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# Changes in accessibility of cellulose during kraft pulping of wood in deuterium oxide

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ABSTRACT

Fresh birch chips were treated with different concentrations of sodium hydroxide and sodium sulfide in deuterium oxide in typical kraft pulping conditions and the extent of irreversible deuteration of the chips/pulps was followed by Fourier transform infrared (FT-IR) spectroscopy. Water retention values (WRV) of pulps were measured to evaluate accessibility of cellulose. The kraft pulping with deuterium oxide led to significant proton-deuterium exchange that was not reversed when the chips/pulps were washed with water. The deuteration followed a first order dynamics with a maximum obtained in the beginning of delignification stage. Higher dosages of effective alkali resulted in a higher degree of deuteration and lower WRV. An inverse relationship between the extent of deuteration and WRV suggests that both were induced by cellulose microfibril aggregation. Results also indicate that hemicellulose dissolution plays an important role in the induction of cellulose microfibril aggregation, while lignin dissolution has less influence.



## 1. Introduction

Accessibility of cellulose is an important factor in industrial processing of wood and other cellulosic materials, especially with the advent of novel cellulosic products that require heterogenous chemical modifications. These include, for example, chemical modification of cellulosic fibers prior to their disintegration to nanofibrillar cellulose (Henriksson, Henriksson, Berglund, & Lindström, 2007; Isogai, Saito, & Fukuzumi, 2011; Pääkkö et al., 2007; Spence, Venditti, Habibi, Rojas, & Pawlak, 2010), dissolution of dissolving grade chemical pulps and their regeneration into textile fibers (Chanzy, Paillet, & Hagège, 1990; Sixta, 2000), and hydrolysis of cellulose into glucose to produce biofuels (Liu et al., 2011; Zhang & Lynd, 2004). The most accepted explanation for possible reduction in accessibility of cellulose during its processing is microfibril aggregation (Pönni, Vuorinen, & Kontturi, 2012), promoted by the formation of hydrogen bonds between adjacent cellulose microfibrils (Higgins & McKenzie, 1963; Matsuda, Isogai, & Onabe, 1994; Newman, 2004). Cellulose microfibril aggregation in wood and pulp has been reported during many technical treatments, such as, drying (Jayme, 1944; Suchy, Kontturi, & Vuorinen, 2010) and thermal treatments (Borrega & Kärenlampi, 2010; Kato & Cameron, 1999; Pönni, Kontturi, & Vuorinen, 2013). Some studies have also addressed aggregation during kraft pulping (Fahlén & Salmén, 2003; Hult, Larsson, & Iversen, 2001), the main aim of which is to separate cellulosic fibers from wood material to pulp for the production of paper and board.

Several parameters have been identified to affect cellulose microfibril aggregation during standard kraft pulping, namely alkalinity, sulphidity, and temperature (Fahlén & Salmén, 2003; Hult, Larsson, & Iversen, 2002; Virtanen, Maunu, Tamminen, Hortling, & Liitiä, 2008). It has been suggested that microfibril aggregation occurs mainly during the heat-up phase, which is associated to dissolution of hemicelluloses (Fahlén & Salmén, 2003; Hult et al., 2001; Oksanen, Buchert, & Viikari, 1997; Virtanen et al., 2008). Swelling in alkaline pulping liquor is also thought to be an important mechanism which promotes microfibril aggregation by loosening hemicellulose–hemicellulose and hemicellulose–cellulose bonding, thus increasing surface availability for hydrogen bond formation between microfibrils (Hult et al., 2002). The swelling induced in alkaline environment has been widely studied in wood (Sumi, Hale, Meyer, Leopold, & Ranby, 1964; Zanuttini, Citroni, Martínez, & Marzocchi, 1998), as well as for recycled, mechanical, chemimechanical, and chemical pulps (El-Din, 1993; Katz, Liebergott, & Scallan, 1981; Klungness, 1974; Zanuttini & Marzocchi, 2003). Besides microfibril aggregation, other structural characteristics, such as crystallinity of cellulose, have an influence

