

# Purification of cellulosic pulp by hot water extraction

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**Abstract** Hot water extraction (HWE) of pulp in a flow-through reactor was evaluated as a method to purify paper-grade pulps. About 50–80 % of the xylan and up to 50 % of the lignin in unbleached birch Kraft pulp was extracted by the HWE without losses in cellulose yield. The residual xylan content in the extracted pulps was predominantly too high for dissolving-grade applications, but some of the pulps with a xylan content of 5–7 % might still be suitable as rayon-grade pulps. Increasing extraction temperature lowered the xylan content at which cellulose yield started to decrease. Furthermore, at any given xylan content, increasing extraction temperature resulted in cellulosic pulp with higher degree of polymerization. The extracted xylan was recovered almost quantitatively as xylo-oligosaccharides. The results suggest that HWEs at elevated temperatures may be applied to purify cellulosic pulps, preferably containing a low xylan content, and to recover the extracted sugars.

**Keywords** Birch kraft pulp · Cellulose · Dissolving-grade pulp · Hot water extraction · Xylan

## Introduction

The global demand for dissolving wood pulps to produce regenerated cellulose fibers has seen a steady increase over the last decade. This increase, largely due to the demand for textile fibers but also for other cellulose specialty products like cellulose acetate, is still expected to prevail over the next 20–30 years (Haemmerle 2011; Sixta et al. 2013). Dissolving pulps contain a high cellulose content (>90 % of the dry mass) of uniform degree of polymerization (DP) and low amounts of organic and inorganic impurities. Acetate-grade pulps are the highest purity dissolving pulps, with a hemicellulose content below 2 %, a cellulose content above 97 %, and an intrinsic viscosity between 600 and 800 ml/g (Sixta 2006).

Dissolving wood pulps are traditionally produced by the prehydrolysis Kraft (PHK) process, in which wood is steamed to remove some of the hemicelluloses prior to pulping, or by the acid sulfite process. Post-treatments to further reduce the hemicellulosic content typically include a hot caustic extraction (HCE) for acid sulfite pulps and a cold caustic extraction (CCE) for both acid sulfite and PHK pulps, but these

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purification methods contribute to a considerable increase in production costs (Sixta 2006). An alternative to the acid sulfite-HCE process for the production of viscose-grade pulps may be the SO<sub>2</sub>-Ethanol-Water (SEW) pulping. In addition to a good quality rayon pulp, the SEW process allows high flexibility in terms of raw materials, short cooking times, and a significant recovery of sugars from the pulping liquor (Iakovlev and Heiningen 2012; Sixta et al. 2013). The production of viscose-grade pulps has also been investigated by applying a CCE stage to paper-grade pulps, which allows the removal of substantial amounts of short-chain hemicellulosic sugars while preserving the yield of cellulose (Gehmayr et al. 2011; Schild and Sixta 2011). Recently, the novel IONCELL process has been shown to be successful in the conversion of paper-grade pulps to dissolving pulps. In the IONCELL process, the hemicelluloses in the pulp are selectively dissolved in an ionic liquid with the addition of a co-solvent, leaving a residual pure cellulosic fraction (Froschauer et al. 2013).

In the last years, several research efforts have been directed towards producing dissolving pulp by applying a hot water extraction (HWE) to the lignocellulosic material before alkaline pulping (Borrega et al. 2013a; Li et al. 2010; Reguant et al. 1997; Ribas Batalha et al. 2011; Schild and Sixta 2011). This approach is similar to the existing industrial PHK process, but the vapor phase is replaced by a liquid water prehydrolysis, and Kraft pulping is often replaced by a non-sulphur soda-anthraquinone (SAQ) pulping. Water prehydrolysis is an attractive method because it produces hydrolysates that are rich in sugars and other valuable products like acetic acid (Amidon et al. 2013; Garrote et al. 1999; Testova et al. 2011). Furthermore, no chemicals are required because water is the only solvent used. So far, the formation of sticky lignin precipitates in the hydrolysate has hindered the application of HWE at an industrial scale (Leschinsky et al. 2009). However, lignin precipitation may be overcome with adsorption technologies based on activated carbon (Gütsch and Sixta 2011), or by flocculation with lignin specific polymers like poly ethylene oxide (Shi et al. 2011).

In general, the purity of dissolving pulps produced by a combined HWE and SAQ pulping is rather low, although this largely depends on the selected raw material (Ribas Batalha et al. 2011; Sixta et al. 2013). Increasing the cellulose purity can be realized by increasing the HWE intensity. This is because at

temperatures above 180 °C, HWE has the potential to quantitatively remove the hemicelluloses from wood, whereas the cellulose yield remains mostly unaffected up to higher temperatures (Borrega et al. 2011; Mok and Antal 1992). Under intense extraction conditions, however, the extensive cleavage of glycosidic bonds in cellulose results in a reduction of its DP and the formation of new reducing end-groups. A reduction in cellulose DP appears to occur even when mild extraction conditions are applied (Duarte et al. 2011). In a subsequent alkaline pulping process, particularly following an intense HWE, the yield of cellulose dramatically decreases due to peeling reactions that start at the reducing ends (Borrega et al. 2013a; Testova et al. 2013). Therefore, a combined HWE and alkaline pulping appears to be suitable to produce dissolving pulps for viscose applications, but other specialty products like cellulose acetate may only be produced from lignocellulosic materials with a low hemicellulosic content.

