulas (Janson, 1970).

117 With these formulas, cellulose is defined as the content of anhydroglucose in the sample after subtracting the
118 contribution of glucose to glucomannan, and xylan is defined as the content of anhydroxylose and uronic acid
119 constituents. The amount of Klason lignin was quantified gravimetrically, and the amount of ASL was determined
120 in a Shimadzu (Kyoto, Japan) UV-2550 spectrophotometer at a wavelength of 205 nm, using an adsorption
121 coefficient of 110 L/(g·cm). The kappa number in the unbleached pulps was determined according to the SCAN-
122 C 1:100 method.

123 The chemical composition of aqueous pre- and post-hydrolysates was determined according to the analytical
124 method NREL/TP-510-42623 issued by the US NREL. Monosaccharides were quantified by HPAEC-PAD by
125 direct injection and after total hydrolysis in an autoclave at 121 °C for 60 min. The amount of oligo- and/or
126 polysaccharides was calculated by difference in the monosaccharide content before and after total hydrolysis. The
127 amount of soluble lignin in the hydrolysates was determined in the Shimadzu UV-2550 spectrophotometer at a
128 wavelength of 205 nm, using an adsorption coefficient of 110 L/(g·cm).

129 *2.4. Macromolecular properties*

130 The intrinsic viscosity of the pulps was determined in 0.5 M cupriethylenediamine (CED) according to the SCAN-
131 CM 15:99 method. Detailed information on the macromolecular properties of bleached pulps was provided by gel
132 permeation chromatography (GPC). For the GPC analyses, the pulps were first activated by a sequential addition
133 of water, acetone, and N,N-dimethylacetamide (DMAc). The activated samples were then dissolved in 90 g/L
134 lithium chloride (LiCl) containing DMAc at room temperature and under gentle stirring. The dissolved samples
135 were diluted to 9 g/L LiCl/DMAc, filtered through 0.2 µm syringe filters, and analyzed in a Dionex Ultimate 3000
136 (Sunnyvale CA, USA) system, equipped with a guard and four analytical Agilent (Santa Clara, USA) PL-gel
137 Mixed-A columns (7.5 X 300 mm), and coupled with a Shodex (Tokyo, Japan) RI-101 refractive index detector.
138 The flow rate was 0.75 mL/min, and the temperature was 25 °C. Narrow pullulan standards (343 Da - 2350 kDa;
139 PSS, Mainz, Germany) were used to calibrate the system. The molar masses of the pullulan standards were
140 modified to correspond to those of cellulose, as reported in Borrega, Tolonen, Bardot, Testova, & Sixta (2013).

141 The molar mass characteristics in selected aqueous pre- and post-hydrolysates were determined by size exclusion
142 chromatography (SEC) in a PSS (Mainz, Germany) instrument, equipped with MCX 1000 and 100 000 columns
143 with a pre-column, and coupled with a Waters (Milford, USA) 2414 refractive index detector. Prior to the analyses,
144 the samples were dissolved in 1 M NaOH and filtered through 0.45 µm filters. The SEC measurements were
145 performed in 0.1 M NaOH as eluent, at pH 13, and with a flow rate of 0.5 mL/min at 25 °C temperature. The
146 molar mass distribution (MMD) of the dissolved compounds were calculated against 8 pullulan standards (6.1 -
147 708 kDa), using the Waters Empower 3 software.

148 *2.5. Supramolecular structure*

149 Structural characterization of the bleached pulps was performed by cross-polarization magic angle spinning
150 carbon-13 nuclear magnetic resonance (CP/MAS ¹³C-NMR) and by wide-angle X-ray scattering (WAXS). For
151 the CP/MAS ¹³C-NMR analyses, the pulp samples (water content > 40%) were packed uniformly in a zirconium
152 oxide rotor. The NMR spectra were recorded in a Bruker Avance III AQS 400 SB instrument operating at 9.4 T.
153 All measurements were carried out at 295 (±1) K with a magic angle spinning (MAS) rate of 10 kHz. A 4-mm
154 double air-bearing probe was used. Data acquisition was performed using a cross-polarization (CP) pulse

155 sequence, i.e., a 2.95 microseconds proton 90-degree pulse and an 800 microseconds ramped (100–50 %) falling
156 contact pulse, with a 2.5 s delay between repetitions. A SPINAL64 pulse sequence was used for ¹H decoupling.
157 The Hartmann-Hahn matching procedure was based on glycine. The chemical shift scale was calibrated to the
158 TMS-scale (tetramethylsilane, (CH₃)₄Si) by assigning the data point of maximum intensity in the alpha-glycine
159 carbonyl signal to a shift of 176.03 ppm. Four thousand ninety-six transients were recorded on each sample leading
160 to an acquisition time of about 3 h. The software for spectral fitting was developed at Innventia AB and is based
161 on a Levenberg-Marquardt algorithm (Larsson, Wickholm, & Iversen, 1997). All computations were based on
162 integrated signal intensities obtained from spectral fitting (Wickholm, Larsson, & Iversen, 1998). The errors given
163 for parameters obtained from the fitting procedure are the standard error of the mean with respect to the quality
164 of the fit.

165 For the WAXS analyses, the pulps (air-dried) were hand-pressed into 2.1 mm thick metal rings and sealed with 6
166 μm thick Mylar foils. The analyses were performed in a custom-built scattering instrument, consisting of an X-
167 ray generator (Siemens), an X-ray tube with a Cu anode (λ=1.541 Å) and point focus, a collimating Montel
168 multilayer monochromator, and a two-dimensional image plate detector (MAR345, Marresearch GmbH). A 20-
169 min measuring time was used to record a two-dimensional powder scattering pattern that was averaged over the
170 azimuthal angles to obtain the intensity as a function of the scattering angle (Copper Kα energy, 8.0 keV). The
171 data were corrected for the noise of the detector, and normalised with the primary beam transmission before Mylar
172 and air background subtraction. Flat panel, polarization and angle-dependent absorption corrections were then
173 applied to the data. The sample crystallinity was estimated by fitting an amorphous background and the 15
174 strongest reflection of cellulose Iβ (Nishiyama, Langan, & Chanzy, 2002) to the measured intensities, using the
175 amorphous fitting method presented in Ahvenainen, Kontro, & Svedström (2016). The Gaussian peak fits were
176 used to estimate the average crystallite size based on the 110, 110 and 200 reflections using the Scherrer equation
177 with K=0.9.

