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Hot water treatment of hardwood kraft pulp produces high-purity cellulose and polymeric xylan

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Abstract Hot water treatments (HWTs) of unbleached hardwood kraft pulps under various process conditions were conducted to extract the xylan and thus produce a high-purity cellulosic pulp that could be used in dissolving applications. Increasing treatment temperature up to 240 °C increased the removal of xylan over the degradation of cellulose in birch pulp, but this effect was minor at higher temperatures. Addition of acetic acid lowered the treatment intensity needed to reach a certain degree of pulp purity, but did not improve the selectivity in xylan removal compared to water-only experiments. HWTs of eucalyptus pulp, with lower xylan content than birch pulp, produced cellulosic fibers with higher degree of polymerization at a given pulp purity. Under selected operational conditions (240 °C for 10 min) in a flow-through reactor, and provided that the HWTs were applied before bleaching, the chemical and

macromolecular properties of water-treated pulps may be suitable for their conversion to viscose. Moreover, at high flow rates (200–400 mL/min), the extracted xylan was recovered from the aqueous hydrolysate in high yield and with relatively high molar mass (~10 kDa). Based on the results of this study, HWTs of hardwood kraft pulp are suggested as a simple and green method to produce high-purity cellulose and polymeric xylan for high value-added applications.

Keywords Cellulose · Dissolving pulp · Hot water treatment · Kraft pulping · Viscose · Xylan

Introduction

Kraft pulping is the dominant industrial process for the production of paper-grade pulps. In the last decade, an increase in production capacity due to new pulp mills established in Brazil and China has strengthened the competition in the forest industries sector. This situation, coupled with a global economic crisis, has resulted in the closure of many pulp mills, especially in Europe and North America, where production costs are higher and feedstock growing rates are lower than those in most Asian and Latin American countries. Simultaneously, the demand for dissolving-grade pulps has almost doubled; the total world consumption has increased from 3.3 million tons in 2007 to 6.2 million tons in 2014 (FAO Yearbook 2007, 2014).

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Dissolving pulps, with high cellulose content (>90 wt%) and low amounts of impurities, are used in the manufacture of cellulose specialty products for textiles, films, lacquers, food, drugs, etc. The high demand for dissolving pulps, mostly driven by the production of viscose fibers for textile applications, is partly related to the growing world population and the increasing purchasing power in developing markets, and thus is expected to continue increasing in the future (Haemmerle 2011; Liu et al. 2016). Dissolving wood pulps are commercially produced by acid sulphite pulping or by prehydrolysis kraft (PHK) pulping; the latter is a modified kraft process that incorporates a water prehydrolysis step to remove some of the hemicelluloses from wood and thus reach a higher cellulose purity in the pulp. Given the current and expected trends in pulp consumption, some kraft mills are being converted into PHK mills. The conversion also allows the mills adjusting their pulp production, either paper- or dissolving-grade, based on market demands.

An alternative to the introduction of a pretreatment step like prehydrolysis prior to kraft pulping to enhance the purity of the pulp may be the application of a post-treatment. Several methods have been studied to remove the hemicelluloses from paper pulps, including enzymatic hydrolysis and cold caustic extraction (Gehmayr et al. 2011; Ibarra et al. 2009; Köpcke et al. 2008), nitren extraction (Janzon et al. 2006, 2008), and ionic liquid extraction (Froschauer et al. 2013; Roselli et al. 2014). Despite their varying success in producing a high-purity pulp for dissolving applications, their high operational costs and/or their toxicity have limited the utilization of these methods in industrial scale. Recently, we demonstrated that hot water treatments (HWTs) of unbleached birch kraft pulp in a flow-through reactor could remove up to 80% of the xylan without losses in cellulose yield (Borrega and Sixta 2013). Some of the water-treated pulps, with xylan content about 7% and intrinsic viscosity around 400 mL/g, may be suitable for their conversion to viscose. Further reduction of the xylan content was still possible at extended treatment times, but the cellulose yield and intrinsic viscosity of the pulp were then compromised. The HWT also reduced the lignin content in the unbleached pulp by 50%, which may facilitate the subsequent bleaching process.

One of the main benefits of HWTs of pulp, compared to other post-treatments reported in the

literature, is that no chemicals are required since water is the only solvent used. However, the removal of hemicelluloses from paper pulps for their conversion to dissolving-grade pulps should follow not only green chemistry principles but also advanced biorefinery concepts. In other words, the side-stream containing the extracted hemicelluloses should be recovered for its subsequent valorization. In a flow-through reactor, the pulp xylan removed during HWTs can be quantitatively dissolved in the aqueous hydrolysate in oligomeric and/or polymeric form (Borrega and Sixta 2013). These xylan-based compounds are valuable products used in a wide variety of applications, ranging from films to foams and food ingredients (Deutschmann and Dekker 2012; Moure et al. 2006). Their potential application comes mostly determined by physico-chemical properties such as composition (i.e. heterogeneity), degree of substitution, and molar mass. The separation and recovery of oligo- and polymeric xylan from the hydrolysates may be easily accomplished by membrane ultrafiltration. In this respect, HWTs of pulp are anticipated to be advantageous over water prehydrolysis of wood, since the complexity of wood prehydrolysates, derived from its heterogenous chemical composition, poses a challenge to the recovery of xylan-based compounds using membrane separation techniques (Koivula et al. 2011).

In our previous study, we observed that increasing temperature from 200 to 240 °C during HWT of birch kraft pulp favored the removal of xylan over the degradation of cellulose (Borrega and Sixta 2013). Moreover, under similar operational conditions, the efficiency of xylan removal from birch wood was higher than from pulp, most likely because of the presence of acetyl groups in the wood xylan, which formed acetic acid and catalyzed the removal of the carbohydrate. Therefore, in this study, we have investigated the application of temperatures up to 280 °C and the addition of acetic acid as ways to further enhance the purity of water-treated pulps. For a selected treatment, four different flow rates have been utilized, and the chemical composition and molar mass characteristics of the hydrolysates have been determined to assess potential applications for the extracted xylan. Unbleached birch kraft pulps have been used as starting raw material because birch wood is the most abundant hardwood species in the Nordic countries and is intensively utilized in pulping for the

production of writing and printing paper. However, the high xylan content in birch makes it a challenging material for its conversion to high-purity pulp. For this reason, HWTs of unbleached eucalyptus kraft pulp containing a lower xylan content have been also performed, and the results are compared to those obtained from HWTs of birch. The application of HWTs on bleached pulps has also been evaluated, and the feasibility of utilizing water-treated pulps for the production of viscose fibers is finally discussed.