Considering their effect on wood carbohydrates, HWEs at elevated temperatures might be used to remove the hemicelluloses from paper-grade pulps and thus convert them into dissolving pulps. Furthermore, in the case of unbleached pulp, the HWE may also remove some of the residual lignin. Such HWE is likely to cleave some of the glycosidic bonds in cellulose, reducing its DP. However, the cellulose yield should be largely preserved because a subsequent alkaline pulping is no longer required. The extracted hemicelluloses may also be recovered from the hydrolysate to be transformed into value-added products. A similar approach but using an acidic hydrolysis on pulp to recover xylose has already been suggested by Heikkilä et al. (2004). In a batch system, HWEs at elevated temperatures induce significant degradation of the extracted hemicelluloses, as they are converted into degradation products like furans and carboxylic acids (Borrega et al. 2013b). In a flow-through system, the hemicelluloses are continuously removed from the reaction chamber before they can degrade further, resulting in a considerable increase in sugar yield (Liu and Wyman 2005; Yang and Wyman 2004).

One of the main challenges of converting a Kraft paper-grade pulp into a dissolving pulp by HWE may be to achieve acceptable pulp reactivity, even if the xylan content is low. The chemical reactivity, one of the most important properties of any dissolving pulp,

is defined by a combination of molecular, ultrastructural and fibrillar features (Sixta 2006). Determining the pulp reactivity in a subsequent chemical conversion process, however, is beyond the scope of the present study. In this paper, we evaluate the potential of HWEs at elevated temperatures to purify paper-grade pulp in a flow-through reactor. Birch (*Betula pendula* and *B. pubescens*) Kraft pulp is selected as starting raw material because birch is the most abundant hardwood in the Nordic countries and is extensively utilized in pulping. The HWE efficiency towards xylan removal is evaluated and compared to the xylan removal from birch wood meal under similar extraction conditions. The effects of HWE on the yield and DP of the cellulose fraction in the pulp are also investigated. Finally, the recovery of dissolved sugars from the hydrolysate is quantified.

## Experimental

### Cellulosic material

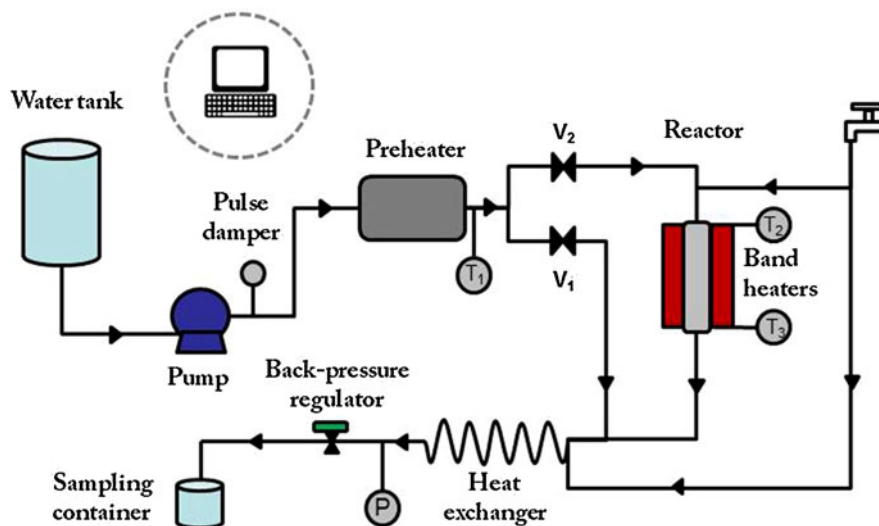
Unbleached birch Kraft pulp and birch wood meal were the raw materials used in this study. The pulp, produced by Stora Enso Oyj (Finland), was taken from the production line before the oxygen delignification stage and delivered unscreened and unwashed. Pulp washing and screening in a rotating laboratory screener were conducted at Aalto University. The identified chemical composition of the pulp was:

21.9 % xylose, 63.9 % glucose, 1.9 % Klason lignin and 1.2 % acid-soluble lignin (ASL). On the other hand, coarse sawdust from silver birch (*B. pendula*) wood felled in Southern Finland was ground in a Wiley mill to a particle size  $<0.6$  mm. The identified chemical composition of the wood meal was: 0.6 % galactose, 1.6 % mannose, 20.8 % xylose, 42.2 % glucose, 19.1 % Klason lignin, 3.6 % ASL, 3.5 % acetyl groups and 2.4 % extractives. The dry matter content of both pulp and wood meal was determined by oven-drying representative samples in a convection oven at 103 °C overnight.