178 2.6. Accessibility by dynamic vapor sorption

179 The accessible -OH groups in the pulps were quantified after deuteration in a dynamic vapor sorption (DVS)
180 apparatus (Surface Measurement Systems, UK). About 10 mg of air-dry bleached pulp were placed in a small
181 aluminum pan in a climate-controlled chamber of 100 cm³ volume. The pan was connected to a microbalance
182 with a measuring accuracy of 0.1 μg. The pulp was first dried at 25 °C by lowering the relative humidity (RH) in
183 the chamber down to 0% with nitrogen gas (flow rate 200 cm³ min⁻¹), until the change in pulp mass over a 10-
184 minute period (dm/dt) was less than 0.0005 %. Thereafter, the RH in the chamber was increased to 95% in a
185 deuterium oxide (D₂O) atmosphere and kept constant for 10 hours, during which the pulp mass reached an
186 equilibrium. Finally, the RH was lowered again to 0% with dry nitrogen gas until the change in pulp mass over a
187 10-minute period (dm/dt) was less than 0.0005 %. Because of the relative difference in molar mass between
188 hydrogen and deuterium, the amount of accessible -OH groups in the pulp sample was calculated according to Eq.
189 1:

$$190 \quad A = \frac{m_f - m_i}{m_i} \times 1000 \left(\frac{mmol}{g} \right) \quad [1]$$

191 where A is the amount of accessible -OH groups, m_f is the dry mass of the deuterated pulp sample at the end of
192 the experiment, and m_i is the dry mass of pulp after the first drying sequence (before exposure to D₂O). The atomic

193 mass difference between deuterium (^2H) and protium (^1H) was approximated to 1 g mol^{-1} . Based on the amount
194 of accessible -OH groups and the chemical composition of the pulp, the relative accessibility of -OH groups was
195 calculated from the theoretical value of 18.5 mmol and 15.2 mmol of -OH groups per gram of anhydroglucose
196 (AGU) and anhydroxylose (AXY) units, respectively. It was considered that -OH groups in the C2, C3 and C6 of
197 the AGU unit and those in the C2 and C3 of the AXY unit were accessible.

198 To exclude any hysteresis effects during the drying-rewetting-drying cycle, two pulp samples containing the
199 highest and lowest amount of hemicelluloses were subjected to the same sorption cycle as described above, but
200 the rewetting stage was performed in a water vapor atmosphere, instead of a D_2O atmosphere. In both samples,
201 the difference in dry mass of pulp between the first and second drying sequence was less than 0.1%.

202 *2.7. Reactivity of pulps*

203 The reactivity of the pulps in a viscose conversion process was estimated by the Fock method; the analyses were
204 performed at MoRe Research (Sweden). With this method, about 0.5 grams of pulp are mixed together with a
205 solution containing sodium hydroxide (NaOH) and excess amounts of carbon disulfide (CS_2) to form cellulose
206 xanthate. By addition of sulfuric acid (H_2SO_4), some of the cellulose in the xanthate is regenerated, and the yield
207 of regenerated cellulose is given to express the Fock reactivity. In the analyses of our pulps, the concentration of
208 NaOH was 9%, but other experimental details were not disclosed. More information about the principle and details
209 of the Fock method can be found elsewhere (Engström et al., 2006; Tian et al., 2013).

210 The chemical reactivity of the pulps was further determined by the dissolution-based torque reactivity (DTR) test
211 (Ceccherini & Maloney, 2017). Such test monitors the rheological behavior of pulp fibers during dissolution in
212 CED, and estimates pulp reactivity in terms of dissolution rate and time. Prior to the dissolution tests, the pulps
213 were stored overnight at a solids content of ca. 20%. For each measurement, 0.1875 g (oven dry basis) of pulp
214 were diluted with deionized water to a final solids content of 1.5%. The sample was then placed in a Physica MCR
215 300 rheometer (Anton Paar GmbH) equipped with 4-blades-vane and basket geometry. The vane height was set
216 at 0.5 mm from the basket bottom, and the temperature was adjusted to 23 °C. The fiber suspension was stirred
217 for an interval of 5 min at 200 s^{-1} shear rate, after which the dissolution was started by injecting 12.5 ml of 1 M
218 CED (Sigma Aldrich). While maintaining a constant shear rate, the dissolution of the fibers was monitored by
219 tracking the evolution of torque. The resulting torque vs time rheogram was typically characterized by four
220 consecutive phases: an initial drop, a short linear increase, a nonlinear increase, and a final plateau. The beginning
221 of the plateau corresponded to the completion of the dissolution process. The pulp reactivity was determined by
222 the initial dissolution rate (IDR) and the overall dissolution time (T0.1). The IDR was measured from the linear
223 torque increase, while T0.1 was the time corresponding to a torque/time ratio of 0.1. This value approximated the
224 beginning of the plateau. High IDR and short T0.1 values indicated high pulp reactivity.

