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Assessing the reactivity of cellulose by oxidation with 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium cation under mild conditions

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ABSTRACT

The accessibility and reactivity of cellulose are key parameters in its conversion into various products. Several indirect measures, such as water retention value (WRV), fiber saturation point (FSP) and specific surface area (SSA), are often used to characterize cellulosic samples for their reactivity. In this paper, we report on using oxidation with 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium cation (4-AcNH-TEMPO$^+$) as a probe reaction for the reactivity of cellulose in mild conditions (pH 9, room temperature). 4-AcNH-TEMPO$^+$ is able to selectively convert hydroxymethyl groups into carboxylate groups. The time dependence of the conversion was monitored by iodometric quantification of the residual 4-AcNH-TEMPO$^+$. Soluble substrates, such as 1-propanol and maltose, were quantitatively oxidized in ca. 1 min while 3–16% of cellulose was oxidized in ca. 15 min depending on its origin. Extrapolation of the slow residual oxidation to zero time allowed quantification of the easily reactive or accessible cellulose. The 4-AcNH-TEMPO$^+$ reactivity was correlated with several pulp characteristics, including WRV, FSP, SSA, chemical composition, crystallinity, the pulping process and the drying history.

1. Introduction

The reactivity of cellulosic materials has been a topic of continuous interest in their conversion into various products, such as cellulose derivatives, regenerated textile fibers and monosaccharides for biofuel production (Krässig, 1992). The natural structure of cellulose, which is characterized by the assembly of elementary fibrils (EFs) and their highly ordered crystalline regions stabilized by intramolecular and intermolecular hydrogen bonds, limits its reactivity. Recently EFs in wood cell wall were shown to assemble into helicoidal bundles of several intertwined fibrils, a structure that probably has a significant impact on the accessibility and reactivity of wood biomass (Reza, Bertinetto, Ruokolainen, & Vuorinen, 2017). Besides the crystal surfaces, amorphous regions of EFs are often considered to be accessible to solvents and chemical reagents (Gross & Chu, 2010). The partial crystalline nature of cellulosic materials has been quantified by a number of direct and indirect techniques, like X-ray diffraction, NMR spectroscopy, differential scanning calorimetry, deuterium exchange, and sorption of water vapor, iodine and dyes (Bertran & Dale, 1986; Hofstetter, Hinterstoisser, & Salmén, 2006; Ioelovich & Leykin, 2009; Lindh & Salmén, 2017; Ott, Spurlin, & Grafflin, 1955).

The low porosity and small pore size may also restrict the accessibility of the cell wall towards solvents and reagents, especially macromolecules like proteins. The exclusion volumes of probe molecules of different sizes provide the pore size distribution (PSD) of wet pulp while the exclusion volume by a very large macromolecule (dextran of 2000 kDa), by definition, is the fiber saturation point (FSP). FSP approximates the inaccessible pore volume of wet cell wall. In contrast, the water retention value (WRV) is a measure of the amount of water bound by wet cell wall under standard centrifugal forces. Mechanical fibrillation of cellulosic pulps increases their WRV because the externally fibrillated structure may swell and bind even more water. In general, WRV > FSP (Pönni, Vuorinen, & Kontturi, 2012) and the difference between the values can be considerable as shown also by thermoporosimetry (Maloney, Paulapuro, & Stenius, 1999). The amount of the bound water depends on the chemical composition of the cell wall, especially on the content of hemicelluloses that associate strongly with water (Alince, 2002).

