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ORIGINAL PAPER

Alkali treatment of birch kraft pulp to enhance its TEMPO catalyzed oxidation with hypochlorite

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Abstract Alkali treatment was used to increase the reactivity of birch kraft pulp prior to its 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) catalyzed oxidation with hypochlorite, which is a process commonly applied to prepare nanofibrillated cellulose. On contrary to the traditional use of NaBr as a cocatalyst, TEMPO was activated with HOCl prior to the oxidation. Commonly, the lack of bromide increases the oxidation time and impairs the formation of carboxylic groups. However, the reaction time of the bromide-free TEMPO catalyzed oxidation could be shortened from 2.5 to 0.5 h when the pulp was treated with 1 M NaOH prior to the oxidation (2.4 mmol NaOCl/g pulp). The beneficial effect was obtained even if the alkali treatment was executed at room temperature and only for few minutes. Moreover, the alkali pretreatment enabled selective production of a pulp with carboxylate content as high as 1.6 mmol/g with NaOCl dosage of 4.4 mmol/g. The changes in the cellulosic raw material during the alkali treatment were assessed by water retention value and carbohydrate analysis.

Keywords Birch · Hypochlorite · Nanofibrillated cellulose · TEMPO catalyzed oxidation · Water retention value · Xylan

Introduction

The catalytic conversion of the primary hydroxyl groups to carboxylates via aldehydes has been studied widely during the last two decades (de Nooy et al. 1995a, b; Zhao 1999; Bragd et al. 2000, 2004; Ibert et al. 2002). 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its derivatives (e.g. 4-methoxy-TEMPO, 4-acetamido-TEMPO, 4-hydroxy-TEMPO) are widely studied catalysts for oxidation of carbohydrates and pulp (Bragd et al. 2001; Isogai 2011a; Watanabe et al. 2012). TEMPO catalyzed oxidation of pulp has been found to be an efficient chemical pretreatment for the production of nanofibrillated cellulose (NFC) (Isogai 2011a; Saito and Isogai 2004; Saito et al. 2007, 2009, 2010). The oxidized pulp can be converted to a transparent gel NFC by homogenization with, e.g., an ultrasonic treatment

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(Saito et al. 2006, 2007, 2009; Okita et al. 2009, 2010). The oxidation of the hydroxymethyl groups of cellulose to carboxylates via aldehydes reduces drastically the energy consumption during the homogenization. The carboxylate content obtained during the oxidation determines the amount of energy required to defibrillate the pulp (Besbes et al. 2011). NFC has a vast variety of potential applications, for instance, in composites (Bulota et al. 2011; Fujisawa et al. 2012), microelectronics, gas-barrier films, cosmetics, flame-resistant materials, and other high-tech materials (Isogai 2011a).

Radical TEMPO, which is available as a commercial product, is typically activated with NaBr that is used as a cocatalyst in stoichiometric oxidation of pulp with NaOCl at pH range from 10 to 11 (Isogai 2011a; Saito and Isogai 2004; Saito et al. 2006, 2007; Okita et al. 2009, 2010; Kitaoka et al. 1999; Iwamoto et al. 2010). However, TEMPO catalyzed oxidation can also be executed under neutral conditions (Saito et al. 2009, 2010). In addition, some procedures without the cocatalysis by NaBr have been introduced, such as an electromediated oxidation (Isogai 2011b) and an acid-neutral process applying TEMPO/NaOCl/NaClO$_2$ (Hirota et al. 2009). The electromediated oxidation applying TEMPO or its derivative with an amperometric system is reported to produce pulps with carboxylate content of 1 mmol/g. However, the reaction requires 48 h to complete. Acid-neutral conditions with the TEMPO/NaOCl/NaClO$_2$ system have been reported to yield extremely high carboxylate contents, even 4 mmol/g with regenerated cellulose (Hirota et al. 2009) and 1.3 mmol/g with softwood pulp (Tanaka et al. 2012). Similarly to the other bromide-free oxidations, this reaction system is also slow requiring a reaction time of 48–80 h depending on the raw material (Hirota et al. 2009; Tanaka et al. 2012). It can be concluded that bromide-free TEMPO catalyzed oxidations are slow in comparison with the bromide assisted TEMPO catalysis. Another drawback within the current oxidation process is the decrease in the formation rate of new carboxylate groups in pulp as the oxidation proceeds (Saito et al. 2007, 2009; Saito and Isogai 2004; Okita et al. 2009).