Experimental

Lignocellulosic materials

Bleached and unbleached birch (*Betula spp.*) kraft pulps were delivered by Stora Enso Oy, Finland. The bleached pulp was delivered as dry sheets, and its identified chemical composition was 71.3% glucose, 27.7% xylose, and 0.3% mannose. The unbleached pulp was taken from the production line before the oxygen delignification stage. Washing and screening in a table-top plate screener (0.35 mm opening) was conducted at Aalto University. The identified chemical composition of the unbleached pulp was 71.5% glucose, 24.6% xylose, 0.1% mannose, 1.8% acid-insoluble (Klason) lignin and 1.3% acid-soluble lignin (ASL).

Wood chips from *Eucalyptus globulus* were delivered by ENCE, Spain. The chips were screened according to the SCAN-CM 40:01 method and stored in the freezer until further use. The identified chemical composition of the wood was 44.7% glucose, 15.2% xylose, 1.2% galactose, 1.1% mannose, 0.3% rhamnose, 0.3% arabinose, 22.5% Klason lignin, 4.7% ASL and 1.1% extractives.

Pulping experiments

Kraft pulping of eucalyptus wood chips was carried out in a rotating air-bath digester (Haato Oy, Finland). Measured amounts of chips and white liquor were added into 2.5 L autoclaves to reach a liquid-to-wood ratio of 4:1 L/kg. White liquor was prepared from concentrated solutions of NaOH and Na₂S in deionized water. The effective alkali (EA) charge was 19% on oven-dry (o.d.) wood, and the sulphidity (S) was

30%. The chips were first impregnated at 120 °C for 60 min to enhance the penetration of the chemicals into the wood structure. Thereafter the temperature was raised to 155 °C and kept constant until an H-factor of 300 was reached. The pulping was ended by submerging the autoclaves in cold water. After cooling, the pulp was thoroughly washed and screened in a table-top plate screener (0.35 mm opening). The amount of rejects was less than 0.2% on dry pulp.

Hot water treatments

HWTs of birch and eucalyptus pulps were carried out in a 190 mL flow-through percolation reactor (Uni-press Equipment, Poland). About 15 g (o.d.) of pulp were placed in the reactor, equipped with a high-pressure pump, preheater and electric heaters, heat exchanger, and back-pressure regulator (BPR). Water at room temperature was initially pumped through the reactor to wet the pulp and to set the BPR to the operating pressure. The preheater was then turned on, and the water was directed to the heat exchanger bypassing the reactor until it reached the selected setup temperature. Once the setup temperature was reached, the incoming hot water was circulated into the reactor. The outgoing hydrolysate was immediately cooled by the heat exchanger, and after passing through the BPR, collected in a sampling container. After a predetermined amount of time, the pump was stopped and the pulp was washed by circulating cold tap water through the reactor (the washing water was not collected). The reactor was then opened and the pulp was recovered for subsequent analyses. The hydrolysate in the sampling container was weighed, and an aliquot was taken for further analyses. Treatment temperatures ranged from 200 to 280 °C, and times ranged from 2 to 180 min. A flow rate of 100 mL/min was used in all experiments; however, for a selected treatment at 240 °C for 10 min, additional flow rates of 50, 200 and 400 mL/min were also used. A summary of the experimental parameters used for the HWTs of pulps is shown in Table 1. More information about the equipment and operational procedure can be found in Borrega and Sixta (2013).

HWTs of unbleached birch pulps were also carried out in a 500 mL batch reactor (Parr Instrument Company, USA). About 15 g (o.d.) of pulp were placed in the reactor together with deionized water, reaching a 4% consistency. In some experiments,

Table 1 Summary of experimental parameters for the hot water treatments of hardwood kraft pulps

Pulp material	Reaction system	Temperature (°C)	Treatment time (min)	Flow rate (mL/min)	Residence time (min)*	Water to pulp ratio (g/g)**	Acetic acid, (mol/L)
Unbleached birch	Flow-through	200–280	2–180	100	1.9	13.3–1200	–
Unbleached birch	Flow-through	240	10	50–400	3.8–0.48	33.3–266.7	–
Bleached birch	Flow-through	240	2–30	100	1.9	13.3–200	–
Unbleached eucalyptus	Flow-through	240	3–15	100	1.9	20–100	–
Unbleached birch	Batch	200–240	10–60	–	–	24	–
Unbleached birch	Batch	180–240	15–60	–	–	24	0.1

* Residence time of water/hydrolysate in the 190 mL flow-through reactor

** Water to pulp ratio for about 15 g of initial dry pulp

0.1 M acetic acid was added to the mixture. The reactor, equipped with electric heaters and a mechanical stirrer, was purged with nitrogen and then the temperature was raised to the setup temperature. After a predetermined isothermal reaction time, the reactor was cooled by circulating cold tap water around it. The pulp and the hydrolysate were separated by filtration, and the pulp was washed before being stored for subsequent analyses. Treatment temperatures ranged from 180 to 240 °C, and times ranged from 10 to 60 min (Table 1). The combined effect of treatment temperature and time was described by a modified P-factor ($\log P_x$), determined with an Arrhenius equation and using an activation energy of 180 kJ/mol, corresponding to the removal of the recalcitrant xylan fraction in birch wood (Borrega et al. 2011).