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in its accessibility, since only the crystal surfaces and amorphous parts of cellulose are accessible to water (Aulin et al., 2009; Müller, Czihak, Schober, Nishiyama, & Vogl, 2000; Wickholm, Larsson, & Iversen, 1998). Thermal alkaline treatments of pulp have been suggested to induce equilibrium between the crystalline and amorphous regions of cellulose (Pönni et al., 2013). Increase in the ordering of cellulose is known to occur during kraft pulping (Evans, Newman, Roick, Suckling, & Wallis, 1995; Hult, Larsson, & Iversen, 2000) and to be affected by hemicelluloses (Liitiä et al., 2003).

Different methods have been used in the past to evaluate the extent of cellulose microfibril aggregation based on indirect measurements, such as water retention value (WRV) (Jayme, 1958), fiber saturation point (FSP) (Stone & Scallan, 1967), and pore size distribution by differential scanning calorimetry (DSC), inverse size-exclusion chromatography (ISEC), or nuclear magnetic resonance (NMR) cryoporosimetry (Berthold & Salmén, 1997; Maloney, Paulapuro, & Stenius, 1998; Östlund, Köhnke, Nordstierna, & Nydén, 2010). In addition, direct methods to determine microfibril and microfibril aggregate sizes in chemical pulps by NMR spectroscopy and atomic force microscopy (AFM) have been applied (Fahlén & Salmén, 2003; Hult et al., 2001). Transmission electron microscopy (TEM) has also enabled the detection of cellulose microfibril aggregation in native wood (Awano, Takabe, Fujita, & Daniel, 2000). More recently, deuteration followed by FT-IR spectroscopy has been applied as a new way to evaluate the changes in the accessible OH groups in cellulose during various treatments in both native wood and pulp fibers (Suchy, Kontturi, & Vuorinen, 2010; Suchy, Virtanen, Kontturi, & Vuorinen, 2010). This method is based on the exchange of accessible OH groups to OD groups when exposing the sample to deuterium oxide (Frilette, Hanle, & Mark, 1948; Mann & Marrinan, 1956) and detection of the non-overlapping OD band after reprotonation by FT-IR spectroscopy. The combination of deuteration and FT-IR spectroscopy has been applied widely for studies on cellulose accessibility in native cellulose, cellulose derivatives, pulp, and wood (Hofstetter, Hinterstoisser, & Salmén, 2006; Jeffries, 1963; Tsuchikawa & Siesler, 2003a, 2003b).

In this study, the progress of the proposed cellulose microfibril aggregation in kraft pulping was followed by deuteration combined with FT-IR spectroscopy throughout the heat-up and cooking phases. The dynamics of deuteration was modeled during kraft pulping of fresh birch chips in deuterium oxide and the influence of the effective alkaline dosage and sulphidity, was also analyzed. WRV was analyzed for the pulp samples as a reference measure for cellulose accessibility.

## 2. Experimental

### 2.1. Materials

Fresh birch chips obtained from a Finnish pulp mill were used as raw material. Prior to cooking, the chips were screened according to the standard SCAN-CM 40:01. The accepted chips were collected from the 7 mm plate screen preceded by a 45 mm plate screen, a 8 mm hole screen, and a 13 mm plate screen. Thickness of the chips was less than 8 mm and the width between 7 and 13 mm.

The cooking liquors were prepared using solid NaOH (99%, VWR (Radnor (PA), USA)), $Na_2S{\cdot}xH_2O$ (60%, VWR (Radnor (PA), USA)), and deuterium oxide (99.9 atom% D, Sigma–Aldrich (St. Louis, USA)). The concentration of the cooking liquor was analyzed according to the standard SCAN-N 2:88. Ion exchanged water was used for the washings. For converting the pulp to $Na^+$-form for the WRV determination, a 0.001 M solution of $NaHCO_3$ (99.5%, Merck (Darmstadt, Germany)) was prepared. Aqueous solutions of NaOH and HCl (0.1 M) were obtained from Merck (Darmstadt, Germany). Water purified in a Milli-Q system (Millipore Corporation, resistivity 18.2 MΩ cm) was used in dilutions.