Various hydrothermal treatments used in processing of lignocellulose may lead to characteristic EF aggregation, so-called hornification, which increases in the degree of coalescence of EFs and further reduces the reactivity of cellulose (Pönni et al., 2012). The term hornification originally referred to an irreversible decrease in WRV of a pulp caused by its drying. Hemicelluloses seem to hinder EF

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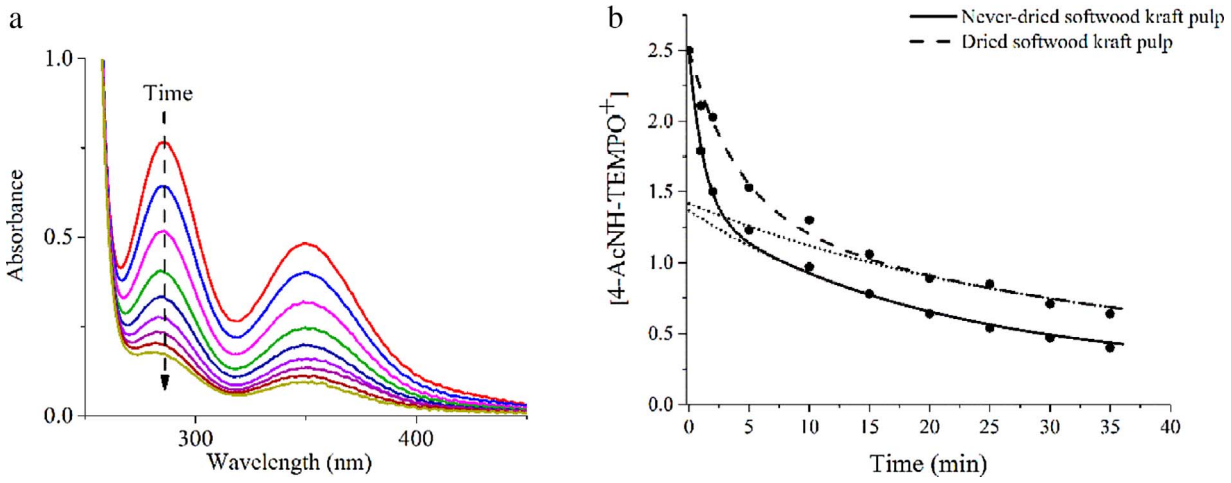

Fig. 1. (a) UV–vis spectra for iodometric analysis of 4-AcNH-TEMPO$^+$ from its reaction mixture with never-dried softwood kraft pulp and (b) consumption of 4-AcNH-TEMPO$^+$ during oxidation of never-dried and dried softwood kraft pulp at pH 9 at room temperature.

aggregation and therefore WRV may decrease less during drying of hemicellulose-rich pulps. Hornification does not only happen during dehydration (Minor, 1994; Suchy, Kontturi, & Vuorinen, 2010) but also in various chemical (Fahlén & Salmén, 2003; Meng, Wells, Sun, Huang, & Ragauskas, 2015; Pönni, Galvis, & Vuorinen, 2014) and hydrothermal treatments (Borrega & Kärenlampi, 2010; Pönni, Kontturi, & Vuorinen, 2013) of lignocellulosic materials. Besides the lower WRV, hornification reduces the accessibility and reactivity of the cell wall in various treatments, such as hydrolysis by cellulases (Duan, Long, Li, Ma, & Ni, 2015). Although the drying-induced collapse of cell wall can be suppressed by critical point drying, the specific surface area (SSA) measured by N_2 adsorption on dried pulp is still lower than could be estimated from PSD of wet pulp (Jayme, 1944; Jeffries, 1963; Lovikka, Khanjani, Väisänen, Vuorinen, & Maloney, 2016; Stone & Scallan, 1967). In contrast, many treatments such as mechanical, enzymatic and oxidative pretreatments were investigated to improve the reactivity of cellulose (Li et al., 2013).

The definition of chemical reactivity of cellulose depends on its application. In textile fiber production the reactivity of dissolving pulps from different raw materials and with different processes has been assessed by a microscale viscose process (Fock, 1959; Gehmayr & Sixta, 2012; Kaur, Bhardwaj, & Sharma, 2016; Quintana et al., 2015). 2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO) catalyzed oxidation of chemical pulps has been studied for production of oxidized cellulose nanofibrils. The actual cellulose oxidant is 2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium cation (TEMPO$^+$) that can be quantified in the reaction system by iodometry. The oxidation rate varies between pulps depending on several factors, such as the drying history or possible pretreatment.