Pulp bleaching

Selected birch and eucalyptus pulps, treated in the flow-through reactor at 240 °C with a flow rate of 100 mL/min, were bleached following a D₀–Ep–P sequence. The bleaching conditions were: D₀: temperature 50 °C, 60 min, kappa factor 0.25; Ep: temperature 70 °C, 60 min, 1.5% NaOH, 0.5% H₂O₂; P: temperature 70 °C, 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 bleaching stages. The

bleaching was performed in plastic bags heated by steam in a water-bath.

Analytical determinations

The extractives content in eucalyptus wood was determined after extraction in acetone for 6 h in a Soxhlet apparatus according to the SCAN-CM 49:03 method. The carbohydrates and lignin composition of wood and pulps was determined after a two-stage acid hydrolysis, according to the analytical method NREL/TP-510-42618 issued by the US National Renewable Laboratory (NREL). The amount of Klason lignin was quantified gravimetrically, and the amount of ASL was determined in a Shimadzu (Kyoto, Japan) UV-2550 spectrophotometer at a wavelength of 205 nm, using an adsorption coefficient of 110 L/(g cm). Monosaccharides were determined by high-performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 (Sunnyvale CA, USA) system, equipped with a CarboPac™ PA-20 (3.0 × 150 mm) analytical column. Milli-Q water was the eluent used, the flow rate was 0.4 mL/min, and the column temperature was 30 °C. Based on the amount of neutral monosaccharides, the cellulose and xylan fractions in the lignocellulosic material were calculated using the formulas by Janson (1970). With these formulas, cellulose is defined as the content of

anhydroglucose in the sample after subtracting the contribution of glucose to glucomannan, and xylan is defined as the content of anhydroxylose and uronic acid constituents. The kappa number and intrinsic viscosity of the pulps were determined according to the SCAN-C 1:100 and SCAN-CM 15:99 methods, respectively.

The molar mass distribution of selected pulps was determined by gel permeation chromatography. The pulp samples were first activated by a sequential addition of water, acetone, and *N,N*-dimethylacetamide (DMAc). The activated samples were then dissolved in 90 g/L lithium chloride (LiCl) containing DMAc at room temperature and under gentle stirring. The dissolved samples were diluted to 9 g/L LiCl/DMAc, filtered through 0.2 μm syringe filters, and analyzed in a Dionex Ultimate 3000 (Sunnyvale CA, USA) system, equipped with a guard and four analytical Agilent (Santa Clara, USA) PL-gel Mixed-A columns (7.5 \times 300 mm), and coupled with a Shodex (Tokyo, Japan) RI-101 refractive index detector. The flow rate was 0.75 mL/min, and the column temperature was 25 °C. Narrow pullulan standards (343 Da–2350 KDa; PSS, Mainz, Germany) were used to calibrate the system. The molar masses of the pullulan standards were modified to correspond to those of cellulose ($\text{MM}_{\text{cellulose}} = q \text{MM}_{\text{pullulan}}^p$), with the coefficients $q = 12.19$ and $p = 0.78$ determined by a least-squares method using the data from Berggren et al. (2003).

The chemical composition of the hydrolysates was determined according to the analytical method NREL/TP-510-42623 issued by the US NREL. Monosaccharides were quantified by HPAEC-PAD by direct injection and after total hydrolysis in an autoclave at 121 °C for 60 min. The amount of oligo- and/or polysaccharides was calculated by difference in the monosaccharide content before and after total hydrolysis. Furfural and 5-hydroxymethylfurfural (HMF) were determined by high-performance liquid chromatography (HPLC) in a Dionex Ultimate 3000 (Sunnyvale CA, USA) system, equipped with an Acclaim[®] Organic Acid (4.0 \times 250 mm) analytical column and a DAD-3000 UV–vis diode array detector. Furfural and HMF were determined at a wavelength of 280 nm. Milli-Q water and acetonitrile were the eluents used, the flow rate was 0.6 mL/min, and the column temperature was 30 °C.

The molar mass characteristics of dissolved carbohydrates in selected aqueous hydrolysates were determined by size exclusion chromatography (SEC) with an HPLC–SEC (Agilent 1100, USA) instrument, equipped with a guard column (Ultrahydrogel 6 mm \times 40 mm, Waters, Milford, USA) and two columns (Ultrahydrogel 120 7.8 mm \times 300 mm and Ultrahydrogel 500 7.8 mm \times 300 mm, Milford, USA) connected in series, and a refractive index detector (RID-10A Shimadzu, Tokyo, Japan). The eluent was 0.1 M NaNO_3 , the flow rate was 0.5 mL/min, and the column temperature was 40 °C. A pullulan standard set (342 Da–708 kDa, certified according to DIN BCBH33056V, Fluka, Switzerland) was used to calibrate the system. Average molar masses of the carbohydrates in the hydrolysates were calculated from the entire peak area of the molar mass distribution.

Results and discussion

Effect of treatment temperature on the degradation and dissolution of carbohydrates

HWTs of unbleached birch kraft pulp were conducted at temperatures between 200 and 280 °C, with a flow rate of 100 mL/min. At any temperature, increasing treatment time decreased the xylan content in pulp. The amount of cellulose remained rather constant until a particular xylan content was reached, but thereafter a further reduction in xylan content was accompanied by a rapid reduction in cellulose yield (Fig. 1a). At 200 °C, this reduction in cellulose yield occurred at a xylan content of about 13%, considerably higher than the 5–8% reached at 240–280 °C. The decrease in xylan content with increasing treatment time was also accompanied by a decrease in the intrinsic viscosity of the pulp, but at a given xylan content, the viscosity of pulps treated at 200 °C was clearly lower than that of pulps treated at 240–280 °C (Fig. 1b). The decrease in intrinsic viscosity was due to the cleavage of glycosidic bonds in the cellulose chains, and the consequent reduction of their degree of polymerization (DP). The results in Fig. 1 confirmed our previous observation that increasing temperature up to 240 °C favored the removal of xylan over the degradation of cellulose (Borrega and Sixta 2013). Above 240 °C, increasing temperature resulted in a somewhat better