### 2.2. Deuteration

Scheme 1 illustrates the principle of deuteration degree assessment in the kraft pulping experiments in $D_2O$. The fresh birch chips were first impregnated in $D_2O$ in plastic bags overnight with an excess of $D_2O$ (10 ml of $D_2O$ per 1 g of dry chips) to convert the accessible hydroxyl groups to OD groups. The excess of $D_2O$ was removed and the cooking was performed using white liquor prepared in $D_2O$. After the cooking, the samples were washed overnight in excess of water to convert the accessible OD groups back to OH groups. After the washing the OD-band observed by FT-IR spectroscopy at 2500 $cm^{-1}$ represents the protonation-resistant, inaccessible OD bonds formed during kraft pulping in the chips/pulp. The complete conversion of accessible OD groups back to hydroxyl groups during the washing phase was verified by deuteration followed immediately by a washing phase, which did not result in observable increase in the OD-band at 2500 $cm^{-1}$.

### 2.3. Kraft pulping

A rotating oil bath series digester (HAATO 43427, Haato-Tuote Oy (Finland)) equipped with 200 ml stainless steel pressure vessels was used for the cooking experiments. The amount of chips in the cooking batches varied between 3 and 10 g (dry matter content). The effective alkali dosage was calculated as percentage of NaOH on dry wood taking into account the equimolar amount of NaOH formed when $Na_2S$ is dissolved in $D_2O$. Sulphidity was calculated as molar percentage of $Na_2S$ on the dosage of NaOH and $Na_2S$. Stock solutions of NaOH in $D_2O$ and $Na_2S$ in $D_2O$ together with $D_2O$ were used to acquire the desired chemical dosage and a liquid-to-wood ratio of 4. Temperature of the digester was raised from room temperature to 170 °C at a rate of 3 °C/min. H-factor, which models the influence of temperature and time during kraft pulping, was calculated according to the equation (Vroom, 1957):

$$H = \int_0^t e^{(43.2-(16{,}115/T))}dt,$$

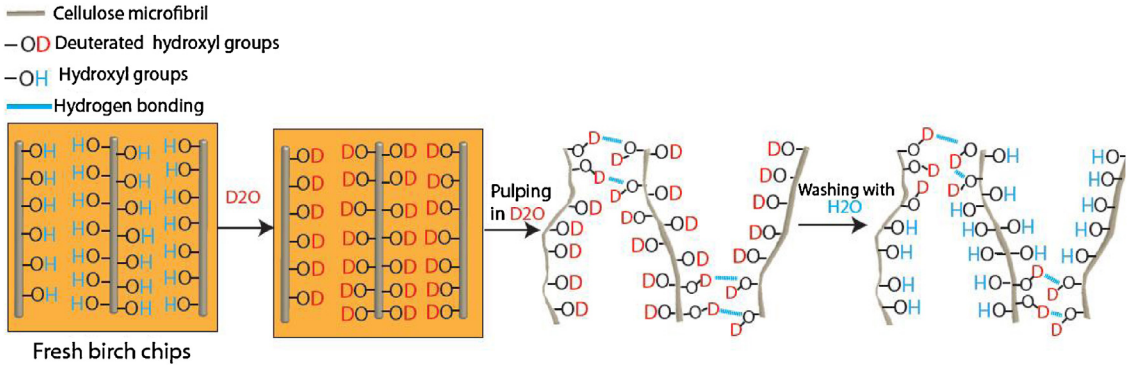
where $t$ is time (s) and $T$ is temperature (K). The heat-up period is considered to begin at 80° and to last until the cooking temperature is reached. In the performed experiments, the heat-up period was 30 min (H factor from 0 to 59). After cooking the chips/pulps were washed with an excess of water overnight at room temperature. All pulps were disintegrated manually. The precise yields could not be determined due to the small sample amount.