The reaction rate of TEMPO catalyzed pulp oxidation is typically dependent on the concentrations of TEMPO, NaOCl and NaBr, pH, and reaction temperature (de Nooy et al. 1995a; Bragd et al. 2000; Saito et al. 2010; Sun et al. 2005; Lai et al. 2013). In addition, the properties of the cellulosic raw material including the applied wood species and the processing history affect the reaction rate (Rodionova et al. 2013). Significance of the pulp properties is emphasized when the carboxylate content target of the oxidized pulp is high (Hirota et al. 2009). Oxidation is most effective when there are abundantly non-oxidized surface of fibers available. Some cellulose fibril surfaces existing in the cellulose fibers are resistant to TEMPO catalyzed oxidation (Saito et al. 2007). Amorphous cellulose is easier to oxidize than crystalline cellulose as the former is accessible to water (Müller et al. 2000). Never-dried pulps are more reactive compared to dry pulps due to the cellulose microfibril aggregation that takes place as water is removed from the cellulosic material (Jayme 1944). This aggregation reduces the amount of accessible hydroxyl groups due to hydrogen bond formation between the cellulose microfibrils (Higgins and McKenzie 1963; Matsuda et al. 1994; Newman 2004). A pretreatment of pulp, which lowers the penetration threshold of the catalyst into the fiber, would be beneficial for the production of NFC.

Strongly alkaline pretreatments of cellulosic raw materials have been studied widely since the mercerization process was developed (Mercer 1851). To date, such pretreatments are used in many chemical processes, including the production of carboxymethyl cellulose (Ambjörnsson et al. 2013) and viscose for textile fibers (Mozdyniewicz et al. 2013). Originally, the strongly alkaline mercerization was applied to improve the strength and appearance of cotton fibers. This treatment causes native cellulose or cellulose I to become swollen and after washing to shrink back to another allomorph, cellulose II, through Na-cellulose (Klemm et al. 1998; Van de Weyenberg et al. 2006). The conversion of cellulose I to Na-cellulose takes place rapidly (Crawshaw et al. 2002). The most severe changes in the crystallinity of cellulose occur (McKenzie and Higgins 1958; Kljun et al. 2011) under the conditions of mercerization, corresponding NaOH concentrations above 8–9 % (Philipp et al. 1959; Dinand et al. 2002). These changes are dependent on the alkalinity but also on the treatment time (Philipp et al. 1959; Borysiak and Doczekalska 2008).

Alkaline treatment of pulp alters the pulp properties by increased swelling already at mild conditions (Lindström and Carlsson 1982). Mild alkaline treatments are used for several purposes, including regaining the bonding properties of recycled pulps (Klungness 1974) and improving the prospects of natural fibers in composites (Crawshaw et al. 2002). Swelling, in general, refers to the loosening of the intermolecular interactions in cellulose and enhancement of competing interactions with the swelling agent. In neutral aqueous systems, the swelling is limited to the amorphous parts of cellulose and the fibril surfaces. Swelling is diffusion controlled and, thus, very rapid occurring in only a few minutes (Schwabe and Philipp 1954, 1955). The maximum extent of swelling is reached at around 10 % NaOH concentration, slightly depending on the cellulosic raw material (Saito 1939). In addition, temperature has a significant effect on the phenomenon as swelling is favored under low temperature (Porro et al. 2007). In novel processes' point of view, swelling improves cellulose accessibility and, thus, makes it more reactive in many heterogeneous chemical and enzymatic treatments. Alkaline treatments have also been suggested to increase cellulose accessibility by increasing the surface area as the crystallite size decreases (Wadsworth et al. 1979).

In this paper, we introduce a short and mild alkali treatment as a powerful pretreatment for both never-dried and dried birch kraft pulps prior to their bromide-free TEMPO catalyzed oxidation with NaOCl. The mild alkaline conditions do not alter the morphology of the pulp, which is beneficial for its further processing. The effects of alkali concentration, reaction time, and reaction temperature are reported. The quality of the pulp after the alkali treatment is estimated through analyses for carbohydrate composition and water retention value (WRV). The efficacy of the pretreatment is evaluated both by the oxidation time needed as well as the final carboxylate content of the pulp.

Experimental

Materials

Never-dried and industrially dried bleached birch kraft pulps were obtained from a Finnish pulp mill. A xylan-poor pulp was prepared by selective and targeted hydrolysis of the never-dried pulp with commercial Ecopulp TX800A xylanase (AB Enzymes Oy, Finland). The hydrolysis was performed in two phases (2 × 24 h) in deionized water at a consistency of 5 % under mild mixing (50 rpm) at pH 5 and 45 °C. After the first 24 h period, the pulp was filtered. Then, the pulp was washed twice with deionized water and suspended back into deionized water for the second hydrolysis, which was performed under the same conditions as described above. After 24 h, the enzymatic action was terminated by immersing the pulp into a boiling water bath for 15 min. Finally, the pulp was filtered and washed with excess deionized water.