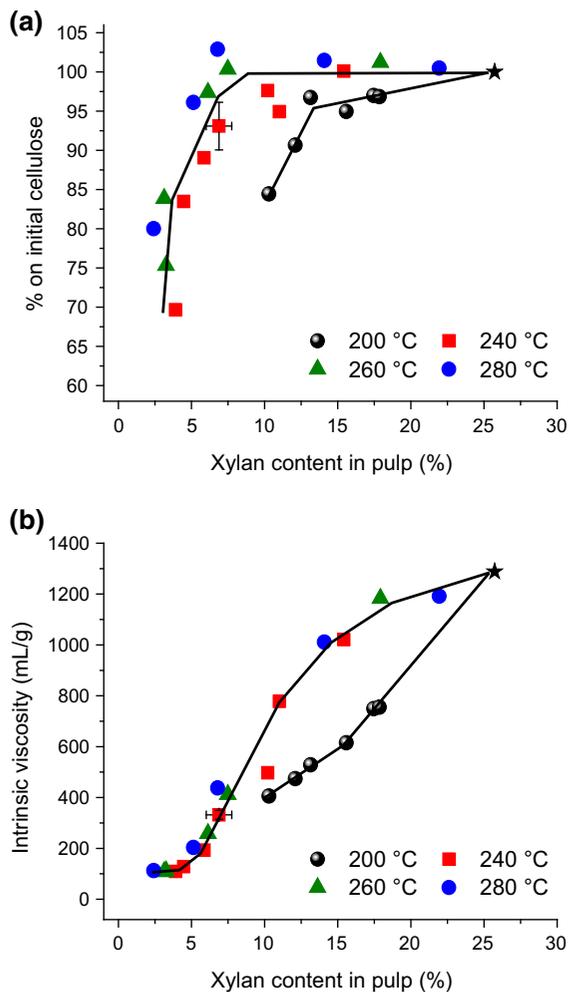


Fig. 1 **a** Residual cellulose and **b** intrinsic viscosity in unbleached birch kraft pulps treated with hot water in a flow-through reactor, using a flow rate of 100 mL/min. The initial kraft pulp is identified with a star symbol. Lines are included to show the prevailing trends

preservation of cellulose yield (Fig. 1a), but no differences were observed in terms of intrinsic viscosity (Fig. 1b). In addition to the degradation of carbohydrates, the HWTs also removed some of the lignin in the unbleached pulp. The lignin content was reduced from 3.1% to about $1.9 \pm 0.4\%$, but a correlation between lignin content and treatment intensity could not be found.

The removal of xylan from birch kraft pulp during the HWT was followed by its dissolution in the aqueous hydrolysate. The chemical composition of selected hydrolysates produced at temperatures of 240–280 °C is shown in Table 2. These treatments

were chosen because of their potential to produce pulps with properties similar to those required in commercial viscose-grade pulps, which typically have a hemicellulosic content of about 3–6% and an intrinsic viscosity in the range of 400–500 mL/g. The terms gluco-oligosaccharides (GOS) and xylo-oligosaccharides (XOS) in Table 2 refer to glucose- and xylose-based compounds with a DP ≥ 2 . At a flow rate of 100 mL/min, the amount of XOS in the selected hydrolysates was about 15% on dry pulp, while the amount of xylose monomers was less than 0.5%. In other words, the xylan recovery was about 60% of the initial pulp xylan, similar to that reported by alkaline extraction of bleached hardwood kraft pulp (Hakala et al. 2013). In addition to xylan-based sugars, small amounts of glucose and GOS were also found in the hydrolysates (Table 2). These amounts probably originated from the residual glucomannan fraction in pulp, but also from the minor degradation of cellulose that occurred during the HWT.

Under hydrothermal conditions, furfural is typically the main degradation product from xylose, but several organic acids and other intermediates formed by side reactions during the conversion (dehydration) of xylose to furfural are also found in aqueous media (Danon et al. 2014; Zeitsch 2000). At a flow rate of 100 mL/min, the amount of furfural in the hydrolysates was only less than 0.5% on dry pulp, and thus the mass balances indicate that about 5% of the initial xylan could not be identified (Table 2). The presence of residual amounts of acetic, levulinic and formic acid in the hydrolysates was indeed detected by our HPLC, but they could not be reliably quantified due to poor signal to noise ratios. It is also likely that some of the extracted xylan remained entrapped within the pulp pores, and was washed away during the cooling of the pulp with cold tap water. Based on the results from Fig. 1 and Table 2, and from a practical point of view, the use of temperatures higher than 240 °C in HWTs of kraft pulp might not be recommended because of the higher costs associated to higher energy demands, and the small differences in cellulose preservation and xylan recovery with increasing temperature.

Effect of flow rate on the recovery of xylan from pulp

In flow-through systems, the selection of a flow rate has direct implications on the formation of

Table 2 Identified composition of pulp and hydrolysates for selected hot water treatments of unbleached birch and eucalyptus kraft pulps in flow-through (FT) and batch reactors

Treatment number	Raw material	Temperature (°C)	Time (min)	Reactor system	Flow rate (mL/min)	Pulp yield (%)	Pulp composition (%)		
							Cellulose	Xylan	Lignin
1	Birch	–	–	–	–	–	70.9	25.7	3.1
2	Birch	280	4	FT	100	80.2	73.0	5.4	1.5
3	Birch	260	5	FT	100	78.5	71.2	5.9	1.1
4	Birch	240	10	FT	100	72.4 (2.9)	66.0 (2.2)	5.0 (0.8)	1.2 (0.2)
5	Birch	240	10	FT	50	75.6 (5.3)	67.5 (2.8)	6.2 (2.1)	1.8 (0.5)
6	Birch	240	10	FT	200	76.0 (1.7)	68.9 (1.1)	5.9 (0.5)	1.2 (0.2)
7	Birch	240	10	FT	400	75.7 (0.5)	69.2 (0.5)	5.4 (0.1)	1.1 (0.0)
8	Birch	220	30	Batch	–	75.9	68.3	5.6	1.9
9	Birch	200*	60	Batch	–	73.2	65.3	5.7	2.2
10	Eucalyptus	–	–	–	–	–	80.0	17.5	2.5
11	Eucalyptus	240	5	FT	100	83.6	75.0	7.1	1.4
12	Eucalyptus	240	6	FT	100	77.0	71.1	4.8	1.1