### 2.4. Kappa number

Kappa number was determined according to the standard SCAN-C 1:00. Parallel measurements were not done because of the limited sample amount.

### 2.5. WRV analysis

Prior to WRV analysis the pulp samples were converted into their $Na^+$-form. All of the subsequent treatments were done at 1% consistency and the change of solution was invariably done after filtration on a Büchner funnel. First, the samples were converted to their protonated form through a treatment in 0.01 M HCl for 1 h. Then the samples were washed twice with water. Conversion to $Na^+$-form was done in 0.001 M $NaHCO_3$ for 2 h with pH adjusted to 9.5–10 with 0.1 M NaOH. Then, the samples were washed with water until the conductivity of the slurry was less than 5 μS/cm.




**Scheme 1.** Schematics of the deuteration of the fresh birch chips to convert the hydroxyl groups to OD groups followed by kraft pulping in $D_2O$ and subsequent washing.

The WRV analysis was done according to the standard SCAN-C 102 XE with a Jouan GR 4.22 centrifuge. The standard deviation was determined from four parallel measurements of a pulp cooked in $H_2O$. The pulps cooked in $D_2O$ were measured only once.

### 2.6. Carbohydrate analysis

The carbohydrate composition of the chips/pulps was determined by quantitative saccharification upon acid hydrolysis according to the standard procedure reported by Sluiter et al. (2011). The monosaccharides were determined by high performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 system (Sunnyvale (CA), USA). The contents of cellulose and xylan were calculated from the monosaccharide contents using a correction factor reported by Sluiter et al. (2011). As the contribution of glucomannan was considered insignificant for this hardwood sample, glucose was considered to originate exclusively from cellulose.

### 2.7. FT-IR spectroscopy

Prior to the FT-IR spectroscopy, the samples were dried at 40 °C in an oven. The spectra were collected using a Bio-Rad FTS 6000 spectrometer (Cambridge (MA), USA) with a Gasera PA301 photoacoustic cell (Turku, Finland) at a constant mirror velocity of 5 kHz, 1.2 kHz filter, and 8 $cm^{-1}$ resolution. In the beginning of each set of measurements, a background spectrum was collected using a standard carbon black. The samples were transferred to the photoacoustic cell and purged with helium gas for 30 s before each measurement including the duplicate measurements. 200 scans per spectrum were collected using the Win-IR Pro 3.4 software (Digilab (Holliston (MA), USA)). Every sample was measured in duplicate and the averaged spectra were processed with Grams/AI 9.00 software (Thermo Fischer Scientific Inc. (Waltham (MA), USA)). The average spectra were baseline corrected and normalized at 1424 $cm^{-1}$. This absorption band is mainly due to the $CH_2$ scissor motion in cellulose and should be essentially unaltered during kraft pulping (Yin, Berglund, & Salmén, 2011).

The spectral interpretation is based on the detection of the protonation resistant OD groups in FT-IR spectrum (Suchy et al., 2010b). The characteristic IR band of OD groups corresponds to γ stretching vibration located at 2500 $cm^{-1}$. This band does not overlap with any other band in the spectrum. The effective washing of the samples prior to the FT-IR analysis ensured that the area of the OD stretch band at around 2500 $cm^{-1}$ can be considered to be a measure of the irreversible deuteration of the sample during kraft pulping. The area of the OD stretch band was integrated using Grams/AI 9.00 software (Thermo Fischer Scientific Inc. (Waltham (MA), USA)). Standard deviation was determined from four different chip samples cooked in similar conditions.