225 **3. Results and discussion**

226 *3.1. Yields, chemical composition and macromolecular properties*

227 The yield of birch wood chips after water pre-hydrolysis decreased along with increasing the P-factor (Table 1).
228 The decrease in wood yield was mainly caused by the removal of the hemicelluloses (predominantly xylan), since
229 the cellulose and lignin yields remained rather similar under the present pre-hydrolysis intensities (supplementary
230 material). This was in agreement with numerous studies dealing with the effects of water pre-hydrolysis on the

231 chemical composition of various woods (Borrega, Tolonen, Bardot, Testova, & Sixta, 2013; Liu, Li, Luo, Chen,
 232 & Huang, 2015; Song, Pranovich, Summerskiy, & Holmbom, 2008; Testova, Chong, Tenkanen, & Sixta, 2011).
 233 After kraft pulping, the pulp yield decreased even further (Table 1), due to the concomitant removal of lignin and
 234 carbohydrates from the fiber cell wall. The cellulose yield after pulping decreased with increasing pre-hydrolysis
 235 intensity (supplementary material), probably due to peeling reactions in alkaline media, following the cleavage of
 236 glycosidic bonds in cellulose during pre-hydrolysis and the consequent formation of new reducing end-groups
 237 (Borrega, Tolonen, Bardot, Testova, & Sixta, 2013). This partial degradation of cellulose was accompanied by a
 238 slight decrease in pulp viscosity (Table 1). As for the removal of lignin, the wood chips pre-hydrolysed at higher
 239 intensities (P-factor) needed lower pulping intensities (H-factor) to reach a similar degree of delignification. The
 240 enhanced delignification of pre-hydrolysed wood is often explained by the cleavage of covalent bonds in the lignin
 241 structure during pre-hydrolysis, as well as by the increased accessibility of lignin to pulping chemicals resulting
 242 from the removal of hemicelluloses (Rauhala, King, Zuckerstätter, Suuronen, & Sixta, 2011; Yoon & van
 243 Heiningen, 2008). As shown in Table 1, increasing pre-hydrolysis intensity led to pulps with higher cellulose and
 244 lower hemicellulose contents, while the lignin content was about 3-4% in all pulps, corresponding to kappa
 245 numbers between 13 and 19. Differences in kappa number for similar lignin contents might be due to different
 246 amounts of hexenuronic acids in the pulps, as these acids are known to consume permanganate and thus affect the
 247 determination of the kappa number (Li & Gellerstedt, 1998).

248 **Table 1.** Yields of birch wood chips after water pre-hydrolysis, and yields and composition of unbleached pulps
 249 after kraft pulping.

Sample	P-factor	^a Wood yield (%)	H-factor	^a Pulp yield (%)	Cellulose (%)	Xylan (%)	^b GM (%)	Lignin (%)	Kappa	Intrinsic viscosity (mL/g)
Kraft	0	100	1 000	55.5	69.2	26.7	0.4	3.8	19.4	1 346
P170	170	92.1	650	44.6	79.5	16.2	0.7	3.7	17.4	1 329
P550	550	78.3	400	37.9	87.1	9.2	0.5	3.3	13.7	1 296
P1000	1 000	74.3	200	31.0	91.3	4.8	0.3	3.5	12.8	1 237

250 ^aWood yield after water pre-hydrolysis; pulp yield after water pre-hydrolysis and kraft pulping

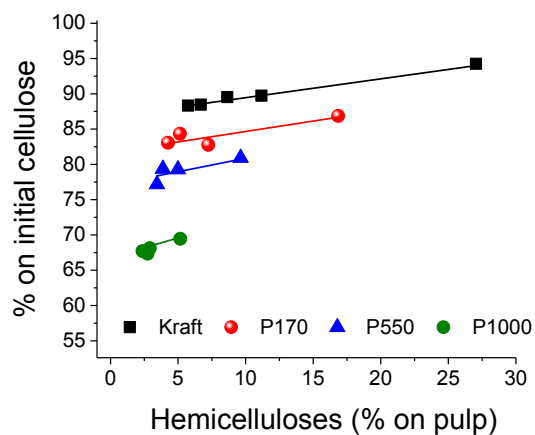
251 ^bGM: glucomannan

252 The unbleached kraft and PHK pulps were then subjected to water post-hydrolysis to extract the residual xylan
 253 fraction. The operational conditions for the post-hydrolysis were selected based on the results of our previous
 254 study (Borrega, Concha-Carrasco, Pranovich, & Sixta, 2017). In all pulps, the hemicelluloses (xylan) content
 255 decreased with increasing post-hydrolysis time, while the cellulose yield decreased only slightly (Fig. 1a).
 256 However, because of the partial degradation of cellulose during pre-hydrolysis and kraft pulping, the cellulose
 257 yield at a given hemicellulosic content was considerably lower in those pulps subjected to higher pre-hydrolysis
 258 intensities. For instance, at a hemicelluloses content of about 5%, the cellulose yield for the post-hydrolysed kraft
 259 pulp (without pre-hydrolysis) was about 90% of the initial cellulose in wood. In comparison, the cellulose yield
 260 for the P1000 pulp was only about 70%.

261 Despite the minor losses in cellulose yield with increasing post-hydrolysis time (Fig. 1a), the intrinsic viscosity
 262 of the unbleached pulps severely decreased with increasing the duration of the post-hydrolysis treatment, and thus
 263 with decreasing the hemicellulosic content (Fig. 1b). This decrease in pulp viscosity, indicating a decrease in the
 264 degree of polymerization (DP) of cellulose, was the result of hydrolytic cleavage of glycosidic bonds in the
 265 cellulose chains that occurs in high-temperature water (Bobleter, 1994). Contrary to the cellulose yield, the

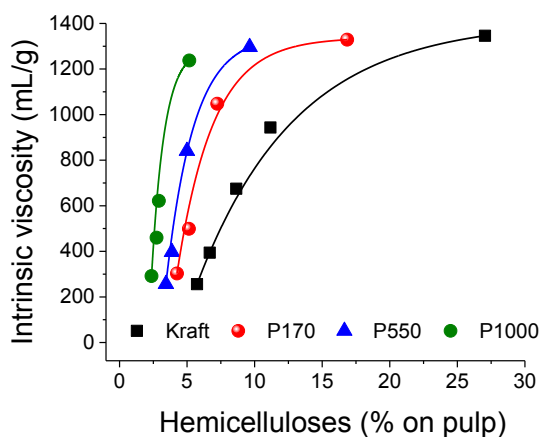
266 intrinsic viscosity at a given xylan content was higher in those pulps subjected to higher pre-hydrolysis intensities,
 267 because these pulps had a lower initial xylan content before post-hydrolysis, and thus needed shorter post-
 268 hydrolysis times to reach a similar purity level.