Treatment number	Raw material	pH	Hydrolysate composition (%)					
			Glucose	Xylose	GOS	XOS	HMF	Furfural
1	Birch	–	–	–	–	–	–	–
2	Birch	4.4	0.0	0.3	0.3	14.9	0.0	0.2
3	Birch	4.4	0.1	0.4	0.5	14.5	0.1	0.3
4	Birch	4.5 (0.2)	0.2 (0.0)	0.4 (0.1)	0.9 (0.2)	14.8 (1.6)	0.2	0.3
5	Birch	4.3 (0.4)	0.1 (0.1)	0.6 (0.3)	0.5 (0.4)	10.0 (1.7)	0.1	0.5
6	Birch	5.1 (0.1)	0.0 (0.0)	0.1 (0.0)	0.5 (0.1)	17.1 (0.5)	0.0	0.0
7	Birch	5.2 (0.1)	0.0 (0.0)	0.0 (0.0)	0.8 (0.7)	20.3 (2.6)	0.0	0.0
8	Birch	3.7	0.4	0.5	0.8	0.2	0.5	3.0
9	Birch	3.0	0.5	0.9	0.5	0.1	0.5	6.9
10	Eucalyptus	–	–	–	–	–	–	–
11	Eucalyptus	5.0	0.0	0.1	0.3	8.4	0.0	0.0
12	Eucalyptus	4.6	0.1	0.2	0.4	9.5	0.1	0.1

Pulp and hydrolysate values are shown as % on initial pulp, with standard deviation in parentheses

* Water treatment conducted in the presence of 0.1 M acetic acid

degradation products as well as on their concentration in the hydrolysate. The higher is the flow rate, the lower is the retention time in the reactor, which means that the dissolved products are released faster from the reaction chamber and their degradation is minimized (Borrega and Sixta 2015; Liu and Wyman 2003). Moreover, the higher is the flow rate, the lower is the products concentration in the hydrolysate

because of higher volumes of water used. In this study, the effect of flow rate on the degradation of carbohydrates and their recovery from the hydrolysate was evaluated on a selected treatment at 240 °C for 10 min, in view of the potential of this particular treatment to produce a viscose-grade pulp and to recover considerable amounts of oligo- and/or polymeric xylan.

For all flow rates investigated, from 50 up to 400 mL/min, the xylan content in pulp was about 7–8% while the intrinsic viscosity was about 330–470 mL/min. Small differences in pulp composition and viscosity were probably due to differences in treatment intensity, as uniform temperature profiles along the reaction chamber were reached faster at higher flow rates. On the other hand, the composition of the hydrolysates was very much dependent on the flow rate. Increasing flow from 50 to 400 mL/min doubled the recovery of XOS, from 10 to 20% on dry pulp, and reduced the recovery of xylose monomers and furfural (Table 2). Increasing flow, however, also led to lower concentrations of the XOS in the hydrolysate, owing to higher volumes of water used. The mass balance for xylan was closed at the highest flow rate (400 mL/min), but was increasingly open with decreasing flow. At the lowest flow rate (50 mL/min), the formation of furfural was only about 0.5% on dry pulp, while the amount of unknown degradation products was as high as 8% on dry pulp. As mentioned above, this may be due to the formation of organic acids, humins and other degradation products which were not here identified. It is also possible that some of the furfural polymerized or was involved in condensation reactions with intermediates formed during the conversion of xylose to furfural (Zeitsch 2000), and therefore was not detected by our HPLC.

The flow rate had a clear effect not only on the amount of sugars recovered, but also on their molar mass characteristics (Fig. 2). Since XOS were by far the dominant compound in the hydrolysates (see Table 2), particularly at the highest flow rates, the molar mass values determined by HPLC–SEC may be assigned to correspond mostly to those of XOS. Figure 2 shows that the extracted xylan had a relatively high molar mass, with weight average values (M_w) increasing from 6 to 11 kDa with increasing flow. The weight fraction of polymeric xylan (above 5 kDa) was about 30–35% at the lowest flow rates (50 and 100 mL/min), and 55–60% at the highest flow rates (200 and 400 mL/min). Despite the relatively high molar mass, the average values obtained here were considerably lower than the 18–36 kDa reported for alkali-extracted xylan from bleached hardwood pulp by Hakala et al. (2013) and Rosa-Sibakov et al. (2016).

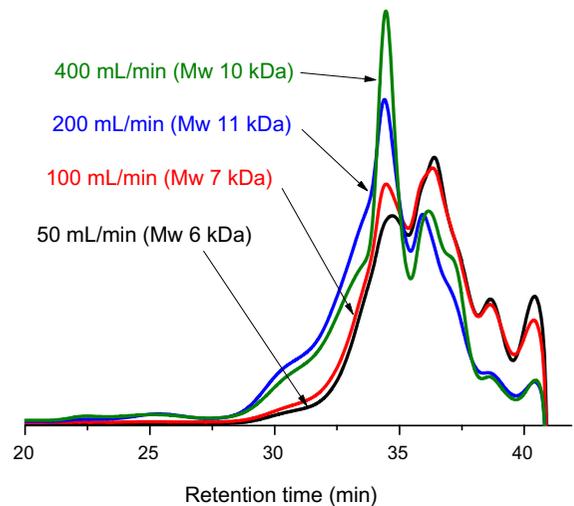


Fig. 2 HPLC–SEC chromatograms of hydrolysates produced by water treatment of unbleached birch kraft pulps at 240 °C for 10 min, with flow rates between 50 and 400 mL/min. The weight average molar mass (M_w) of dissolved carbohydrates in the hydrolysate is indicated in *parenthesis*

Acid-catalyzed treatments of pulp

In our previous study, it was observed that under similar treatment conditions of temperature, time and flow, the removal efficiency of xylan from birch wood during HWTs was higher than from birch kraft pulp (Borrega and Sixta 2013). This superior efficiency in xylan removal was partly explained by the presence of an easy-to-remove xylan fraction in wood, but more importantly, by the presence of acetyl groups, which formed acetic acid and catalyzed the degradation of the xylan. Based on this observation, the addition of acetic acid to enhance xylan removal from pulp and thus reach higher purity levels than those shown in Fig. 1 was here investigated in a batch reactor.