## 3. Results

### 3.1. H factor

Fig. 1 illustrates as an example the FT-IR spectra of deuterated and washed fresh birch chips and a pulp cooked in $D_2O$ in conditions typical of birch pulps. The band at 2500 $cm^{-1}$ is associated to OD groups bound to the pulp. Fig. 2 represents the integrated OD-band area as a function of H-factor in 10 samples taken at different stages during the heat-up and cooking phases. Deuteration proceeds rapidly during the heat-up phase and equilibrates soon after cooking temperature is reached (H-factor 59). Therefore, the extent of deuteration levels off, even though delignification continues to proceed (Smook, 1992). It was assumed that deuteration would follow first order dynamics according to the following equation, as observed also earlier by our group during treatment of alkaline pulp suspensions at elevated temperatures (Pönni et al., 2013):

$$A_{OD} = A_{OD,eq}(1 - e^{-kH})$$

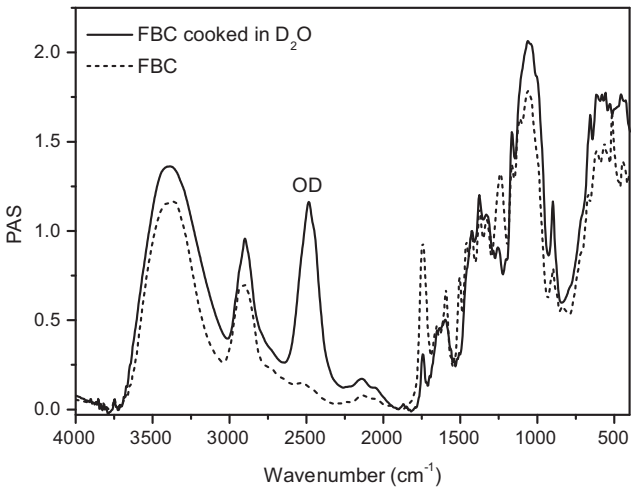



**Fig. 1.** The FT-IR spectra (photo acoustic cell (PAS)) of the reference sample, deuterated fresh birch chips with subsequent washing with water (dotted line) and kraft pulp of deuterated fresh birch chips produced in $D_2O$ followed by washing with water (continuous line). The cooking conditions were: effective alkali 22%, sulphidity 35%, liquid-to-wood ratio 4, H-factor 1200, and cooking temperature 170 °C. OD-band at 2500 $cm^{-1}$ represents the protonation resistant OD groups formed during pulping.

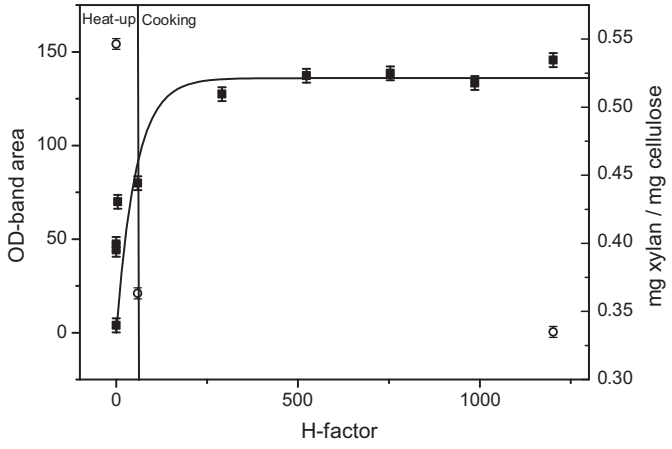



**Fig. 2.** Level of deuteration (square) as observed by the OD-band area (at 2500 $cm^{-1}$) and xylan/cellulose content (circle) as a function of H-factor during the heat-up (H-factor from 0 to 59) and cooking phase (H-factor from 59–1400) of kraft pulping of fresh birch chips in $D_2O$.