### Hot water extractions

About 15 g (oven-dry mass) of pulp were placed in a flow-through percolation reactor of 190 ml volume constructed by Unipress Equipment (Poland) (Fig. 1). Water at room temperature was pumped through the reactor to wet the pulp and to set the back-pressure regulator to the operating pressure. The preheater was then turned on and water was pumped through the bypass line ( $V_1$ ) to reach a predetermined temperature, measured by the thermocouple  $T_1$ . Subsequently, the band heaters were turned on to pre-heat the reactor walls and thus minimize heat losses during the extraction process. As soon as the thermocouple  $T_2$  measured 100 °C, the valve  $V_2$  was opened, allowing the incoming hot water to pass through the reactor. The temperature of the hydrolysate leaving the reactor was measured by the thermocouple  $T_3$ . Because of the high

**Fig. 1** Schematic diagram of the flow-through percolation reactor and associated elements used for the hot water extractions of pulp and wood



**Table 1** Experimental parameters for the hot water extractions of birch Kraft pulp and birch wood meal

Raw material	Temperature (°C)	Extraction time (min)	Flow rate (ml/min)	Pressure (bars)
Kraft pulp	200	5, 15, 30, 60, 90	400	30 ± 5
Kraft pulp	220	5, 10, 15, 30, 45	400	40 ± 5
Kraft pulp	240	1, 2, 5, 10, 15, 30	400	50 ± 5
Wood meal	200	5, 10, 20, 45, 60	400	30 ± 5
Wood meal	240	2, 5, 8, 12, 20, 30	400	50 ± 5

flow rate selected (400 ml/min), a uniform temperature gradient along the reactor was rapidly reached. The hot hydrolysate was cooled by a heat exchanger and collected in a sampling container. After a predetermined amount of time, the valve  $V_2$  was closed, the pump was stopped and the heating elements (pre-heater + band heaters) were turned off. The pressure was then released and the remaining hydrolysate within the reactor was collected. The pulp was cooled by circulating cold tap water through the reactor before being recovered. Some HWEs on 30 g (oven-dry mass) of wood meal were also conducted following the same procedure as described above. The pulp and wood yield after the extraction were determined on a dry-mass basis after oven-drying representative samples at 103 °C overnight. The experimental parameters for the HWEs are shown in Table 1.

#### Analytical determinations

The chemical composition of pulp and wood meal, before and after the HWE, was determined according to the analytical method NREL/TP-510-42,618 issued by the US National Renewable Energy Laboratory (NREL). Monosaccharides were determined by high-performance anion exchange chromatography with pulse amperometric detection in a Dionex ICS-3000 system. Based on the amount of glucose and xylose mono saccharides, the cellulose and xylan (polymeric xylose) content was calculated with the Janson formula (Janson 1974). Acetyl groups (acetic acid) were determined by high-performance liquid chromatography (HPLC) in a Dionex 3000 Ultimate system. The ASL was determined in a Shimadzu UV-2550 spectrophotometer at a wavelength of 205 nm, and using an adsorption coefficient of 110 l/(g cm) (Swan 1965). The extractives content in wood meal was determined after extraction with acetone for 6 h in a Soxhlet apparatus. The kappa number and the intrinsic viscosity

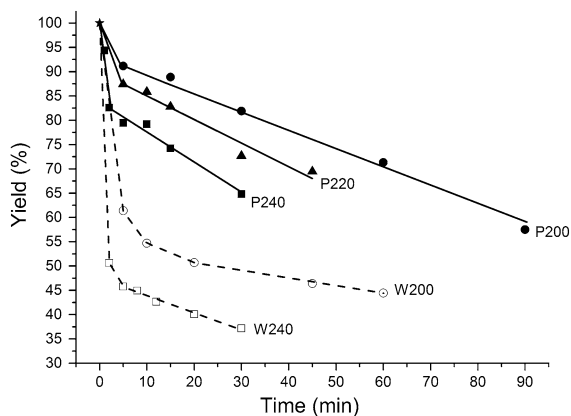
of the pulp were determined according to the SCAN-C 1:100 and SCAN-CM 15:99 methods, respectively.

The molar mass distribution (MMD) of selected pulps was determined by gel permeation chromatography. Prior to the analyses, the samples were activated by a water—acetone—*N,N*-dimethylacetamide (DMAc) sequence. The activated samples were dissolved in 90 g/L lithium chloride (LiCl) containing DMAc at room temperature, and under gentle stirring. The samples were then diluted to 9 g/L LiCl/DMAc, filtered through 0.2 µm syringe filters, and analyzed in a Dionex Ultimate 3000 system with a guard column, four analytical columns (PLgel Mixed-A, 7.5 × 300 mm) and RI-detection (Shodex RI-101). Flow rate and temperature were 0.75 ml/min and 25 °C, respectively. Narrow pullulan standards (343 Da–2,500 kDa, PSS GmbH) were used to calibrate the system. The MM of the pullulan standards were modified to correspond to those of cellulose ( $MM_{cellulose} = q \cdot MM_{pullulan}^p$ ), with the coefficients  $q = 12.19$  and  $p = 0.78$  being determined by a least-squares method using the data published by Berggren et al. (2003).