269 a)



270

271 b)



272

273 **Figure 1.** (a) Cellulose yield and (b) intrinsic viscosity of unbleached kraft and PHK pulps after water post-
 274 hydrolysis at 240 °C in a flow-through reactor, with a flow rate of 400 mL/min. The PHK pulps were pre-
 275 hydrolysed at P-factors of 170, 550 and 1000. For each pulp, different hemicellulose contents correspond to
 276 different post-hydrolysis times. Lines are included to indicate the prevailing trends.

277 Commercial viscose-grade pulps typically have a hemicellulosic content of about 3-6%, while their intrinsic
 278 viscosity is predominantly within the range of 400-500 mL/g. Here, based on the results from Fig. 1, selected
 279 pulps with potential for viscose conversion were bleached following a D₀-E_p-P sequence. The yield of the bleached
 280 pulps was not determined, but yield losses up to 5% may be expected during bleaching (Suess, 2010), particularly
 281 in those pulps with higher xylan content and/or higher amounts of low molar mass cellulose. The bleached pulps
 282 had an ISO brightness of about 83-86% (Table 2), lower than the >90% required in pulps for dissolving
 283 applications. Since it was not the purpose of this study to optimize the bleaching stages, the brightness may still
 284 be improved by selecting more appropriate bleaching sequences or by adjusting the chemical charges. This is
 285 particularly true in the case of the kraft and P1000 pulps, where an oxygen delignification stage prior to the

286 chlorine dioxide (D₀) bleaching would be typically implemented to reduce the kappa number down to 6-8, similar
 287 to the kappa values of the post-hydrolysed pulps. On the other hand, oxygen delignification would not be
 288 recommended for pulps with low intrinsic viscosity, on order to avoid further degradation of the cellulose fraction
 289 by oxidation (Sixta, 2006). It should be mentioned that the optimization of bleaching may affect some of the
 290 chemical, molecular and structural properties of the pulps as discussed in this study. Nonetheless, the results
 291 presented in the following sections may be considered representative of the effects of pre- and post-hydrolysis on
 292 pulp properties.

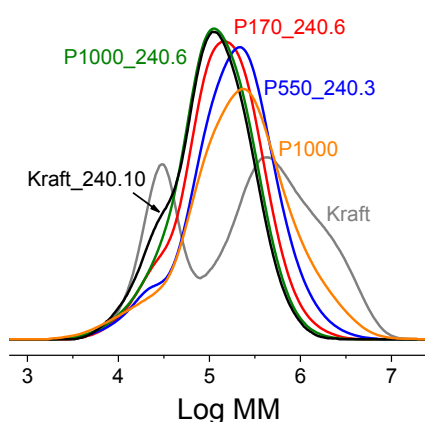
293 The chemical composition and viscosity data of the bleached pulps is shown in Table 2. The pulp Kraft_240.10,
 294 i.e., the kraft pulp after post-hydrolysis at 240 °C for 10 min, had a xylan content of about 7% and a viscosity of
 295 about 300 mL/g. In agreement with our previous results (Borrega & Sixta, 2013; Borrega, Concha-Carrasco,
 296 Pranovich, & Sixta, 2017), it appears that water post-hydrolysis of kraft pulp cannot lower the hemicelluloses
 297 content below 7% without compromising the pulp quality by extensive degradation of the cellulose fraction.
 298 Although the xylan content of the Kraft_240.10 pulp was on the higher end, it may be still acceptable for viscose
 299 conversion because PHK pulps from birch containing 6-7% xylan content have previously shown satisfactory
 300 performance in a viscose process simulation (Testova et al., 2014). Moreover, although the viscosity of this pulp
 301 was relatively low, it should be sufficient for viscose conversion because in the manufacture of viscose the pulp
 302 viscosity is decreased to 230-240 mL/g by pre-aging of the alkali-cellulose. The pulps P170_240.6 and
 303 P550_240.3, both produced by a combination of pre- and post-hydrolysis, showed purity and viscosity values
 304 similar to those required in viscose-grade pulps (Table 2), but the need for two separate water treatments (pre-
 305 and post-hydrolysis) is not very attractive from an industrial point of view. The pulp P1000, produced only by
 306 pre-hydrolysis, showed high purity as well as high viscosity. The addition of an oxygen delignification stage prior
 307 to bleaching would probably be required to lower the viscosity to suitable levels for entering the conversion
 308 process to viscose fibers. Alternatively, the viscosity of the pulp P1000 could be adjusted with a water post-
 309 hydrolysis treatment, which not only decreases viscosity but also increases pulp purity, as shown by the properties
 310 of the P1000_240.6 pulp in Table 2. Water post-hydrolysis of PHK pulps could be considered as an alternative
 311 method to acid hydrolysis for the adjustment of viscosity through controlled degradation of cellulose.

312 **Table 2.** Chemical and macromolecular properties of bleached kraft pulp and selected pre- and post-hydrolyzed
 313 pulps. Pre-hydrolysis was conducted at 170 °C at different intensities (P-factor), while post-hydrolysis was
 314 conducted at 240 °C and various treatment times.

	Kraft	Kraft_240.10	P170_240.6	P550_240.3	P1000	P1000_240.6
P-factor	0	0	170	550	1 000	1 000
Post-hydrolysis time (min)	0	10	6	3	0	6
Cellulose (% on pulp)	73.6	93.2	94.9	94.6	95.4	97.2
Xylan (% on pulp)	26.4	6.8	5.1	5.4	4.6	2.8
ISO brightness (%)	82.7	84.2	83.3	83.7	86.4	84.0
Intrinsic viscosity (mL/g)	969	296	356	507	671	324
Mw (kg/mol)	770	163	218	308	464	178
PDI	11.6	2.8	3.0	3.6	5.8	2.8
DP > 2000	0.48	0.12	0.19	0.29	0.37	0.14
DP < 100	0.05	0.05	0.03	0.03	0.04	0.01

315 In addition to viscosity values, the macromolecular properties of the selected bleached pulps were further studied
 316 by determining their molar mass distribution by GPC (Fig. 2). The peak in the low molar mass region,
 317 corresponding to the hemicelluloses, was clearly visible for the kraft pulp but largely disappeared from the molar