The chemicals used for the oxidations were TEMPO [Sigma Aldrich (St. Louis, USA)], 13 % NaOCl {VWR [Radnor (PA), USA]}, $NaClO_2$ [Sigma Aldrich (St. Louis, USA)], 1 M NaOH [Merck (Darmstadt, Germany)], 1 M HCl [Merck (Darmstadt, Germany)], and H_2SO_4 [Emsure (Darmstadt, Germany)]. An 8 M NaOH solution was prepared from solid NaOH pellets [VWR (Leuven, Belgium)] to adjust the alkalinity in the pretreatments of the pulps. Water was purified in a Milli-Q system (Millipore Corporation, resistivity 18.2 MΩcm) for reagent solution preparations. Deionized water was used for all washings.

Alkali treatment of pulps

The treatments were executed mainly at room temperature (RT). For the samples treated at elevated temperatures, a water bath with a temperature control was applied. First, an 8 M NaOH solution together with water was added to the pulp to obtain the desired alkalinity and pulp consistency of 5 %. The pulp suspension was stirred with a mechanical stirrer throughout the reaction time. After the desired reaction time, the pulp was washed immediately with deionized water to a desired pH. The pH of the suspension was measured with a pH meter (Mettler Toledo) at 5 % pulp consistency. Finally, the pulp was manually pressed to a dry matter content of approximately 20 % and homogenized mechanically.

TEMPO catalyzed oxidation of pulps

The oxidations were performed in a Büchi reactor (volume 1.6 dm^3), with a Metrohm 718 Stat Titrino titrator for the pH adjustment. TEMPO was mixed with an excess of NaOCl in water. The pH of the TEMPO solution was adjusted to 7.5 with H_2SO_4. The final concentration of NaOCl was titrated with 0.005 M thiosulphate. Due to the formation of HOCl from NaOCl, TEMPO was oxidized to the oxoammonium cation and dissolved in the aqueous medium. First, the pulp (48 g dry matter content) and the activated TEMPO (2.4 mmol) were mixed well in a closed vessel. Then, the pulp suspension and water were added to the Büchi reactor to make a total volume of 1.2 dm^3. The reactor was provided with a continuous mixing and temperature control at 25 °C. NaOCl (58–218 mmol) was added to the reactor with a pump during (5–32 min) and the acidity was adjusted to pH 9 with 1 M NaOH. After the addition of NaOCl, pH was kept constant (pH 9) by adding 1 M NaOH with the automatic titrator. The oxidation was performed at pH 9 which was found to be optimal for HOCl which is a stronger acid (pKa 7.5) than HOBr (pKa 8.7). The bromide assisted oxidations are commonly conducted at pH 10.

NaBr/TEMPO/NaOCl oxidations were conducted similarly as the oxidations described above. However, the activation of TEMPO was excluded and a higher pH level of 10 was applied. TEMPO (2.4 mmol) and NaBr (4.8 mmol) were diluted into 40 ml of water and mixed with the pulp prior the oxidation. The NaOCl addition was 97 mmol.

The oxidation rate was followed by iodometric titration until all active chlorine was consumed. The standard deviation for the oxidation time was determined from four parallel measurements. After the reaction, the pulp was washed with deionized water.

Conversion of residual aldehydes to carboxylates by chlorous acid

The oxidized pulp suspension at 1 % consistency was adjusted to pH 3 with 1 M HCl. $NaClO_2$ was added to the suspension (10 mM final concentration) which was then mixed in the Büchi reactor for 2 h at 50 °C. Finally, the pulp was washed with deionized water. Viscosity of the pulp was analyzed according to the standard SCAN-CM 15:99.

Conductometric titration

The conductometric titration was conducted according to the standard SCAN-CM 65:02. The titration was executed using an automatic titrator (Metrohm 751 GPD Titrino) together with Tiamo 1.2.1. software. The data were processed with Origin 9 [OriginLab Corporation (MA, USA)]. The standard deviation is according to the standard.

Iodometric titration

The HOCl concentration (mol/l) of the pulp solution was determined by an iodometric titration described by Wartiovaara (1982).

WRV analysis

Prior to the WRV analysis, the pulp samples were converted to their Na^+-form. All of the subsequent treatments were done at 1 % consistency and the change of solution was 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 <5 μS/cm. 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.

Carbohydrate analysis

The carbohydrate composition of the 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 content of xylan was calculated from the monosaccharide content using a correction factor reported by Sluiter et al. (2011). The standard deviation was determined from four parallel measurements.