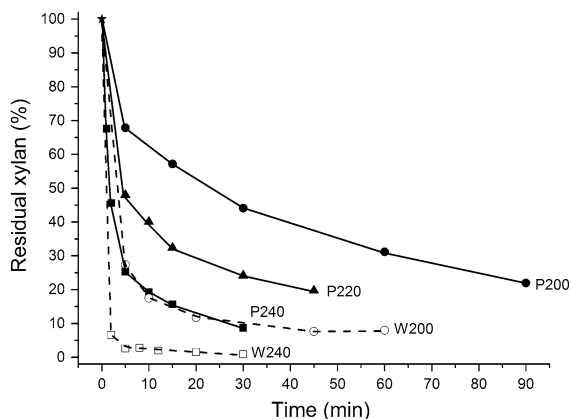
## Results and discussion

### Efficiency of hot water extraction towards xylan removal

The pulp and wood yield after HWE decreased with increasing extraction temperature and time (Fig. 2). Under similar extraction conditions, the pulp yield was considerably higher than the yield of birch wood meal. This yield difference can be partly explained by the effect of HWE on xylan removal. As shown in Fig. 3, xylan was more extensively removed from wood than from pulp, despite both having a similar initial amount (about 27 % xylan content). Xylan in wood is often considered as two separate fractions, one that is easily



**Fig. 2** Yield of birch Kraft pulp (P) and wood meal (W) after hot water extraction at temperatures of 200, 220 and 240 °C



**Fig. 3** Residual xylan in birch Kraft pulp (P) and wood meal (W) after hot water extraction at temperatures of 200, 220 and 240 °C

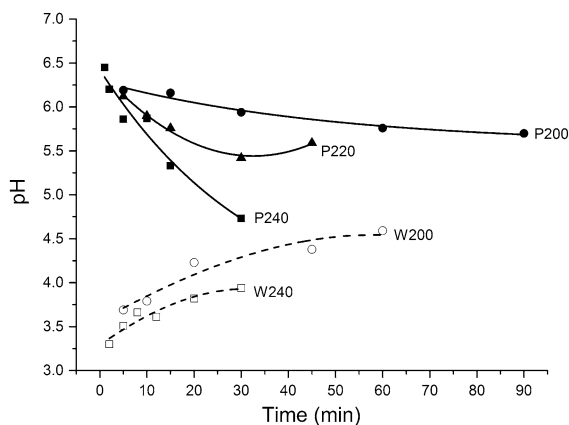
degraded and one that is more difficult to remove (Conner 1984). In pulp, a larger proportion of the recalcitrant xylan fraction may be expected because some (or most) of the easily degradable xylan in wood is already dissolved during Kraft pulping. Therefore, a larger amount of recalcitrant xylan might explain to some extent the lower extraction efficiency in pulp.

In addition to different proportion of xylan fractions in wood and pulp, the main factor contributing to the xylan removal efficiency is likely to be found in the chemical structure of the xylan. In hardwoods, the hemicellulosic 4-*O*-methyl-glucuronoxylan contains acetyl groups bound to the C2 or C3 carbons of the xylose units (Fengel and Wegener 2003). During a HWE, hydronium ions from water auto ionization cleave the acetyl groups in wood, and the consequent

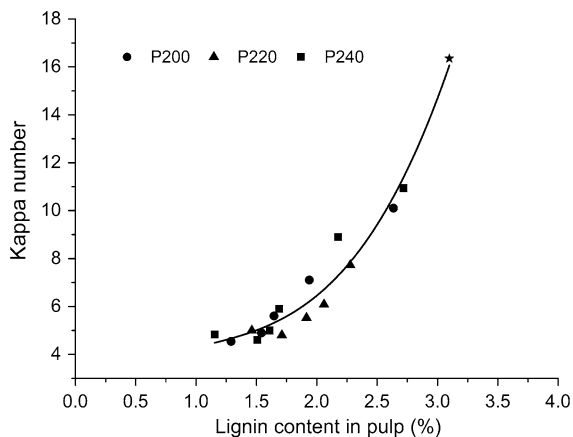
formation of acetic acid promotes the hydrolytic degradation of wood components, primarily the hemicelluloses (Garrote et al. 1999). On the other hand, in Kraft pulp, the xylan is not acetylated because acetyl groups are readily removed during alkaline pulping (Sixta 2006). The absence of acetyl groups in our unbleached pulp was confirmed by HPLC analyses. Therefore, during HWE of pulp, acetic acid from acetyl groups could not be formed and xylan degradation was minimized (Fig. 3).

Despite the lower extraction efficiency, as compared to wood, large amounts of pulp xylan were removed during the HWE, particularly with increasing temperature. This probably occurred through cleavage of glycosidic bonds in xylan by hydronium ions from water auto ionization, and along with time, by the release of low molar mass xylo-oligosaccharides (XOS) and their solubilization in the high-temperature water (Chen et al. 2010). The formation of hydronium ions by water auto ionization and the solubilization of low molar mass XOS were enhanced by an increase in water temperature (Kruse and Dinjus 2007).