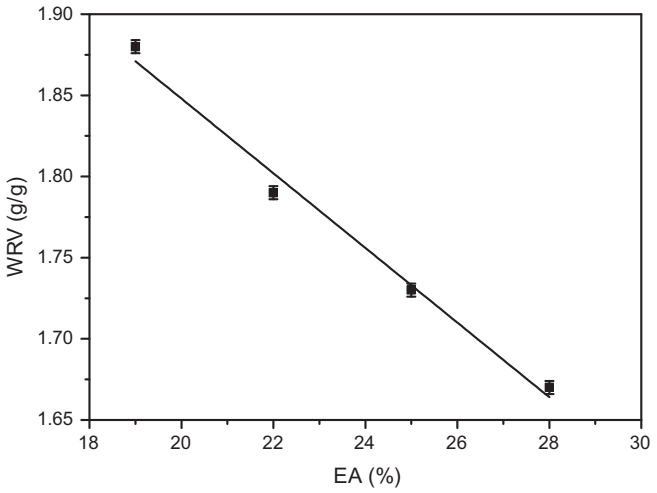



**Fig. 3.** Linear correlation between water retention value (WRV) and effective alkali (EA) dosage during kraft pulping of fresh birch chips.

where $A_{OD}$ is the OD-band area, $H$ is the H factor, $A_{OD,eq}$ is the OD-band area in equilibrium (136 in this fitting) and $k$ is rate constant (0.02 in this fitting) (Fig. 2). Subsequently, the formation of protonation resistant OD groups occurs rapidly and reaches equilibrium already in the beginning of the cooking.

Fig. 2 also illustrates the xylan/cellulose content in the sample prior to cooking, after the heat-up phase, and in the final pulp cooked to H-factor of 1200. It is possible to observe that the major portion of xylan dissolution occurs during the heat-up phase simultaneously with the increase in the deuteration level. Similar dissolution of xylan during birch kraft cooking has also been reported earlier (Aurell, 1964).

### 3.2. Alkalinity

During this study, five different effective alkali (EA) dosages in kraft pulping were applied. Sulphidity was kept constant at 35%, liquid-to-wood ratio at 4, and H-factor at 1200. The cooking temperature was 170 °C. The range of EA levels (16, 19, 22, 25, and 28%) was broader than the ones used in normal birch pulping. The washed and disintegrated pulps were analyzed for the extent of deuteration, WRV, xylan content, and kappa number. As the chips were not totally disintegrated at the lowest EA level (16%), WRV and kappa number were not analyzed for this sample. Fig. 3 shows the changes in WRV as function of EA dosage. Increase in EA dosage led to linear decrease in WRV within the studied range. The effects of the EA dosage on OD-band area, WRV, and kappa number are summarized in Table 1. The level of deuteration also increased by increasing alkalinity at the normal kraft pulping range (below EA 28%) (Fig. 4). Simultaneously, xylan content in relation to cellulose content decreased (Fig. 4). However, lignin content decreased also with increasing EA as reported in Table 1. Interestingly, when the effective alkaline content was increased to a level much higher than conventional kraft pulping (EA 28%), the level of deuteration collapsed, even though WRV continued to decrease.

**Table 1**
Characteristics of birch kraft pulps cooked with different effective alkali dosages. The cooking conditions were: sulphidity 35%, liquid-to-wood ratio 4, H-factor 1200, and cooking temperature 170 °C.

| EA (%) | OD-band area [std ±4] | WRV (g/g) [std ±0.01] | Kappa number [std ±1] |
|---|---|---|---|
| 16 | 112 | * | * |
| 19 | 125 | 1.88 | 23 |
| 22 | 132 | 1.79 | 15 |
| 25 | 142 | 1.73 | 17 |
| 28 | 122 | 1.67 | 12 |

* Analysis not performed because sample could not be disintegrated to pulp.