X-ray diffraction (XRD) analysis

The samples were pressed into tablets prior the analysis. The diffractograms were recorded with a Philips X'Pert MPD X-ray diffractometer in the powder method in a range 5–40° 2θ with Graphitemonochromatized Cu Kα radiation (λ = 0.1541 nm). The working conditions were 40 kV and 50 mA tube power. The crystallinity indexes were calculated using the Segal method.

Fluidization

The fluidization was carried out with a Microfluidics M-110P device applying two chambers: 200 and 100 µm. The pulp was diluted to 1.5 % concentration at pH 9. The pressure during the fluidization was 1,000 bar. 1 pass was conducted.

Turbidity and Brookfield viscosity

Turbidity was measured with a HACH P2100 Turbidometer with a 50 ml measuring vessel. The NFC sample was diluted in water to 0.1 % concentration for the measurement. Three parallel measurements were carried out. The apparent viscosity of NFC was measured with a Brookfield viscometer. The NFC sample was diluted in water to 0.8 % concentration for the measurement. Temperature during the measurement was adjusted to 20 ± 1 °C and a low rotational speed of 10 rpm was applied. Two parallel measurements were carried out.

Results

Alkalinity of the pretreatment

The progress of the catalytic oxidation was monitored by iodometric titration of the residual NaOCl in the reaction mixture. Without any pretreatment of a never-dried birch kraft pulp its oxidation was relatively slow and it took several hours to complete the reaction (Fig. 1). A short pretreatment of the pulp with 0.25 M NaOH, followed by washing with water to pH 9, did not change the reactivity. When 0.5 M or higher concentration of NaOH was applied in the pretreatment, a marked increase in the reaction rate was observed. Thus, the total reaction time, corresponding to the time needed to consume all NaOCl, could be reduced from 2.5 to 0.5 h by applying a pretreatment with 0.75 M NaOH at RT (Fig. 2). A similar 80 % reduction of reaction time took place when a dry birch kraft pulp was pretreated with 1 M NaOH prior to the catalytic oxidation at RT. The reduction in the reaction time was smaller (50 %) when the alkali treated pulp (1 M NaOH at RT) was oxidized by applying the bromide assisted TEMPO catalysis.

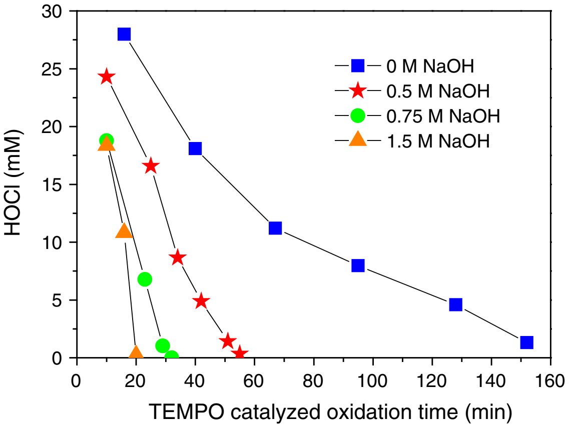

Fig. 1 The progress of TEMPO catalyzed oxidation observed as the residual concentration of HOCl. The reaction is considered to end when the all of the added NaOCl is consumed. The performance of the never-dried bleached birch pulp (*square*) can be substantially improved by an alkali treatment prior the oxidation at RT for 15 min as observed for pulps treated under 0.5 M (*star*), 0.75 M (*circle*), and 1.5 M (*triangle*) NaOH concentration. TEMPO dosage was 0.05 mmol/g, pulp consistency 4 %, and reaction temperature 25 °C

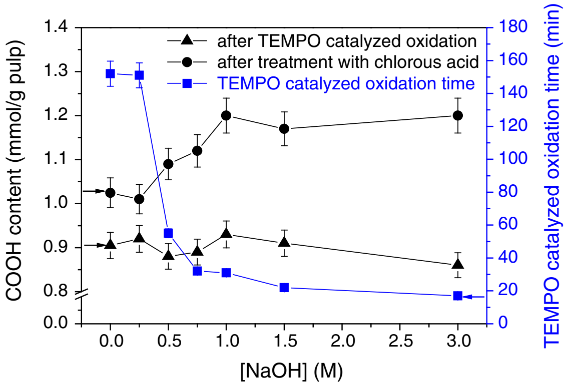

Fig. 2 Effect of NaOH concentration in pretreatment (15 min at RT) of never dried birch pulp (5 % consistency) on its TEMPO (0.05 mmol/g) catalyzed oxidation with NaOCl (2.4 mmol/g). The carboxylate content of the pulp is shown after the oxidation (*triangle*) and a post-treatment with chlorous acid that converts aldehydes to carboxylic acids (*circle*). The total reaction time (*square*) refers to the time during which NaOCl was fully consumed. Pulp consistency was 4 % and reaction temperature 25 °C during the TEMPO catalyzed oxidation