The acidic conditions generated during HWE of pulp and wood were investigated by measuring the pH in the collected hydrolysates (Fig. 4). It should be noted that the pH was measured at room temperature, and thus the actual pH of the liquid phase in the reactor may be considerably lower than that shown in Fig. 4 (Kruse and Dinjus 2007). The hydrolysates from wood were clearly more acidic than the ones from pulp, which supports the superior efficiency of HWE towards xylan hydrolysis shown in Fig. 3. In wood,



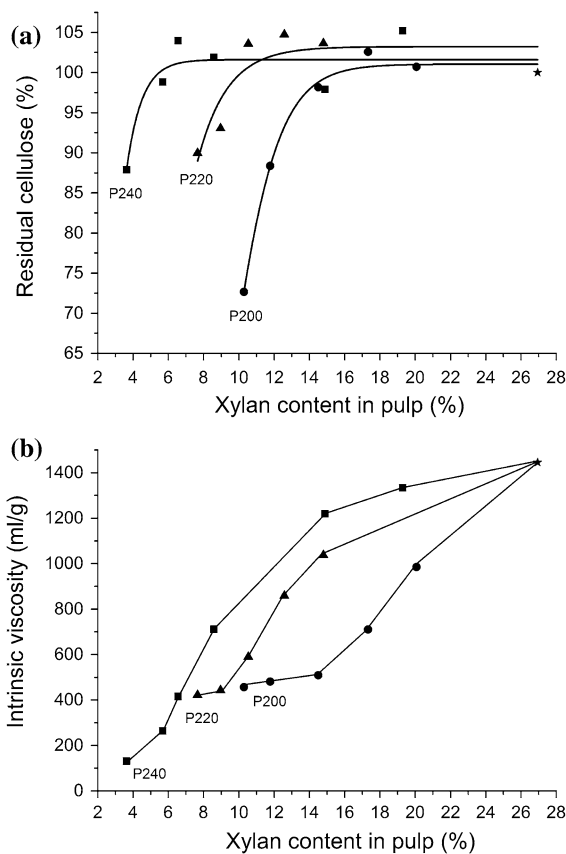
**Fig. 4** Measured pH at room temperature in hydrolysates after hot water extraction of birch Kraft pulp (P) and wood meal (W) at temperatures of 200, 220 and 240 °C



**Fig. 5** Kappa number versus lignin content in birch Kraft pulp after hot water extraction at temperatures of 200, 220 and 240 °C

the rapid cleavage of acetyl groups followed by the formation of acetic acid resulted in highly acidic hydrolysates. Thereafter their acidity decreased along with increasing extraction time, due to large volumes of water used and the consequent dilution of the acids formed. Previous studies on HWE of wood in a continuous flow-through system have also shown the pH to increase with extraction time (Chen et al. 2010; Liu and Wyman 2005). Surprisingly, the pulp hydrolysates became more acidic along with increasing extraction temperature and time (Fig. 4). Although the absence of acetyl groups in pulp prevented the formation of acetic acid, a large variety of low MM carboxylic acids may have formed through degradation of carbohydrates, particularly at increased extraction intensities (Borrega et al. 2013b). However, one might expect a similar acid formation during HWE of wood. The discrepancies in the evolution of pH in pulp and wood hydrolysates are not yet fully understood.

The removal of xylan from the unbleached pulp during the HWE was accompanied by some delignification (Fig. 5). The lignin content in the pulp, expressed as the sum of Klason lignin and ASL, was reduced about 60 %. This was also shown as a decrease in kappa number, from an initial value of 16 down to about 4. Pulp delignification during the HWE possibly occurred, as in the case of wood, by homolytic cleavage of  $\alpha$ -O-4 and  $\beta$ -O-4 bonds (Bobleter 1994; Leschinsky et al. 2008). The removal of lignin from pulp during the HWE is of interest because it might facilitate the subsequent bleaching stage by, for instance, reducing the amount of chemicals or the



**Fig. 6** Residual cellulose (a) and intrinsic viscosity (b) of birch Kraft pulp as a function of xylan content after hot water extraction at temperatures of 200, 220 and 240 °C

number of bleaching sequences needed to attain certain brightness.

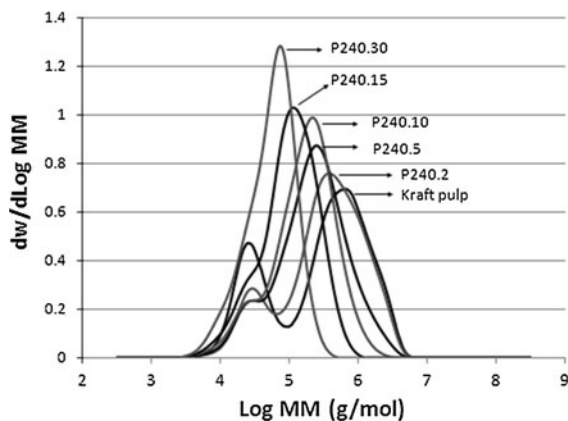
#### Effects of hot water extraction on the cellulose fraction

The use of HWE to purify paper-grade pulps and produce dissolving-grade pulps obviously requires that cellulose is preserved. Moreover, the xylan content should be primarily lower than 5 % in order to avoid discoloration and filterability problems during the subsequent processing of the pulp (Sixta 2006). It can be seen in Fig. 6a that at 200 and 220 °C, HWEs did not remove sufficient xylan from the pulp. At 240 °C, only one of the HWEs gave an extracted pulp with a xylan content lower than 5 %, but at the expense of up to 12 % losses in cellulose yield. However, two of the pulps extracted at 240 °C showed a xylan content between 5 and 7 % and negligible

losses in cellulose yield. These pulps may probably be used as lower quality rayon-grade pulps. At any temperature, the cellulose yield appeared to remain mostly unaffected down to a particular xylan content, and thereafter it started to decrease (Fig. 6a). The degradation of cellulose was, to some extent, likely related to the acidic conditions generated during the HWE, particularly at increased extraction intensities (Fig. 4). Controlling the acidity of the hydrolysate may limit the degradation of cellulose by cleavage of glycosidic bonds, but it would also reduce the xylan extraction efficiency.