**Table 2**
Characteristics of birch kraft pulps cooked with varying sulphidities. Cooking conditions were: effective alkali 22%, liquid-to-wood ratio 4, H-factor 1200, and cooking temperature 170 °C.

| S (%) | OD-band area [std ±4] | WRV (g/g) [std ±0.01] | Kappa number [std ±1] |
|---|---|---|---|
| 25 | 121 | 1.81 | 15 |
| 30 | 124 | 1.80 | 13 |
| 35 | 132 | 1.79 | 15 |

### 3.3. Sulphidity

There was no significant correlation between the level of deuteration and sulphidity when it varied between 25 and 35% (Table 2). Moreover, WRV was little if not at all affected by sulphidity within this range (Table 2). This finding is in accordance with previous studies by NMR spectroscopy on changes in cellulose microfibril size (Virtanen et al., 2008).

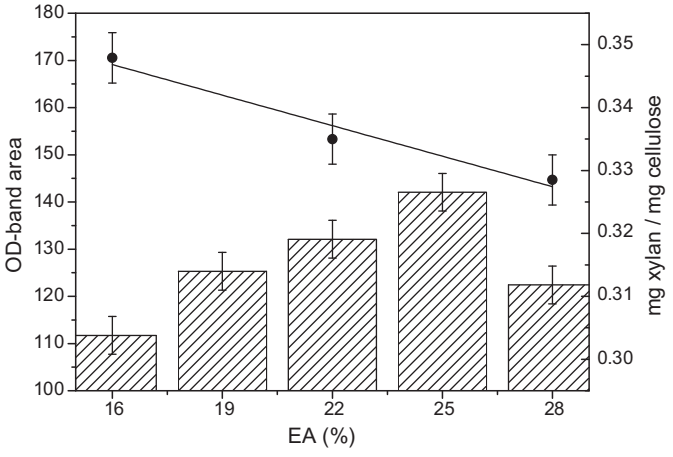



**Fig. 4.** Level of deuteration (bar) as observed by the OD-band area (at 2500 $cm^{-1}$) and xylan/cellulose content (circle) for fresh birch kraft pulps cooked with varying effective alkali (EA) dosage.

## 4. Discussion

This study introduces deuteration combined with FT-IR spectroscopy to kraft pulping. Lately, this method has been applied in studies concerning the changes in accessibility during various treatments on both wood and pulp and the observed irreversible deuteration has been suggested to be due to cellulose microfibril aggregation (Suchy, Kontturi, et al., 2010; Suchy, Virtanen, et al., 2010; Pönni et al., 2013). The method is based on the deuteration of the free hydroxyl groups prior to cooking followed by reprotonation after the cooking. The level of irreversible deuteration is followed by FT-IR spectroscopy. This method was selected for this study due to its simple and fast implementation provided by the use of photoacoustic detection that requires minimal sample pretreatment. In addition, the method was considered one of the most promising methods, to date, to assess cellulose microfibril aggregation occurring during kraft pulping. The earlier studies on kraft pulping have applied NMR spectroscopy and AFM to assess changes in cellulose microfibril size (Fahlén & Salmén, 2003; Hult et al., 2001, 2002; Oksanen et al., 1997; Virtanen et al., 2008).

In this study, we were able to monitor protonation resistant deuteration during the heat-up and cooking phases of kraft pulping of fresh birch chips in deuterium oxide. When the time was corrected for the varying temperature by using H-factor, the deuteration followed first order kinetics. This resembles our earlier studies on deuteration of alkaline pulp fiber suspensions at high temperature (Pönni et al., 2013). Therefore, we suggest that this irreversible deuteration of the pulp is due to the aggregation of cellulose microfibrils.