At low and intermediate treatment intensities (\log of $Px_s < 6$), the residual xylan content in pulp was lower in acid-catalyzed than in water-only experiments (Fig. 3). At the highest intensities, corresponding to residual xylan contents below 10% and pulp yields below 70%, the addition of acetic acid had negligible effects on improving xylan removal. A similar behavior was observed during water and dilute acetic acid prehydrolysis of southern red oak wood, where the addition of acetic acid improved the removal of xylan only until intense prehydrolysis conditions were applied (Conner and Lorenz 1986).

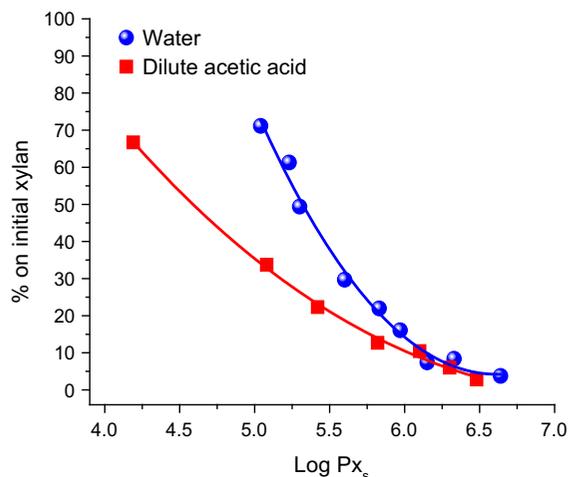


Fig. 3 Residual xylan in unbleached birch kraft pulps treated with hot water and dilute acetic acid in a batch reactor, at temperatures between 180 and 240 °C. The Log Px_s is a measure of the treatment intensity that combines the effect of temperature and time. Lines are included to show the prevailing trends

The higher efficiency in xylan removal for some of the acid-catalyzed experiments was, however, not accompanied by a higher selectivity, since the degradation of cellulose at a given xylan content in pulp was the same as in the water-only experiments (Fig. 4). The abrupt decrease in cellulose yield at xylan contents below 10%, as shown in Fig. 4a, was also observed when unbleached birch pulps were treated in the flow-through system at temperatures of 240–280 °C (see Fig. 1a). This appears to indicate that the removal of large amounts of xylan from the fibers' cell wall enhanced the exposure of cellulose chains to high-temperature water, promoting their hydrolytic degradation. Moreover, the residual xylan present in the fibers at low xylan contents is closely associated to the cellulose, and thus the removal of this recalcitrant xylan fraction was not possible without the concomitant degradation of cellulose.

In Fig. 4b, the intrinsic viscosity of unbleached pulps with xylan contents below 10% was lower than 300 mL/g, which practically renders these pulps unsuitable for commercial dissolving applications. It appears that, at a given xylan content, the viscosity of pulps treated in a batch reactor was lower than that of pulps treated in the flow-through reactor (see Figs. 1b and 4b). This may be explained by the more acidic conditions in the batch reactor, as indicated by the lower pH values in Table 2.

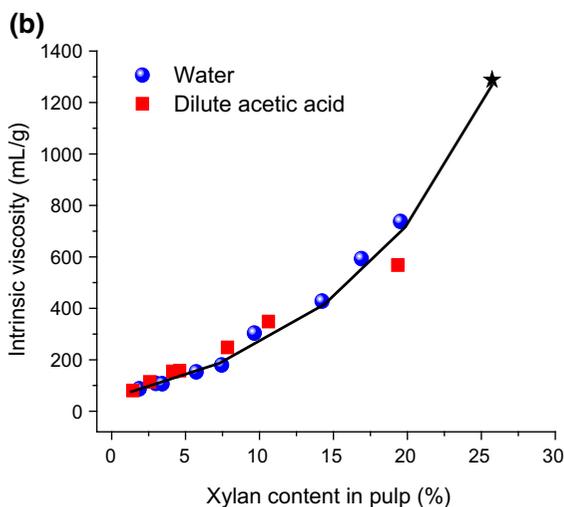
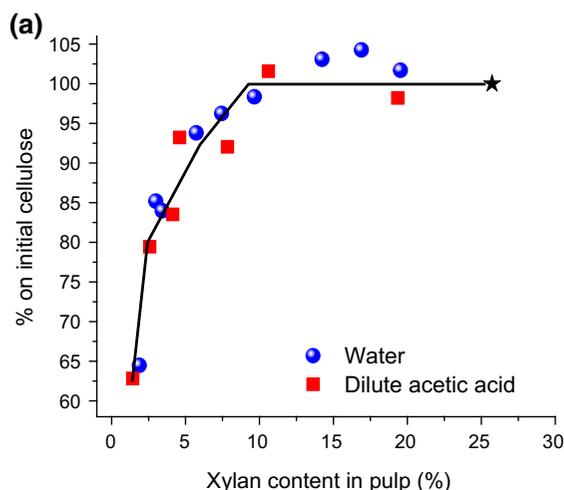


Fig. 4 a Residual cellulose and **b** intrinsic viscosity in unbleached birch kraft pulps treated with hot water and dilute acetic acid in a batch reactor, at temperatures between 180 and 240 °C. The initial kraft pulp is identified with a star symbol. Lines are included to show the prevailing trends

The composition of selected hydrolysates from the water-only and the acid-catalyzed experiments is shown in Table 2. Compared to the hydrolysates from the flow-through experiments, and for a similar removal of pulp xylan, the amount of sugars in the hydrolysates from the batch reactor was only minor, with less than 1% of the initial pulp being recovered as xylose and XOS. This low sugar recovery was due to the extensive formation of degradation products, as demonstrated by the relatively high furfural content (Table 2). In addition to furfural, a substantial amount

of other xylan degradation products, including organic acids and humins, were most likely formed (Danon et al. 2014; Zeitsch 2000). Therefore, based on the effects on pulp quality and sugar recovery, the use of a flow-through system to perform HWTs of pulps is recommended over a batch system.

