



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.

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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 heterogeneous 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, & Liittä, 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)), Na₂S·xH₂O (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 NaHCO₃ (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 D₂O. The fresh birch chips were first impregnated in D₂O in plastic bags overnight with an excess of D₂O (10 ml of D₂O per 1 g of dry chips) to convert the accessible hydroxyl groups to OD groups. The excess of D₂O was removed and the cooking was performed using white liquor prepared in D₂O. 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 Na₂S is dissolved in D₂O. Sulphidity was calculated as molar percentage of Na₂S on the dosage of NaOH and Na₂S. Stock solutions of NaOH in D₂O and Na₂S in D₂O together with D₂O 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 NaHCO₃ 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.

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