318 mass distribution of all water-treated pulps. The peak corresponding to the cellulose fraction shifted towards lower
319 molar mass regions by increasing the intensity of the pre-hydrolysis and/or post-hydrolysis treatment. The
320 degradation of cellulose was also evident by a decrease in the weight average molar mass (M_w) and in the number
321 of molecules with a $DP > 2000$ (Table 2). The pulp P1000_240.6 had the lowest amount of molecules with $DP < 100$,
322 while the pulps produced by pure pre-hydrolysis (P1000) or pure post-hydrolysis (Kraft_240.10), together with
323 the kraft pulp, had the highest amount of this $DP < 100$ fraction. The presence of these short-chain molecules in
324 the pulp, originating from the hemicelluloses and from degraded cellulose fragments, appears to have a negative
325 effect on the mechanical properties of viscose fibers (Sixta, 2006). Finally, increasing the intensity of the
326 hydrothermal treatment resulted in pulps with narrower molar mass distribution (see Fig. 2 and PDI values in
327 Table 2), a desired feature in dissolving pulps because it relates to the homogeneity of the cellulosic material.



328
329 **Figure 2.** Molar mass distribution of bleached kraft pulp and selected pre- and post-hydrolysed pulps. Pre-
330 hydrolysis was performed at P-factors of 0, 170, 550 and 1000, while post-hydrolysis was performed at 240 °C
331 for 3, 6 or 10 min.

332 3.2. Supramolecular pulp properties

333 The supramolecular structure of the bleached pulps was investigated by solid state NMR and WAXS. The NMR
334 data showed that the lateral fibril dimension (LFD), a measure of the cellulose crystallite size, was about 4-5 nm
335 in all pulps (Table 3). These values were in agreement with published data on fibril dimensions in kraft pulps
336 produced under different pulping conditions (Duchesne et al., 2001; Virtanen, Liisa Maunu, Tamminen, Hortling,
337 & Liitiä, 2008). The LFD appeared to increase slightly from 3.9 nm in the kraft pulp to 4.1 nm in the P1000 pulp.
338 Interestingly, all pulps that were subjected to post-hydrolysis clearly showed a higher LFD, with values around
339 4.5-4.7 nm. It has been previously reported that water pre-hydrolysis of birch wood induces an increase in the
340 cellulose crystal size, particularly with increasing pre-hydrolysis temperature (Penttilä et al., 2013; Testova et al.,
341 2014). The increase in crystal size in both pre- and post-hydrolyzed pulps might be explained by the crystallization
342 of cellulose chains on the surfaces of the crystals as well as by agglomeration (coalescence) of neighboring
343 cellulose chains. These molecular re-arrangements would be favored in the presence of water (plasticizer), and
344 further promoted by the use of elevated temperatures during the hydrothermal treatment (Atalla, Ellis, &
345 Schroeder, 1984). Nonetheless, the crystallization or coalescence of cellulose chains would probably imply the
346 splitting and thus shrinking of neighboring crystallites, which would then leave the average LFD unchanged. At
347 this stage, the mechanism for the increase in LFD still remains unclear. In any case, the increase in LFD was also

348 accompanied by an increase in cellulose crystallinity, from 50% for the kraft pulp to about 57% for all post-
 349 hydrolyzed pulps (Table 3). These crystallinity values are well in agreement with several studies on the
 350 supramolecular structure of kraft and PHK pulps (Hult, Liitiä, Maunu, Hortling, & Iversen, 2002; Wollboldt,
 351 Zuckerstätter, Weber, Larsson, & Sixta, 2010; Testova et al., 2014). The differences in the supramolecular
 352 structure of cellulose in the kraft, pre-hydrolyzed, and post-hydrolyzed pulps were evident from the recorded
 353 NMR spectra originating from the C4 carbon (supporting information).

354 **Table 3.** Supramolecular properties of bleached kraft pulp and selected pre- and post-hydrolyzed pulps. Pre-
 355 hydrolysis was conducted at 170 °C at different intensities (P-factor), while post-hydrolysis was conducted at 240
 356 °C and various treatment times.

	Kraft	Kraft_240.10	P170_240.6	P550_240.3	P1000	P1000_240.6
<i>Solid state NMR</i>						
Crystallinity index ($\pm 1\%$)	50 \pm 1	57 \pm 1	57 \pm 1	57 \pm 1	52 \pm 1	56 \pm 1
Lateral fibril dimension (± 0.1 nm)	3.9	4.6	4.7	4.6	4.1	4.5
Aggregate dimension (nm)	37 \pm 4	27 \pm 2	28 \pm 2	26 \pm 1	22 \pm 1	24 \pm 1
Specific surface area (m ² /g)	73 \pm 9	99 \pm 6	95 \pm 6	104 \pm 5	119 \pm 4	113 \pm 6
<i>X-ray diffraction</i>						
Crystallinity (%)						
Sample	45	53	51	50	46	52
Cellulose	61.1	56.9	53.7	52.9	48.2	53.5
Crystal width (± 0.5 nm)						
1-10	4.1	4.0	4.2	4.0	3.8	4.1
110	3.9	4.7	4.8	4.9	5.2	5.0
200	4.0	5.0	5.0	4.9	4.3	5.0

357 Cellulose fibrils in the fiber cell wall tend to aggregate and form larger structures, typically called microfibrils.
 358 Here, the fibrils in the kraft pulp formed the largest aggregates, as indicated by the lateral fibril aggregate
 359 dimensions (LFAD), while the P1000 pulp had the smallest aggregates despite having rather similar fibril
 360 dimensions as the kraft pulp (Table 3). It has been reported that pulps produced by an alkaline process tend to
 361 show larger aggregates than those produced or subjected to an acidic treatment (Wollboldt et al., 2010). The acidic
 362 conditions generated during water pre-hydrolysis of wood may thus explain the difference in aggregate
 363 dimensions between the kraft and P1000 pulp samples. It should also be mentioned that the aggregate dimensions
 364 for the kraft pulp (37 nm) were significantly higher than the 15-25 nm commonly found in pulps (Hult, Larsson,
 365 & Iversen, 2001; Hult, Liitiä, Maunu, Hortling, & Iversen, 2002; Wollboldt, Zuckerstätter, Weber, Larsson, &
 366 Sixta, 2010). The kraft pulp in this study was bleached with a rather unconventional bleaching sequence, with the
 367 absence of an oxygen delignification stage, and this might have had an effect on fibril aggregation. According to
 368 the fibrillar model used for the determination of the supramolecular structure in cellulose I, the surface of the
 369 fibrils are assumed to be easily accessible while the inner surfaces may have restricted access due to aggregation.
 370 The specific surface area (SSA) in the wet state, which was computed from the LFAD, obviously showed that the
 371 SSA was the lowest for the kraft pulp and the highest for the P1000 pulp, with SSA values for all post-hydrolyzed
 372 pulps laying in between.