Interestingly, Fig. 6a shows that increasing extraction temperature decreased the xylan content threshold at which cellulose started to degrade. This is further supported by Fig. 6b, which shows that for a given xylan content, increasing extraction temperature resulted in cellulosic pulp with higher DP, expressed by the intrinsic viscosity. At any extraction temperature, the intrinsic viscosity decreased along with decreasing the xylan content. The fact that, given a xylan content, an increase in extraction temperature resulted in a better preservation of the cellulose might be explained by the higher activation energy reported for the hydrolytic degradation of the recalcitrant xylan fraction, as compared to that of cellulose (Borrega et al. 2011). In other words, increasing extraction temperature favoured the removal of xylan over the degradation of cellulose. The results shown in Fig. 6 suggest that HWE of pulp at temperatures above 240 °C might be a suitable method to reduce the xylan content to levels below 5 % whilst keeping the cellulose yield unaffected. However, the intrinsic viscosity should be kept high enough to comply with requirements for dissolving-grade pulp applications. Furthermore, the use of such elevated temperatures clearly imposes a challenge with regard to energy demands and design of equipment at an industrial scale.

The reduction in the DP of cellulosic pulp during the HWE, as indicated by the decreasing intrinsic viscosity, was further investigated by comparing the MMD of unbleached Kraft pulp before and after HWE at 240 °C (Fig. 7). The peak in the low MM region, corresponding to the hemicelluloses present in the unbleached pulp, disappeared gradually with increasing extraction time. It can also be seen that increasing extraction time resulted in cellulosic pulps with lower MM and narrower MMD. The degradation of cellulose



**Fig. 7** Molar mass distribution of birch Kraft pulp before and after hot water extraction at 240 °C and several extraction times (2, 5, 10, 15 and 30 min)

is also supported by a decreasing weight average molar mass ( $M_w$ ) and polydispersity index (PDI), as well as by a decreasing mass fraction of molecules with a DP higher than 2,000 (Table 2). The mass fraction of molecules with a DP lower than 100 decreased at first, due to the degradation of the xylan, but increased at extended extraction times, due to the degradation and shortening of cellulose chains. Increasing the intensity of HWE of wood prior to soda-AQ pulping has been reported to have similar effects on the MMD of pulp (Borrega et al. 2013a).

#### Recovery of sugars from the hydrolysate

The removal of xylan from paper-grade pulp by HWE was aimed at producing a dissolving-grade pulp, but the recovery of the extracted sugars from the hydrolysates was also of interest. Hemicellulosic mono- and oligosaccharides are valuable compounds that could be converted into films, fuels or food additives, among others (Girio et al. 2010; Hansen and Plackett 2008; Parajó et al. 2004). Acidic post-hydrolysis of pulp has been suggested as a method to extract the residual hemicelluloses and convert the extracted monosaccharides into chemical building blocks (Heikkilä et al. 2004), or alternatively, as a method to hydrolyze the cellulosic pulp and produce microcrystalline cellulose (Dahl et al. 2011). In order to evaluate the recovery of xylan, the carbohydrate composition of selected hydrolysates was analyzed. The mass balances in Table 3 indicate that the extracted xylan was recovered as XOS, with xylose monomers accounting to less

**Table 2** Chemical composition and macromolecular properties of birch Kraft pulp before and after hot water extraction at 240 °C

	Kraft pulp	P240.2	P240.5	P240.10	P240.15	P240.30
Extraction conditions						
Temperature (°C)	–	240	240	240	240	240
Time (min)	–	2	5	10	15	30
Yield (%)	100	82.6	79.4	79.2	74.2	64.8
Chemical composition on pulp (%)						
Cellulose	70.0	82.9	89.7	91.8	93.2	94.9
Xylan	26.9	14.9	8.6	6.6	5.7	3.6
Lignin	3.1	2.2	1.7	1.6	1.2	1.5
Macromolecular properties						
Viscosity (ml/g)	1445	1220	711	415	264	131
M <sub>w</sub> (kg/mol)	650	627	387	258	146	73
PDI	9.3	6.1	4.3	3.3	2.6	2.0
DP < 50	0.01	0.00	0.01	0.01	0.01	0.02
DP < 100	0.05	0.03	0.03	0.04	0.05	0.09
DP > 2,000	0.54	0.54	0.36	0.26	0.09	0.00

**Table 3** Mass balances of xylan and cellulose for selected hot water extractions of birch Kraft pulp. All values are based on initial pulp