In this paper we introduce a method to assess the chemical reactivity of cellulose under mild conditions (room temperature, pH 9) by using 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium cation (4-AcNH-TEMPO$^+$) as a stoichiometric oxidant of hydroxymethyl groups. The method provides an absolute amount (mmol/g) or fraction (percentage on theoretical maximum) of hydroxymethyl groups that react easily (in ca 15 min) with 4-AcNH-TEMPO$^+$. Bleached softwood and hardwood pulps as well as bacterial cellulose (BC) were analyzed for their chemical reactivity and a number of indirect measures of reactivity. BC has unique properties such as high water binding capacity, tensile strength, and biocompatibility, which are important for potential application of BC in the food and cosmetic industry, drug delivery, etc. (Numata, Sakata, Furukawa, & Tajima, 2015; Tabarsa, Sheykhnazari, Ashori, Mashkour, & Khazaeian, 2017).

2. Experimental

2.1. Materials and methods

Bleached never-dried and dried birch kraft, birch prehydrolysis kraft and softwood (mixed pine and spruce) kraft pulps were obtained from Finnish pulp mills. Suspensions of the pulps in water/buffer solution were prepared with 10 min ultrasonic treatment. Nata de coco was used as raw material for bacterial cellulose (BC). 1-Propanol, maltose, potassium iodide (KI) and 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium (4-AcNH-TEMPO$^+$) tetrafluoroborate were purchased from Sigma-Aldrich. A pH 9 buffer solution was prepared by dissolving 185 mg boric acid (VWR) and 80 mg of NaOH (VWR) in 500 ml of distilled water. The pH 2 citrate buffer solution (AVS TITRINORM) was purchased from VWR. Research quality dextran (T2000, 2000 kDa) and acetone (99.8%) were provided by Pharmacosmos A/S and WVR International, respectively. CO_2 (99.8%) was delivered by Oy Aga AB. UV/Vis absorption spectra were measured with a Shimadzu UV/2550 spectrophotometer.

2.2. Oxidation with 4-AcNH-TEMPO$^+$

The oxidations were carried out at room temperature (23 °C) in pH 9 buffer solution and 100 ml reaction volume. The initial concentration of 4-AcNH-TEMPO$^+$ was 2.5 mM. The substrates and their concentrations were: 1-propanol (0.5 mM), maltose (0.2 mM), pulps (0.5 g/l) and BC (0.5 g/l).

The change in the concentration of 4-AcNH-TEMPO$^+$ was monitored by its reaction with KI (Pääkkönen et al., 2015). A sample (1 ml) of the reaction solution and 1 ml of a 10% KI were diluted to 40 ml with pH 2 buffer solution. The formed I_2 was quantified by absorption spectrophotometry at the absorption maximum of I_3^- at 288 nm (Bichsel & von Gunten, 1999) (Fig. 1a). 4-AcNH-TEMPO$^+$ was found to consume an equivalent amount of I^- and to produce half an equivalent of I_3^- (I_2) (Eq. (1)). Iodide thus reduced 4-AcNH-TEMPO$^+$ to 4-AcNH-TEMPO radical (Rozantsev & Sholle, 1971).

$$2\ \text{4-AcNH-TEMPO}+ + 3\,I^- \rightarrow 2\ \text{4-AcNH-TEMPO} + I_{3^-} \quad (1)$$

The values of reactivity (mmol/g) and initial reaction rate (min^{-1}) were obtained by nonlinear fitting to the oxidant decay data according to Eq. (2).

$$c = c_0 - 2\alpha + \alpha e^{-k_1 t} + \alpha e^{-k_2 t} \quad (2)$$

where c_0 and c refer to the concentration of 4-AcNH-TEMPO$^+$ after reaction time 0 (2.5 mM) and t, respectively, k_1 and k_2 are first-order