373 In general, qualitative variations in the supramolecular structure of cellulose detected by NMR tend to agree well
 374 to those detected by x-ray scattering, even if the absolute values determined by these methods may differ (Lee et
 375 al., 2016). The results from the WAXS analyses showed that the cellulose crystal size measured from the 200
 376 reflection increased slightly from 4 nm in the kraft pulp to 4.3 nm in the P1000 pulp, with all post-hydrolyzed

377 samples showing a significantly higher crystal size, about 5 nm (Table 3). In the 110 direction, the crystal size
378 was larger in all water-treated pulps than in the kraft pulp, while in the 1-10 direction the size was similar in all
379 pulps. The differences in the crystalline structure of cellulose, particularly in the 200 reflection, between the post-
380 hydrolysed pulps and the kraft and P1000 pulps could be seen from the WAXS spectra (supplementary material).
381 Overall, the crystallite dimensions and their increase with increasing the intensity of the hydrothermal treatment
382 were in close agreement with those determined by NMR.

383 The sample crystallinity determined by WAXS was between 45-53%, increasing slightly from the kraft to the
384 P1000 pulp, and then further in the post-hydrolyzed pulps. By taking into account the chemical composition of
385 the pulps, the degree of cellulose crystallinity could also be estimated. In all pre- and post-hydrolyzed pulps, with
386 a high cellulose content (>93%), the cellulose crystallinity was similar to the sample crystallinity. Moreover, the
387 cellulose crystallinity determined by WAXS was in good agreement with the crystallinity values from the NMR
388 measurements (Table 3). In the kraft pulp, however, the cellulose crystallinity estimated by WAXS (61%) was
389 considerably higher than that determined by NMR (50%). It is well known that the presence of amorphous
390 polymers such as hemicelluloses interfere with the spectral fitting for the determination of crystallinity in NMR
391 experiments, and thus the removal of hemicelluloses by acid hydrolysis is often performed prior to the analyses
392 (Hult, Larsson, & Iversen, 2000; Liitiä et al., 2003). In order to avoid any hydrolytic degradation of the cellulose
393 fraction, the removal of hemicelluloses from the kraft pulp was not performed in this study, which might have
394 affected the determination of crystallinity.

395 *3.3. Accessibility and reactivity of pulps*

396 Probably the most important property of any dissolving-grade pulp is its reactivity, that is, how well the pulp
397 reacts (dissolves) in a particular chemical solvent system so it can be transformed into the desired final product.
398 The pulp reactivity depends on a variety of chemical, molecular and fibrillar features, but it is strongly related to
399 the accessibility of functional groups in the pulp, mainly -OH groups (Sixta, 2006). In this study, the accessibility
400 of -OH groups was determined after deuteration of the samples at 95% RH in a D₂O atmosphere. This relative
401 humidity should be enough to reach complete exchange of free -OH groups into -OD groups, as it has been
402 previously shown that the deuterium exchange in wood reaches a maximum at 60% RH (Taniguchi, Harada, &
403 Nakato, 1978).

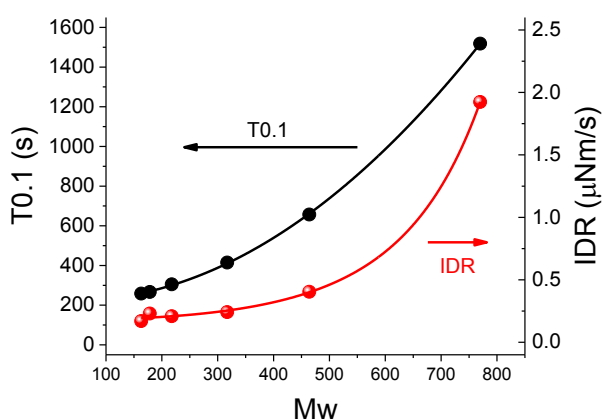
404 The accessibility values for our pulp samples are shown in Table 4. All post-hydrolyzed pulps had a similar
405 accessibility, with 54-58% of their -OH groups being reactive. The P1000 pulp clearly had the highest
406 accessibility, which was probably related to its high SSA, derived from the presence of small fibril aggregates.
407 On the other hand, the accessibility of the kraft pulp was lower than that of the P1000 pulp, but higher than that
408 of the post-hydrolyzed pulps (Table 4). The fibril aggregates in the kraft pulp appeared to be the largest, and
409 correspondingly its SSA was the lowest. Therefore, the high accessibility of the kraft pulp may be related to its
410 high xylan content, because hemicelluloses are amorphous polymers with free -OH groups. It should also be
411 mentioned that in the case of the P1000 and kraft pulps, their accessibility values might be slightly underestimated,
412 because at the end of the deuteration stage (10 hours) the pulp mass did not seem to have reached yet an
413 equilibrium (dm/dt was about 0.001-0.0015%, compared to <0.0008% for the post-hydrolyzed pulps).
414 Nonetheless, differences in accessibility values with extending deuteration time might be expected to be rather
415 small.

416 **Table 4.** Accessible hydroxyl (-OH) groups and reactivity values of bleached kraft pulp and selected pre- and
 417 post-hydrolysed pulps. Pre-hydrolysis was conducted at 170 °C at different intensities (P-factor), while post-
 418 hydrolysis was conducted at 240 °C and various treatment times. The reference pulp is a commercial bleached
 419 birch pulp produced by PHK pulping.