Sample	Xylan in pulp (%)	XOS (%)	Xylose (%)	Total	Cellulose in pulp (%)	COS (%)	Glucose (%)	Total
Kraft pulp	26.9	–	–	26.9	70.0	–	–	70.0
P200.30	11.9	9.3	<0.1	21.2	68.7	0.6	<0.1	69.2
P200.60	8.4	11.5	<0.1	19.9	61.8	2.4	<0.1	64.3
P200.90	5.9	17.6	<0.1	23.6	50.8	8.2	0.1	59.1
P220.10	10.8	13.0	<0.1	23.8	73.3	0.1	<0.1	73.4
P220.15	8.7	14.3	<0.1	23.1	72.5	0.3	<0.1	72.7
P220.30	6.5	15.7	<0.1	22.2	65.1	1.1	<0.1	66.2
P220.45	5.3	18.4	<0.1	23.7	63.0	2.6	<0.1	65.5
P240.5	6.8	18.7	<0.1	25.5	71.3	0.1	<0.1	71.4
P240.10	5.2	21.5	<0.1	26.7	72.8	0.3	<0.1	73.0
P240.15	4.2	19.2	<0.1	23.4	69.1	0.5	<0.1	69.7
P240.30	2.3	19.9	0.1	22.3	61.5	2.5	0.1	64.1

than 0.1 % on initial dry pulp. They also indicate that the degradation of cellulose during the HWE was followed by the release of cello-oligosaccharides (COS), with only small amounts of glucose monomers found in the hydrolysates. The insignificant degradation of XOS into monomers is perhaps best explained by the high flow rates used in the extraction trials. It is plausible to assume that, while transported towards the outlet of the reactor, XOS solubilized in the high-temperature water were degraded into XOS of lower DP. However, because the flow rates were high, the

low DP XOS were removed from the system before they were further degraded to single xylose monomers. A similar behavior could also be expected for the release and recovery of COS from cellulose.

In general, the mass balances for xylan and cellulose were rather closed, although some deviation in the data can be observed. In the case of xylan, losses of about 15 % based on the initial amount of pulp xylan were observed (Table 3). In the case of cellulose, the mass balances at any extraction temperature appeared to be more open along with increasing extraction time, with



losses around 10 % of the initial cellulose. The loss of xylan and cellulose during the extraction may be due to the formation of degradation products such as low MM mass carboxylic acids (Borrega et al. 2013b), which in turn are likely to account for the pH decrease in the hydrolysates as shown in Fig. 4. The high recovery of sugars in the hydrolysates, with only small amounts of degradation products, is typically found during HWE in flow-through systems, as compared to batch systems (Liu and Wyman 2005; Yang and Wyman 2004). Nonetheless, the MM of the extracted XOS should be considered in order to assess their potential applications.

## Conclusions

About 50–80 % of the xylan in birch Kraft pulp was removed by HWE in a flow-through reactor, without losses in cellulose yield. Increasing extraction temperature lowered the xylan content at which cellulose started to degrade, in terms of yield and DP. The HWE also removed some of the lignin, which might allow for subsequent milder bleaching sequences. The results appear to indicate that HWEs at elevated temperatures may be applied to purify paper-grade pulps, preferably containing a low xylan content, for their conversion into dissolving-grade pulps. Moreover, the extracted xylan may be recovered from the hydrolysates almost quantitatively as XOS. The required elevated temperatures, however, impose a challenge with regard to energy demands.