Xylan was observed to dissolve mainly during the heat-up phase of kraft pulping, in accordance with earlier studies on kraft pulping of birch (Aurell, 1964; Saucedo, Josephson, & Krishnagopalan, 2001). On the contrary, delignification is fastest at temperatures higher than 150 °C and continues throughout the cooking (Aurell, 1964; Saucedo et al., 2001). Thus, lignin dissolution was not to the key factor influencing the level of deuteration during kraft cooking, since the level of deuteration stayed constant throughout the bulk delignification cooking phase. We suggest that hemicellulose dissolution plays a more important role than lignin dissolution during kraft pulping. It should be taken into account that xylans readsorb on the fibers during the final stage of kraft pulping (Aurell, 1965). The readsorption is dependent on the conditions, i.e., the xylan content in the black liquor, pH, and temperature (Clayton & Stone, 1963; Danielsson & Lindström, 2005; Hansson & Hartler, 1969; Ribe, Söderqvist Lindblad, Dahlman, & Theliander, 2010). The readsorption is enhanced when the end pH is low. Thus, the lower the EA has been during the cooking, the more readsorption has occurred during the final stage.

Alkalinity had a significant influence on the proposed aggregation observed both by WRV and the level of deuteration. The effect of pH on cellulose microfibril aggregation has already been proposed for pulps treated in wet thermal alkaline conditions at temperatures lower than 100 °C (Pönni et al., 2013). Effective alkaline dosage was shown to affect both lignin and xylan content of the pulp, an observation that had been previously reported (Aurell, 1964). However, as the increase in alkalinity leads to increased dissolution of both lignin and xylan, it is not possible to determine a single cause for this effect. Still, as observed earlier, irreversible deuteration occurs already during the heat-up and early cooking phase simultaneously with xylan dissolution, whereas the change in kappa number during the main cooking phase does not influence the level of deuteration. Therefore, the influence of xylan dissolution can be suggested as a more probable cause for changes in cellulose accessibility observed for the various EA levels as the level of deuteration and WRV. However, the effect of lignin dissolution cannot be neglected. Alkalinity is also known to induce pulp swelling (El-Din, 1993; Klungness, 1974; Lindström & Carlsson, 1982), which presumably further promotes the observed changes in cellulose microfibrils, as swelling supposedly increases the likelihood of cellulose microfibrils aggregation. This observation was also made in previous studies on acidic and neutral sulphite pulping, which were shown to lead to less cellulose microfibril aggregation compared to kraft pulping (Hult et al., 2002).

Although crystallinity has been shown in earlier studies to increase during kraft pulping, it has been reported to be mainly due to the removal of the disordered regions and not to changes in the crystalline structures (Evans et al., 1995). Therefore, deuteration during cooking is not likely to be due to the changes in crystalline structures, but on the changes in cellulose microfibril aggregates. However, when atypically high alkaline dosage is applied (EA 28%), the level of deuteration does not follow the trend. This high alkaline dosage that equals 7% NaOH solution is close to the alkaline conditions where changes in cellulose morphology occur. These changes in the lattice transition of cellulose I via Na-cellulose to cellulose II are reported to begin at NaOH concentrations of 8–9% (Dinand, Vignon, Chanzy, & Heux, 2002; Klemm, Philipp, Heinze, & Heinze, 1998) and even lower for certain cellulosic raw materials (Philipp, Lehmann, & Ruscher, 1959). The most severe alkaline conditions applied in this study are suggested to cause changes in cellulose morphology that affect the level of deuteration.

## 5. Conclusions

The irreversible deuteration of the pulp samples, proposed as cellulose microfibril aggregation, occurs mainly during the heat-up period of kraft pulping for fresh birch chips and follows a first order kinetics. However, dissolution of lignin alone does not explain cellulose microfibril aggregation during kraft pulping, as delignification proceeds throughout the cooking phase. Accordingly, the dissolution of hemicelluloses during the early phases of kraft pulping seems to play a key role in cellulose microfibril aggregation. Effective alkali content has a significant effect on the extent of the proposed cellulose microfibril aggregation. Alkalinity showed a direct relation with irreversible deuteration and an inverse relation with WRV within the common kraft pulping range. Additionally, sulphidity does not affect microfibril aggregation during kraft pulping. Our results show that deuteration, combined with OD-band detection by FT-IR spectroscopy, provides valuable information regarding cellulose aggregation occurring in the very beginning of kraft pulping i.e. prior to chip disintegration.

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