The amount of carboxylic acid groups formed in the catalytic oxidation with TEMPO was nearly independent of the pretreatment applied (Fig. 2). When the oxidized pulps were post-treated with chlorous acid, almost 20 % higher carboxylic acid contents were measured for the pulps pretreated with ≥1 M NaOH. The increase in the carboxylic acid content caused by the post-treatment equals to the amount of residual aldehyde groups in the pulp after the catalytic oxidation as chlorous acid is known to react selectively and stoichiometrically with chlorous acid (Lehtimaa et al. 2010), i.e., the consumption of HOCl during the conversion phase corresponds to the amount of aldehydes in the TEMPO oxidized pulp. Thus, the amount of the residual aldehyde groups was increased as a result of the alkali pretreatment and depending on its alkalinity. This was obviously related with the effect of the pretreatment on the catalytic oxidation time—the pretreatment increased the accessibility of cellulose for the primary oxidation but did not affect the secondary oxidation of the aldehydes formed to carboxylic acid groups. The observed increase in the total amount of the oxidized hydroxymethyl groups after the pretreatment with ≥0.5 M NaOH indicated also an increase in the accessibility of cellulose. However, the increase levelled off at around 1 M NaOH concentration. According to XRD, there were no changes in the crystallinity of the pulp treated with 1 M NaOH concentration. However, a pulp treated with 3 M NaOH solution suffered from changes in its supramolecular structure. This is in accordance with earlier findings that suggest the changes in the supramolecular structure of cellulose to occur only at >2 M NaOH. Thus, the increased reactivity could not be related with any interconversion between the allomorphs of cellulose (Dinand et al. 2002).

NFC was prepared from the TEMPO oxidized pulp pre-treated under 0.5 M NaOH concentration for 15 min at RT. No notable change in the NFC quality measured by turbidity and Brookfield viscosity were observed (Table 1). This was in accordance with the viscosity of the oxidized pulp prior the homogenization (Table 1).

Duration and temperature of the pretreatment

The duration of the pretreatment of the birch kraft pulp with 1 M NaOH at RT did not significantly affect the time needed to complete the TEMPO catalyzed oxidation nor the final carboxylate content measured after the post-treatment with chlorous acid (Table 2). The rapid activation that occurred already during 1 min contact time with alkali indicated the underlying phenomenon was diffusion controlled. Interestingly, swelling of cellulosic fibers is known to occur very rapidly and to be diffusion controlled (Schwabe and Philipp 1954, 1955). On the basis of our results we could not confirm the alkali-induced swelling as a reason for the activation but nevertheless the increase in the reactivity was retained over the subsequent washing with water.

Conducting the alkali pretreatment (1 M NaOH, 15 min) at 60 °C (instead of RT) had effect on neither

Table 1 Effect of alkali pretreatment (0.5 M NaOH for 15 min at RT) on TEMPO-mediated oxidation of never-dried birch pulp and properties of NFC produced from the pulps through fluidization. Charges of TEMPO and NaOCl were 0.05 and 2.4 mmol/g, respectively

		Never-dried birch pulp	Alkali treated pulp
Reaction time of TEMPO catalyzed oxidation	(min) ± 5 %	152	70
Carboxylate content after post-treatment with chlorous acid	(mmol/g) ± 3 %	1.02	1.08
CED viscosity after post-treatment with chlorous acid	(ml/g) ± 1 %	417	473
NFC turbidity	(NTU) ± 6 %	23	28
NFC Brookfield viscosity	(mPas) ± 2 %	9,260	11,350

Pulp consistency was 4 % and reaction temperature 25 °C. NFC was prepared through 1 pass with 1,000 bar pressure

Table 2 Total reaction time of the TEMPO catalyzed oxidation and the final carboxylic acid content for pulps pretreated with 1 M NaOH at RT for varying time. Residual aldehyde groups were converted to carboxylates by chlorous acid before their quantification

Pretreatment time (min)	Reaction time of TEMPO catalyzed oxidation (min) ± 5 %	Carboxylate content after post-treatment with chlorous acid (mmol/g) ± 3 %
1	27	1.18
15	31	1.20
240	27	1.12

Charges of TEMPO and NaOCl were 0.05 and 2.4 mmol/g, respectively. Pulp consistency was 4 % and reaction temperature 25 °C the carboxylate content of the pulp nor the oxidation time. This could further support swelling as an underlying phenomenon, since swelling of cellulosic fibers is known to be enhanced at lower temperatures (Porro et al. 2007).