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## References

- Amidon TE, Bujanovic B, Liu S, Hasan A, Howard JR (2013) Niche position and opportunities for woody biomass conversion. In: Christopher LP (ed) Integrated Forest Biorefineries. Challenges and opportunities, RSC Green Chemistry 18, The Royal Society of Chemistry, pp 151–179
- Berggren R, Berthold F, Sjöholm E, Lindström M (2003) Improved methods for evaluating the molar mass distributions of cellulose in kraft pulp. *J Appl Polym Sci* 88:1170–1179
- Bobleter O (1994) Hydrothermal degradation of polymers derived from plants. *Prog Polym Sci* 19:797–841
- Borrega M, Nieminen K, Sixta H (2011) Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures. *Bioresour Technol* 6:1890–1903
- Borrega M, Tolonen LK, Bardot F, Testova L, Sixta H (2013a) Potential of hot water extraction of birch wood to produce high-purity dissolving pulp after alkaline pulping. *Bioresour Technol* 135:665–671
- Borrega M, Niemelä K, Sixta H (2013b) Effects of hydrothermal treatment intensity on the formation of degradation products from birch wood. *Holzforschung*. doi:10.1515/hf-2013-0019
- Chen X, Lawoko M, Van Heiningen A (2010) Kinetics and mechanism of auto hydrolysis of hardwoods. *Bioresour Technol* 101:7812–7819
- Conner AH (1984) Kinetic modeling of hardwood pre-hydrolysis. Part I. Xylan removal by water pre-hydrolysis. *Wood Fiber Sci* 16:268–277
- Dahl O, Vanhatalo K, Parvianen K (2011) A novel method to produce microcellulose. WO Patent 2011/154600
- Duarte GV, Ramarao BV, Amidon TE, Ferreira PT (2011) Effect of hot water extraction on hardwood Kraft pulp fibers (*Acer saccharum*, sugar maple). *Ind Eng Chem Res* 50:9949–9959
- Fengel D, Wegener G (2003). Wood: chemistry, ultrastructure, reactions. Verlag Kessel, Germany
- Froschauer C, Hummel M, Iakovlev M, Roselli A, Schottenberger H, Sixta H (2013) Separation of hemicellulose and cellulose by means of ionic liquid/cosolvent mixtures. *Biomacromolecules* 14:1741–1750
- Garrote G, Dominguez H, Parajo JC (1999) Hydrothermal processing of lignocellulosic materials. *Holz Roh Werkst* 57:191–202
- Gehmayer V, Schild G, Sixta H (2011) A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. *Cellulose* 18:479–491
- Girio F, Fonseca C, Carvalheiro F, Duarte L, Marques S, Bogel-Lukasik R (2010) Hemicelluloses for fuel ethanol: a review. *Bioresour Technol* 101:4775–4800
- Gütsch JS, Sixta H (2011) Purification of *Eucalyptus globulus* water prehydrolyzates using the HiTAC process (high-temperature adsorption on activated charcoal). *Holzforschung* 65:511–518
- Haemmerle FM (2011) The cellulose gap. *Lenzing Ber* 89:12–21
- Hansen NML, Plackett D (2008) Sustainable films and coatings from hemicelluloses: a review. *Biomacromolecules* 9:1493–1505
- Heikkilä H, Lindroos M, Sundquist J, Kauliomäki S, Rasimus R (2004) Preparation of chemical pulp and xylose, utilizing a direct acid hydrolysis on the pulp. US Patent 6(752):902
- Iakovlev M, Heiningen A (2012) Efficient fractionation of spruce by SO<sub>2</sub>-ethanol-water treatment: closed mass balances for carbohydrates and sulfur. *Chem Sus Chem* 5:1625–1637
- Janson J (1974) Analytik der Polysaccharide in Holz und Zellstoff. *Faserforschung Textiltechnik* 25:375–382
- Kruse A, Dinjus E (2007) Hot compressed water as reaction medium and reactant. Properties and synthesis reactions. *J Supercrit Fluid* 39:362–380
- Leschinsky M, Zuckerstätter G, Weber HK, Patt P, Sixta H (2008) Effect of autohydrolysis of *Eucalyptus globulus*

- wood on lignin structure. Part 1: comparison of different lignin fractions formed during water prehydrolysis. *Holzforschung* 62:645–652
- Leschinsky M, Weber HK, Patt R, Sixta H (2009) Formation of insoluble components during autohydrolysis of *Eucalyptus globulus*. *Lenzing Ber* 87:16–25
- Li H, Saeed A, Jahan MS, Ni Y, van Heiningen A (2010) Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the Kraft-based dissolving pulp production process. *J Wood Chem Technol* 30:48–60
- Liu C, Wyman CE (2005) Partial flow of compressed-hot water through corn stover to enhance hemicellulose sugar recovery. *Bioresour Technol* 96:1978–1985
- Mok WSL, Antal MJ Jr (1992) Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water. *Ind Eng Chem Res* 31:1157–1161
- Parajó J, Garrote G, Cruz J, Domínguez H (2004) Production of xylooligosaccharides by auto hydrolysis of lignocellulosic materials. *Trends Food Sci Technol* 15:115–120
- Reguant J, Martínez JM, Montané D, Salvadó J, Farriol X (1997) Cellulose from softwood via pre-hydrolysis and soda/anthraquinone pulping. *J Wood Chem Technol* 17:91–110
- Ribas Batalha LA, Colodette JL, Gomide JL, Barbosa LCA, Maltha CRA, Borges Gomes FJ (2011) Dissolving pulp production from bamboo. *BioResources* 7:640–651
- Schild G, Sixta H (2011) Sulfur-free dissolving pulps and their application for viscose and lyocell. *Cellulose* 18:1113–1128
- Shi H, Fatehi P, Xiao H, Ni Y (2011) A combined acidification/PEO flocculation process to improve the lignin removal from the pre-hydrolysis liquor of kraft-based dissolving pulp production process. *Bioresour Technol* 102:5177–5182
- Sixta H (2006) *Handbook of Pulp*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
- Sixta H, Iakovlev M, Testova L, Roselli A, Hummel M, Borrega M, van Heiningen A, Froschauer C, Schottenberger H (2013) Novel concepts of dissolving pulp production. *Cellulose* 20:1547–1561
- Swan B (1965) Isolation of acid-soluble lignin from the Klason lignin determination. *Sven Papperstidn* 68:791–795
- Testova L, Chong SL, Tenkanen M, Sixta H (2011) Auto hydrolysis of birch wood. *Holzforschung* 65:535–542
- Testova L, Nieminen K, Penttilä PA, Serimaa R, Potthast A, Sixta H (2013) Cellulose degradation in alkaline media upon acidic pretreatment and stabilization. *Carbohydr Polym*. doi:10.1016/j.carbpol.2013.01.093
- Yang B, Wyman CE (2004) Effect of xylan and lignin removal by batch and flow through pretreatment on the enzymatic digestibility of corn stover cellulose. *Biotechnol Bioeng* 86:88–95