Effect of initial xylan content on the purity of water-treated pulps

The high xylan content in birch kraft pulp makes it an attractive material for HWTs, since large amounts of xylan-derived sugars can be potentially recovered from the aqueous hydrolysates. From the viewpoint of dissolving pulp production, however, the high xylan content is not desirable because of the intense treatment conditions required to reach high levels of cellulose purity, with the consequent partial degradation of the cellulose fraction (see Fig. 1). The effects of HWTs on pulps with lower xylan content were here investigated by producing an unbleached eucalyptus kraft pulp, containing 18% xylan, and applying a series of water treatments at 240 °C. To exclude any effects derived from different lignin contents, kraft pulping of eucalyptus wood was conducted until a kappa number of about 16 was reached, similar to the kappa number of the unbleached birch pulp.

The properties of both unbleached eucalyptus and birch pulps after the HWTs are compared in Fig. 5. The residual cellulose yield was similar in both pulps, and decreased abruptly at xylan contents below 10% (Fig. 5a). The intrinsic viscosity was higher in the eucalyptus pulps (Fig. 5b), which may be partly explained by the somewhat higher initial viscosity, but mostly by the lower initial xylan content, which required shorter treatment times to reach the same level of cellulose purity as in the birch pulps. Shorter treatment times (6 min instead of 10 min) reduced the extent of hydrolysis in the cellulose chains, with the consequent higher preservation of their DP. Therefore, compared to pulps with high xylan content, HWTs of pulps with low xylan content allow for higher viscosities at a given purity, or for higher purity at a given target viscosity. In the latter case, however, the increase in purity may come at the expense of some additional losses in cellulose yield (Fig. 5a). A low initial xylan content in pulp also results in a lower sugar recovery from the hydrolysates, as shown in Table 2.

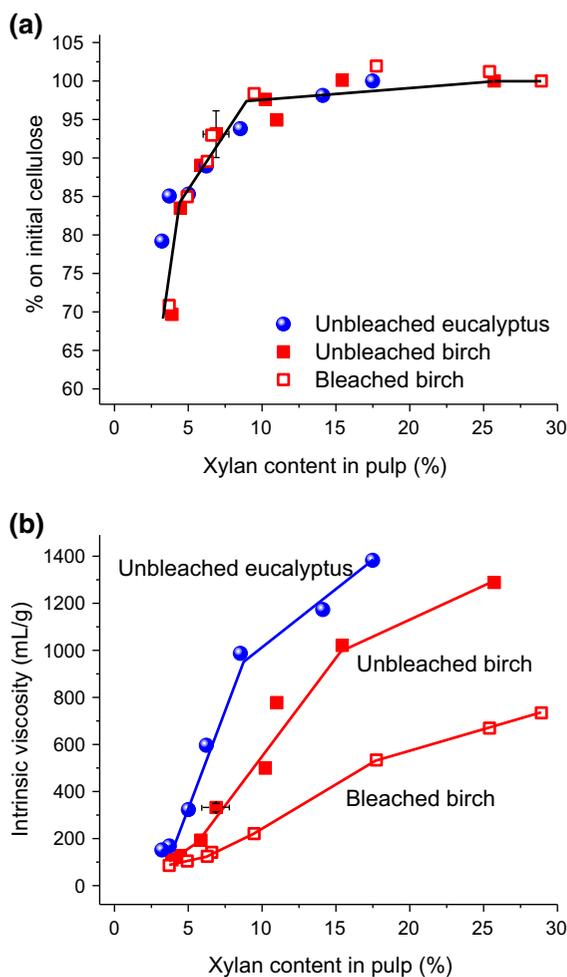


Fig. 5 **a** Residual cellulose and **b** intrinsic viscosity in birch and eucalyptus kraft pulps treated with hot water in a flow-through reactor at 240 °C, with a flow rate of 100 mL/min. Lines are included to show the prevailing trends

Bleached vs unbleached pulps

The use of unbleached pulps for the HWTs is interesting because part of the residual lignin in the pulp is removed, which may then allow for milder bleaching processes. Nonetheless, in this study, we have also investigated the effects of HWTs on bleached birch kraft pulps. As shown in Fig. 5a, the removal of cellulose as a function of decreasing xylan content in pulp followed a similar trend in both unbleached and bleached birch pulps. However, the intrinsic viscosity at any given xylan content was lower in the bleached pulps (Fig. 5b), with values between 100–150 mL/g at about 7% xylan content,

much lower than those required in commercial dissolving applications. The low intrinsic viscosity of the bleached water-treated pulps is due to the lower initial viscosity, although it is also possible that, compared to bleached pulps, the presence of residual lignin in the unbleached pulps played some role in protecting the cellulose fraction from hydrolytic degradation during the HWT (Zhao et al. 2012).