Washing after the pretreatment

The alkali pretreated pulps were usually washed with water to pH of 9. However, the extent of washing in final pH range of 7–12 did not influence the pulp behavior during the oxidation procedure (Table 3). When the initial pH of the pulp was higher, the pH of the added NaOCl solution was reduced to maintain the optimal oxidation conditions.

NaClO dosage in TEMPO catalyzed oxidation

A never-dried birch kraft pulp pretreated with 1 M NaOH for 15 min at RT and then washed to pH 9 was oxidized with varying NaOCl dosage (2.4–4.5 mmol/g) to obtain pulps with varying carboxylate contents (Fig. 3). The oxidation rate of the pretreated pulp remained high when NaOCl dosage was increased from 2.4 to 3.1 mmol/g (Fig. 3). However, further oxidation of the pulp slowed down when higher NaOCl dosages were applied (3.8–4.5 mmol/g), indicating that the number of available unreacted hydroxymethyl groups was clearly reduced. Figure 3 illustrates the consumption of HOCl after the chemical addition. In all cases most of the NaOCl was consumed already during the chemical addition (first <20 min of oxidation) as the concentration of NaOCl added varied between 95 (2.4 mmol/g) and 180 mM (4.5 mmol/g).

Table 3 Total reaction time of TEMPO catalyzed oxidation and the final carboxylic acid content for pulps pretreated with 1 M NaOH for 15 min at RT and then washed to varying pH prior to the catalytic oxidation

pH of pulp washing filtrate after alkaline treatment	Reaction time of TEMPO catalyzed oxidation (min) ± 5 %	Carboxylate content after post-treatment with chlorous acid (mmol/g) ± 3 %
12	32	1.18
11	34	1.17
10	34	1.20
9	31	1.20
8	27	1.16
7	33	1.17

Charges of TEMPO and NaOCl were 0.05 and 2.4 mmol/g, respectively. Pulp consistency was 4 % and reaction temperature 25 °C

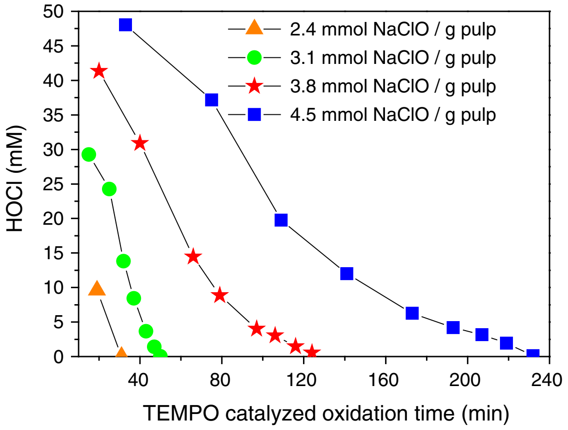

Fig. 3 Decrease in the residual concentration of HOCl with time in TEMPO catalyzed oxidation of alkali treated (1 M NaOH, 15 min, RT) never dried birch pulp with varying initial NaOCl dosage: 2.4 (*triangle*), 3.1 (*circle*), 3.8 (*star*), and 4.5 (*square*) mmol/g. TEMPO dosage was 0.05 mmol/g, pulp consistency 4 %, and reaction temperature 25 °C

The alkaline pretreatment of pulps enabled reaching very high carboxylate contents without using bromide in the catalytic oxidation. Figure 4 illustrates the obtained carboxylate contents for pulps first pretreated at 1 M NaOH concentration for 15 min at RT and the oxidized with varying NaOCl dosages using TEMPO as a catalyst. When NaClO dosage of 4.5 mmol/g was applied, the final carboxylate content was above 1.6 mmol/g (Fig. 4). Previously, the traditional TEMPO catalyzed oxidation with NaBr as cocatalyst and applying NaOCl dosage of 5 mmol/g has produced carboxylate contents ranging from 1.25 to 1.5 mmol/g for bleached hardwood pulp (Saito et al. 2007; Iwamoto et al. 2010). Thus, the procedure introduced in this paper exhibits even better oxidation performance without the use of bromide. In addition, the selectivity of the oxidation was constant up to 3.8 mmol/g dosage (Fig. 4). However, the reaction time (240 min) is still longer compared to the bromide aided oxidation (125 min) reported by Saito et al. (2007). Yet, the reaction time is significantly shorter than the previously reported bromide-free alternatives exhibiting reaction times up to 80 h (Hirota et al. 2009; Tanaka et al. 2012). The amount