	-OH groups (mmol/g pulp)	-OH groups (% on total)	Fock reactivity (%)	DTR reactivity	
				IDR (μNm/s)	T0.1 (s)
Kraft	11.2 ± 0.4	63.5	30 ± 1.7	1.92 ± 0.09	1 518 ± 19
Kraft_240.10	10.7 ± 0.4	58.3	21 ± 3.8	0.17 ± 0.04	258 ± 3
P170_240.6	10.6 ± 0.4	57.9	14 ± 3.9	0.21 ± 0.01	305 ± 5
P550_240.3	10.0 ± 0.1	54.3	nd	nd	nd
P1000	12.1 ± 0.2	65.9	15 ± 2.3	0.40 ± 0.04	657 ± 8
P1000_240.6	10.6 ± 0.3	57.5	18 ± 2.9	0.23 ± 0.06	267 ± 8
Reference	10.2 ± 0.0	55.8	20 ± 1.4	0.24 ± 0.01	415 ± 9

420 The proportion of accessible -OH groups in the reference (commercial) pulp was lower than that in the P1000
 421 pulp, despite the fact that both pulps were produced by PHK pulping of birch wood. However, the process
 422 parameters during pre-hydrolysis, pulping and bleaching differed, which may have affected the accessibility of
 423 the pulp. Moreover, the reference pulp was delivered in dry sheets, and was re-wetted in liquid water before the
 424 DVS experiments. This additional re-wetting and drying cycle probably reduced the accessibility of -OH groups,
 425 due to irreversible hydrogen bonding caused by the closure of pores during water removal (i.e. hornification)
 426 (Weise, 1998).

427 In this study, the reactivity of the pulps in a viscose conversion process was first estimated by the Fock method,
 428 which quantified the amount of regenerated cellulose in the xanthate. All post-hydrolyzed samples gave similar
 429 amounts of regenerated cellulose, as indicated by the Fock reactivity values in Table 4. Moreover, the pulp P1000
 430 also showed similar reactivity than the post-hydrolyzed pulps, even though its accessibility was considerably
 431 higher. The Fock reactivity appears to decrease with increasing the molar mass of the cellulose fraction (Engström
 432 et al., 2006), and thus the higher molar mass of the P1000 pulp, compared to the post-hydrolyzed pulps, may have
 433 resulted in lower Fock values than otherwise expected from the accessibility of its -OH groups. For all dissolving-
 434 grade pulps, including the commercial (reference) PHK pulp, the reactivity was less than 25% (Table 4), much
 435 lower than previously reported for other hardwood PHK pulps (Duan et al., 2015; Miao et al., 2014). In the absence
 436 of detailed information on experimental parameters during the Fock tests, we can only assume that the reactivity
 437 of our pulp samples was strongly affected by the testing conditions (Tian et al., 2013). Surprisingly, the kraft pulp
 438 was the most reactive sample, even though both its molar mass and xylan content were the highest. It is well
 439 established that kraft pulps exhibit poor reactivity during viscose conversion, mainly because the hemicelluloses
 440 react with the derivatizing chemicals and impair the conversion of cellulose (Gehmayr et al., 2011; Wollboldt et
 441 al., 2010). Therefore, the results from the Fock tests should be interpreted with caution, as they may not be
 442 representative of the true behavior of the pulps in a viscose process.



443

444 **Figure 3.** Initial dissolution rate (IDR) and time to complete dissolution (T0.1) of bleached kraft, pre- and post-
 445 hydrolyzed pulp samples in CED solvent, plotted as a function of their average weight molar mass (Mw).

446 The pulp reactivity to derivatizing chemicals was alternatively investigated by monitoring its rheological behavior
 447 during dissolution in CED. According to this method, a pulp shows high reactivity if the initial dissolution rate
 448 (IDR) is high and the time to complete dissolution (T0.1) is short (Ceccherini & Maloney, 2017). Interestingly,
 449 the results in Table 4 indicate that those pulps with a high IDR also showed a high T0.1. In other words, the pulps
 450 that started dissolving at a fast pace required longer time to complete the dissolution process. The pulps could be
 451 roughly classified into three categories, with kraft pulp showing the highest IDR and T0.1 values, followed by the
 452 P1000 pulp and then by all post-hydrolyzed pulps. As shown in Fig. 3, the reactivity parameters determined by
 453 the DTR test were strongly related to the molar mass of the pulp. Adjusting the pulp viscosity prior to the reactivity
 454 tests may thus be required in order to evaluate the effect of other physical and chemical pulp properties on their
 455 reactivity. It should also be considered that the accessibility and reactivity parameters of the pulps determined in
 456 this study may differ if some pulp properties were adjusted by selecting different bleaching conditions.

457 3.4. Recovery of xylan-based sugars from the aqueous hydrolysates

458 The side-streams generated during the hydrothermal treatments of wood and pulp were analyzed to determine
 459 their chemical composition (Table 5). In pre-hydrolysis, increasing the P-factor led to higher amounts of xylan-
 460 derived sugars, although the share of oligo- and/or polysaccharides ($DP \geq 2$) decreased due to their degradation
 461 under elevated temperature and prolonged reaction times (Borrega, Niemela, & Sixta, 2013; Liu, Li, Luo, Chen,
 462 & Huang, 2015). Other sugars originating from the partial degradation of glucomannan and cellulose, as well as
 463 a soluble lignin fraction were also present in the hydrolysates. It is likely that several degradation products such
 464 as furans and carboxylic acids were also formed, particularly with increasing pre-hydrolysis intensity (Borrega,
 465 Niemela, & Sixta, 2013), but were not here analyzed. At a P-factor of 1000, almost 11% of xylose (based on dry
 466 wood) was found in the pre-hydrolysate, with half of it in oligo- and/or polymeric form. These values were well
 467 in agreement with previous reports on xylose yields during water autohydrolysis of birch wood (Testova et al.,
 468 2011).