Commercial dissolving pulps used in the manufacture of cellulose derivatives such as viscose need to be fully bleached. Therefore, in order to evaluate the applicability of HWTs to produce a bleached viscose-grade pulp, selected unbleached birch and eucalyptus pulps treated with water at 240 °C for 10 and 6 min, respectively, were subjected to a D₀–Ep–P bleaching sequence. Since the kappa number of the water-treated pulps was only about 4–5, much lower than the initial kappa number of 16, no oxygen delignification was performed. The oxygen delignification stage was also purposely omitted in order to avoid oxidative degradation reactions in cellulose that may result in a further decrease of its molar mass (see Sixta 2006). The properties of the bleached pulps are compared in Table 3 to those of a commercial viscose-grade pulp, produced by PHK pulping of birch wood. The final xylan content in both water-treated pulps was about 8%, slightly higher than the 6.3% in the commercial pulp. Despite their lower purity, these pulps may still be suitable for the viscose process, as birch pulps with similar xylan content (i.e., 7–8%) have previously shown satisfactory filter values during viscose filterability tests (Testova et al. 2014). The molar mass characteristics of the eucalyptus pulp were similar to those of the commercial viscose-grade pulp, while the cellulose fraction in the birch pulp was clearly

degraded to a higher extent, as indicated by the lower viscosity, average weight molar mass and number of chains with a DP higher than 2000 (Table 3). The low viscosity of the water-treated birch pulp, however, should be sufficient for its viscose conversion, since the pulp viscosity is typically adjusted to about 220–240 mL/g during the viscose process by pre-aging of the alkali-cellulose. It should also be noted that it was not the objective of this exercise to optimize the bleaching process, and thus the properties of the bleached pulps may be improved by selecting more appropriate bleaching sequences and/or adjusting the chemical charges for each sequence.

Yields and potential applications of the cellulose and xylan fractions

In summary, HWTs of unbleached hardwood kraft pulps in a flow-through system were here presented as a simple and chemical-free biorefinery concept for the separation of xylan and cellulose fractions. At 240 °C, up to 75–80% of the xylan in birch pulps and up to 60–65% of the xylan in eucalyptus pulps could be extracted with only minor losses in cellulose yield (Table 2); over 90% of the cellulose present in the initial kraft pulp remained in the water-treated pulp. After bleaching, the water-treated pulps contained 7–8% xylan and had an intrinsic viscosity between 300 and 500 mL/g (Table 3), with birch pulp having a lower viscosity than eucalyptus pulp at a given xylan content. These cellulose-enriched pulps may be utilized in the manufacture of viscose fibers, as their chemical and macromolecular properties were similar to those of commercial viscose-grade pulps. However, one of the most important parameters of any

Table 3 Chemical and molecular properties of unbleached kraft pulps treated with hot water at 240 °C, with a flow rate of 100 mL/min, and then bleached with a D₀–Ep–P sequence. The reference pulp is a commercial prehydrolysis kraft pulp from birch

Sample	Cellulose (%)	Xylan (%)	Glucomannan (%)	ISO brightness (%)	Intrinsic viscosity (mL/g)	Mw (kg/mol)	PDI	DP < 100	DP > 2000
Birch kraft	91.8	7.9	–	87.8	318	187	3.7	0.07	0.14
Eucalyptus kraft	92.0	8.0	–	86.0	442	298	4.2	0.04	0.26
Reference	93.5	6.3	0.2	>90*	484	317	4.5	0.05	0.27

* ISO-brightness provided by the pulp manufacturer

dissolving pulp is its reactivity towards derivatizing chemicals. The pulp reactivity cannot be defined by a single parameter, since it often depends on a combination of molecular, ultrastructural and fibrillar features (Sixta 2006). Therefore, additional information on the physico-chemical and structural characteristics of water-treated pulps is yet needed to fully assess their suitability for viscose conversion.

The xylan extracted from the unbleached kraft pulps during the HWT was dissolved in the aqueous hydrolysate, from which may be recovered for its subsequent valorization. The use of birch pulps, with higher initial xylan content than eucalyptus pulps, obviously resulted in higher sugar recoveries. Increasing flow rate from 50 to 400 mL/min increased the amount of birch xylan found in the hydrolysate, from 10 to 20% on initial pulp (Table 2). Moreover, increasing the flow rate also increased the molar mass (M_w) of the xylan, from 6 kDa to about 10 kDa. The potential applications of xylan-based compounds strongly depend on their physico-chemical properties. Neutral XOS with DPs 2–6 can be utilized as dietary fibers (prebiotics), since they promote the growth of microbiota living in the human colon and exhibiting beneficial health-effects (Aachary and Prapulla 2011; Deutschmann and Dekker 2012). Neutral polymeric xylan may be used as a multifunctional food ingredient, because it improves several technological properties (i.e., texture, water retention) in dairy products and shows a slow fermentation rate, which enhances intestinal comfort (Rosa-Sibakov et al. 2016). These authors reported that xylan obtained after enzymatic hydrolysis of alkali-extracted xylan, and having a M_w of 10 kDa, showed the best colloidal effects and the slower fermentation rate when added to acid-milk gels. The oligo- and/or polymeric xylan recovered from our hydrolysates is expected to have a low degree of substitution, since acetyl groups present in the wood xylan are known to be cleaved during kraft pulping. Moreover, uronic acids formed during pulping may have been partly hydrolyzed under the slightly acidic conditions generated during the HWT, as indicated by the pH values in Table 2. The expected low degree of substitution, coupled with the relatively high molar mass (~ 10 kDa) and the chemical-free extraction process, make water-extracted xylan a strong candidate to be used as food hydrocolloid.

Conclusions

HWT of unbleached hardwood kraft pulp in a flow-through system can be utilized to produce high-purity cellulosic pulp and to recover polymeric xylan. Under selected operational conditions (240 °C for 10 min), the properties of water-treated pulps largely comply with the chemical and macromolecular properties required in viscose-grade pulps. However, none of the water-treated pulps would be suitable for the production of cellulose acetate, since the low xylan content (less than 2%) required in acetate-grade pulps may only be reached at very low viscosities and after substantial losses in cellulose yield. The amount of xylan in the hydrolysate as well as its molar mass increase with increasing flow, but this in turn dilutes the product concentration and may require additional efforts to isolate it. Nonetheless, the rather homogeneous composition of the hydrolysate is expected to facilitate the recovery of the dissolved xylan by ultrafiltration. This neutral polymeric xylan has the potential to be utilized in high value-added applications such as food hydrocolloids.

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