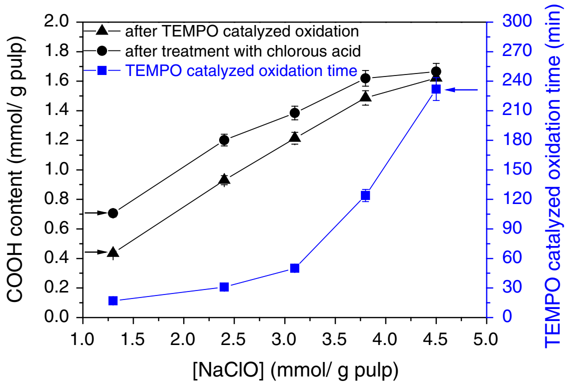

Fig. 4 Effect of NaOCl dosage on the carboxylate content both after the oxidation (*triangle*) and after the post-treatment with chlorous acid (*circle*) of the alkali treated (1 M NaOH, 15 min, RT) and catalytically oxidized (0.05 mmol/g TEMPO, 25 °C, 4 % consistency) never dried birch pulps and on the total reaction time (*square*) of the catalytic oxidation

of residual aldehydes, observed as an increase in the carboxylate content caused by the post-treatment with chlorous acid, decreased as a function of increasing NaOCl dosage. Although this change is indirectly related with the decrease in the number of available unoxidized hydroxymethyl groups, it is more probably caused by the extended reaction time during which the slow secondary oxidation of the already formed aldehydes continues.

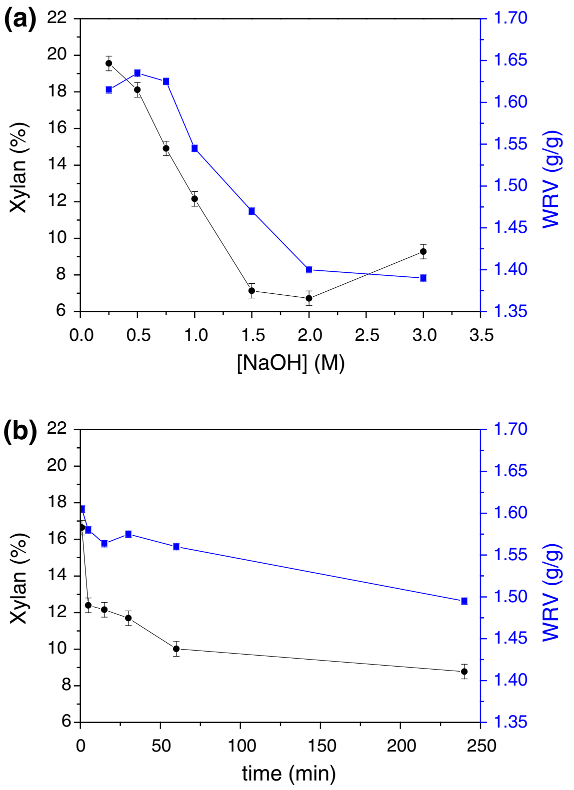

Fig. 5 Effect of **a** alkalinity (15 min treatment) and **b** contact time (in 1 M NaOH) on the residual xylan content (*circles*) and WRV (*squares*) of never-dried birch kraft pulp in aqueous suspension at RT

Pulp characteristics

WRV of dry birch kraft pulp increased by 12 % when it was treated with 1 M NaOH for 15 min at RT, similar to earlier literature (Lindström and Carlsson 1982; Lindström 1992; Weise et al. 1998). However, treating the never-dried birch kraft pulp with ≥1 M NaOH (15 min at RT) decreased its WRV by up to 15 % (Fig. 5a). Increasing the treatment time had a similar but smaller effect (Fig. 5b). The xylan content of both pulps was significantly decreased by the action of alkali as has been reported earlier (Sjöström and Enström 1967). Since the alkali pretreatment activated both the dry and never-dried pulps towards the TEMPO catalyzed oxidation, it seems obvious that the increase in the accessibility of cellulose was affected more by the dissolution of xylan than fiber wall swelling that correlates with WRV. The changes in WRV could be explained by the dissolution of the highly accessible xylan (Pejik et al. 2008) and reversible aggregation of microfibrils in alkali.