469 In the post-hydrolysates, the amount of xylan-based sugars decreased with increasing pre-hydrolysis intensity.
 470 This was obviously a direct consequence of lower xylan content in the unbleached pulps and shorter post-
 471 hydrolysis times needed for pulps pre-hydrolyzed at higher P-factor. Since water post-hydrolysis was performed

472 in a flow-through reactor and under high flow rates, the xylan-based compounds were found quantitatively as
 473 oligo- and/or polymers (Table 5). In pure post-hydrolysis (Kraft_240.10), the amount of xylose recovered from
 474 the hydrolysate was about 10% on initial dry wood, similar to the amount of xylose (11%) recovered from pure
 475 pre-hydrolysis (P1000), and for a similar amount of residual xylan (5-7%) in the pulp. The xylose in the post-
 476 hydrolysate for the Kraft_240.10 sample corresponded to about 17% of the dry pulp mass, slightly lower than the
 477 20% previously reported under similar conditions of temperature, time and flow (Borrega, Concha-Carrasco,
 478 Pranovich, & Sixta, 2017). In those treatments with combined pre- and post-hydrolysis, the total recovery of
 479 xylose was dependent on the pre-hydrolysis intensity. At a P-factor of 550, about 10-11% of xylan-based sugars
 480 (on dry wood) were also found in the aqueous hydrolysates, but at a P-factor of 170, only about 7% of xylan-
 481 based sugars were found. This lower recovery may be explained by extensive xylan dissolution during alkaline
 482 pulping, following the cleavage of xylan chains in wood during the low-intensity pre-hydrolysis.

483 **Table 5.** Chemical and macromolecular composition of selected aqueous pre- and post-hydrolysates. Pre-
 484 hydrolysis was conducted at 170 °C at different intensities (P-factor), while post-hydrolysis was conducted at 240
 485 °C and various treatment times. The amounts of sugars and lignin are shown as % on initial birch wood, unless
 486 otherwise indicated.

	Kraft_240.10	P170_240.6	P550_240.3	P1000	P1000_240.6
<i>Pre-hydrolysate</i>					
Total xylose (%)	na	3.1	9.2	10.9	10.9
DP ≥ 2 (% of xylose)	na	96.1	88.2	49.5	49.5
Mw (kDa)	na	nd	nd	1.2	1.2
PDI	na	nd	nd	1.4	1.4
Concentration (g/L)	na	7.8	22.9	27.2	27.2
Other sugars (%)	na	1.2	2.0	2.3	2.3
Soluble lignin (%)	na	1.8	2.9	2.6	2.6
<i>Post-hydrolysate</i>					
Total xylose (%)	9.8	4.0	1.3	na	0.6
DP ≥ 2 (% of xylose)	>99	>99	>99	na	>99
Mw (kDa)	10.5	nd	nd	na	nd
PDI	3.4	nd	nd	na	nd
Concentration (g/L)	0.6	0.5	0.2	na	0.1
Other sugars (%)	0.3	0.1	<0.1	na	0.1
Soluble lignin (%)	0.4	0.6	nd	na	0.2

487 Despite similar xylose recovery by pure pre- and post-hydrolysis, the molar mass of the xylan-based compounds
 488 in the pre- and post-hydrolysates clearly differed. Since these compounds were the most abundant in the
 489 hydrolysates, it was assumed that the molar masses of the dissolved products largely corresponded to those of the
 490 xylan-based sugars. In pre-hydrolysis (P1000), their average molar mass (Mw) was about 1.2 kDa, while in post-
 491 hydrolysis the xylan had an average molar mass of about 10.5 kDa (Table 5). The molar mass distribution was
 492 also broader for the xylan-based compounds in the post-hydrolysate, as indicated by the polydispersity index
 493 (PDI). According to the molar mass characteristics, the xylan fraction in the post-hydrolysates may be utilized as
 494 multifunctional food ingredient to improve several technological properties in dairy products and to promote
 495 health-related effects (Rosa-Sibakov et al., 2016). Moreover, the amount of impurities (other sugars, lignin) was
 496 less than 1% on wood in the Kraft_240.10 post-hydrolysate, compared to the 5% found in the P1000 pre-
 497 hydrolysate. The higher purity of the xylan fraction in the post-hydrolysates was probably related to the more
 498 homogeneous composition of pulp, as compared to wood, and thus it may be expected to facilitate its recovery
 499 using membrane filtration techniques. It should be mentioned, however, that the concentration of xylan-based

500 sugars in the post-hydrolysates was very low (less than 1g/L), and thus their isolation by membrane filtration
501 would be a highly energy intensive process. Lowering the flow rate in post-hydrolysis may increase the product
502 concentration, but then the total amount of sugars recovered would be lower (Borrega et al., 2017). More data on
503 xylan yields at different flow rates, energy requirements for isolation, and product market price would be needed
504 to assess the economic viability of the recovery process.

505 **4. Conclusions**

506 Water post-hydrolysis of kraft pulp can produce viscose-grade pulp with considerably higher cellulose yield than
507 traditional PHK pulping, but the pulp viscosity at a given hemicellulosic content is considerably lower. This fact
508 limits the application of water post-hydrolysis, particularly on high-hemicellulose containing pulps, because high
509 purity levels cannot be reached without compromising the cellulose quality. Compared to pre-hydrolysis, water
510 post-hydrolysis results in lower accessibility of hydroxyl groups, probably derived from supramolecular re-
511 arrangements in cellulose promoted by high-temperature water. Despite the lower accessibility, the reactivity of
512 post-hydrolysed pulps to derivatising chemicals is not seemingly compromised. However, the bleached pulps in
513 this study did not reach all the required specifications (e.g. brightness) for the viscose process, and thus the
514 variation in some pulp properties by adjusting the bleaching operation may in turn alter the accessibility and
515 reactivity of the pulps. Moreover, the performance of the pulps during the actual conversion to viscose needs yet
516 to be assessed to clearly elucidate the suitability of post-hydrolysed pulps for the viscose process. The use of a
517 flow-through system for pulp post-hydrolysis allows the recovery of a high purity and molar mass xylan fraction
518 for high-value applications.

519 **Supplementary materials**

520 E-supplementary data of this work can be found in the online version of the paper.

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