A xylan-poor never dried birch pulp was produced through a xylanase treatment to confirm the role of xylan removal on the increased reactivity of the pulps during their catalytic oxidation. The xylanase treated pulp had xylan content of 14.7 %, which corresponded to that of the pulp treated in 0.75 M NaOH at RT for 15 min (14.9 % xylan). Table 4 summarizes the oxidation response of these pulps in comparison with the non-treated never-dried birch kraft pulp. Although the xylanase treatment shortened the reaction time, the superior performance of the alkali treated pulp cannot be merely explained by the xylan removal. Moreover, the carboxylate content of the xylanase treated pulp was significantly lower compared to the alkali treated pulp. Thus, the alkali treatment has additional benefits not dependent merely on the reduced amount of xylan.

Table 4 Effect of xylanase and alkali treatments of the never-dried birch pulp on their xylan content and reactivity in TEMPO catalyzed oxidation (0.05 mmol/g TEMPO, 2.4 mmol/g NaOCl, 25 °C) measured by reaction time and the obtained carboxylate content

Pulp	Xylan content (%) ± 0.4 PP	Reaction time of TEMPO catalyzed oxidation (min) ± 5 %	Carboxylate content after post-treatment with chlorous acid (mmol/g) ± 3 %
Never-dried birch pulp	22.4	152	1.02
Xylanase treated pulp	14.7	92	0.93
Alkali treated pulp (0.75 M NaOH, RT, 15 min)	14.9	30	1.20

Discussion

The traditional TEMPO catalyzed oxidation of cellulosic pulps is effective and fast. However, because the use of bromide as a cocatalyst has raised concern, bromide-free oxidations have also been developed (Bragd et al. 2000). Unfortunately, these oxidations are often slow and inefficient (Saito et al. 2010; Isogai 2011b; Tanaka et al. 2012; Liaigre et al. 2005). To overcome this hindrance, we propose a pretreatment with alkali to increase the accessibility of cellulose prior to the oxidation.

Strong alkaline treatments are commonly used in many cellulosic processes (Ambjörnsson et al. 2013; Mozdyniewicz et al. 2013). However, these treatments often alter the crystalline structure of cellulose (Klemm et al. 1998), which is unwanted in the production of NFC. Thus, we introduce a short, mild alkaline treatment to merely improve swelling and accessibility of pulp without altering its properties otherwise. Nevertheless, the treatment dissolves some xylan depending on the alkalinity. In fact the removal of xylan seems to be responsible, in part, for the increased reactivity of cellulose. This is understandable because xylan is known to be unreactive towards TEMPO catalyzed oxidation (Brodin and Theliander 2013; Bowman et al. 2011).

Increase in swelling of fiber wall, typically quantified as WRV, could be another logical reason for the observed alkali-induced increase in the reactivity of cellulose. WRV of a dry pulp was indeed increased by the action of alkali, despite the partial dissolution of hemicelluloses that are known to retain water (Pejik et al. 2008). The decrease in WRV of a never-dried pulp during alkali treatment was unexpected and has not been reported earlier. Conversely, an alkaline treatment has even been reported to increase WRV of a never-dried paper pulp (El-Din 1993). Obviously WRV alone cannot be considered as a good measure of pulp quality for TEMPO catalyzed oxidation.

The alkali pretreatment is not only advantageous in shortening the reaction time but also in increasing selectivity and the extent of oxidation. By applying high enough NaOCl dosage during the oxidation, carboxylate contents comparable to the conventional TEMPO catalyzed oxidation can be achieved. The duration of the pretreatment had no effect on the response of the pulp during the oxidation. The beneficial effects of the pretreatment are resistant to the following washing and, thus, the behavior of the pulp during the oxidation is independent of pH of the pulp after the washing. The possibility to reduce the washing demand after the alkali treatment will be beneficial both economically as well as environmentally. In addition, the oxidation is easier to control at the ideal pH region of around 8–9, since NaClO decomposes faster if pH is lower and undesirable oxidation of C2 and C3 secondary hydroxyls of cellulose to ketones takes place if pH is higher (Saito and Isogai 2004).

Conclusions

Pretreatment with alkali was introduced as a means to intensify bromide-free TEMPO catalyzed oxidation of cellulosic pulps. A very short pretreatment of a never-dried birch pulp with 0.75 M NaOH at RT was shown to decrease the oxidation time from 2.5 to 0.5 h. In addition, the selectivity of the oxidation increased and, when 4.5 mmol/g hypochlorite dosage was applied during the oxidation, a carboxylate content as high as 1.6 mmol/g was reached. Thus, the pretreatment enabled a bromide-free oxidation with similar or even slightly better oxidation outcome compared to the conventional TEMPO catalyzed oxidation. Similar benefits were recorded for dry birch pulps that were pretreated with alkali. As expected, the hemicellulose content decreased as a function of the alkalinity. Surprisingly, WRV was shown to increase for the dry pulps but to decrease for the never-dried pulps.

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