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Activation of TEMPO by ClO₂ for Oxidation of Cellulose by Hypochlorite - Fundamental and Practical Aspects of the Catalytic System

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**ABSTRACT**

Bromine-free TEMPO-catalyzed oxidation of the primary alcohols by sodium hypochlorite (NaOCl) does not proceed without a prior activation of the catalyst. Here we demonstrate an immediate *in situ* activation of the catalyst with an equimolar addition of chlorine dioxide (ClO₂) relative to TEMPO. Sodium bromide (NaBr) had a similar role in activating the catalyst although NaBr was needed in excess and the activation took several minutes depending on the dosage of NaBr. The activation method, or the concentration of NaBr, did not affect the bulk oxidation rate. The selectivity of the ClO₂ initiated oxidation remained high up to NaOCl addition of 3 mol/kg bleached birch kraft pulp after which additional loss in yield and depolymerization of cellulose were emphasized with negligible increase in carboxylate content. A carboxylate content of 0.8-1 mol/kg, sufficient for easy mechanical fibrillation of the pulp, was achieved under mild conditions with NaOCl addition of 2-2.5 mol/kg pulp.

**Keywords:** birch pulp, cellulose, carboxylates, bromide-free, ClO₂ activated TEMPO-mediated oxidation, UV-Vis spectrometry

**Chemical compounds studied in this article:**

- 2,2,6,6-tetramethyl-1-piperidinyloxy (PubChem CID: 2724126)
- Chlorine dioxide (PubChem CID: 24870)
- Sodium hypochlorite (PubChem CID: 23665760)
- Sodium chlorite (PubChem CID: 23668197)
- Sodium hydroxide (PubChem CID: 14798)
- Hydrochloric acid (PubChem CID: 313)
1. Introduction

The highly selective nitroxy radical mediated oxidation of hydroxymethyl groups of polysaccharides was introduced already two decades ago (Davis & Flitsch, 1993; de Nooy, Besemer, & van Bekkum, 1994; de Nooy, Besemer, & van Bekkum, 1995a; de Nooy & Besemer, 1995b; Kitaoka, Isogai, & Onabe, 1999; Rozantsev & Sholle, 1971). A catalytic amount of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical, some sodium bromide (NaBr) and an excess of sodium hypochlorite (NaOCl) are required to selectively convert the primary alcohols to aldehydes and further to carboxylates. More recently fibrillation of TEMPO/NaBr/NaOCl oxidized pulps was described to yield nanofibrillated cellulose (NFC) gels, a discovery that has been widely applied in science and cellulose-based materials development since then (Isogai, Saito, & Fukuzumi, 2011; Iwamoto, et al., 2010; Saito, Okita, Nge, Sugiyama, & Isogai, 2006; Saito & Isogai; 2004, Saito, Shibata, Isogai, Suguri, & Sumikawa, 2005). The extensively oxidized, negatively charged pulps are easy to disintegrate which radically reduces energy use compared to fibrillation of unmodified pulps (Isogai, A, et al., 2011).

Hypobromite, which is formed in a reaction between NaBr and NaOCl, has been claimed to convert the reduced form of TEMPO, the hydroxylamine (TEMPOH), to its oxidized form, the nitrosonium ion (TEMPO⁺), that is the actual oxidant of the primary alcohol groups (Isogai, et al., 2011). To oxidize most of the available hydroxymethyl groups, a large excess of NaOCl is needed, typically more than twice the amount calculated from the reaction stoichiometry (Iwamoto, et al., 2010).

Alkaline mixtures of hypochlorite and hypobromite are somewhat unstable (Lewin & Avrahami, 1955),
and part of the added bromide is inactivated during the catalytic oxidation. Thus, rather significant amounts of NaBr are required, which is a challenge for industrial application of the process (Bragd, et al., 2000).

To overcome the use of bromide several modifications of the original reaction system have been presented. TEMPO can be activated for oxidation without bromide by cyclic voltammetry. However, the electro-mediated oxidation is slow which reduces its applicability (Isogai, T, Saito, & Isogai, A, 2010; Isogai, T, Saito, & Isogai, A, 2011). Low reactivity is also a drawback in the proposed bromide-free catalytic oxidation by sodium chlorite (TEMPO/NaOCl/NaClO₂) under slightly acidic or neutral conditions (pH 3.5-6.8) (Hirota, Tamura, Saito, & Isogai, 2009; Saito, et al., 2009; Saito, Hirota, Tamura, & Isogai, 2010; Tanaka, Saito, & Isogai, 2012). In this system chlorous acid (HClO₂) oxidizes stoichiometrically the initially formed aldehydes to carboxylates which releases an equimolar amount of hypochlorous acid (HOCl) (Lehtimaa, et al., 2010; Chinake, Olojo, & Simoyi, 1998; Isbell & Sniegoski, 1964; Isogai & Saito, 2010; Jeanes & Isbell, 1941; Launer & Tomimatsu, 1959; Launer & Tomimatsu, 1954; Stitt, Friedlander, Lewis, & Young 1954). The oxidation of aldehydes is fastest at low pH (<2) where the equilibrium concentration of the less reactive chlorite ion is low (Lehtimaa, Kuitunen, Tarvo, & Vuorinen, 2010).

Another possibility to eliminate the use of bromide is to apply a separate pretreatment to convert TEMPO to TEMPO⁺ with hypochlorous acid prior to mixing the catalyst with the pulp and NaOCl (Pääkkönen et al., 2015). The efficiency of the catalysis could potentially decrease with time since TEMPO⁺ and TEMPOH can react with each other to form TEMPO (Israeli, et al., 2005; Sen and Golubev, 2009). The rate of this comproportionation reaction increases as a function of pH (Israeli, et al., 2005). However, it was recently shown that the catalyst exists almost exclusively as TEMPO⁺ during the
catalytic oxidation of cellulose, both in the presence and absence of bromide, and therefore the initial activation of TEMPO should be sufficient to maintain the high reactivity throughout the oxidation (Pääkkönen, et al., 2015).

The use of TEMPO with chlorine dioxide (ClO₂) as the bulk reagent to oxidize softwood kraft pulp has also been reported (Komen, Weerawarna, & Jewell, 2006). Because ClO₂ reacts very fast with TEMPO (Ganiev, et al., 1999; Ganiev, et al., 2001), we decided to study this reaction as a means to initiate the TEMPO-mediated oxidation of cellulose with NaOCl. First we studied the stoichiometry of the initiation and then applied it in the oxidation of both simple alcohols (1-propanol, 2-propanol) and a kraft pulp. These experiments enabled us to draw general conclusions on the initiation and selectivity of TEMPO-catalyzed oxidation of cellulose.

2. Experimental

2.1. Materials

Bleached birch kraft pulp (kappa number < 1, xylan content 21.5 %) was obtained from a Finnish pulp mill, TEMPO (Aldrich), ClO₂ water solution (prepared in lab), 3.5 % NaOCl solution (pH over 12, VWR), NaClO₂ (Sigma-Aldrich), n-Propanol (Riedel-deHaen), 1 M NaOH, 1 M HCl, Büchi reactor (volume 1.6 dm³), Metrohm 718 Stat Titrino titrator (pH adjustment), Metrohm 751 GPD Titrino titrator (conductometric titration), Tiamo 1.2.1. software (conductometric titration), Shimadzu 2550 UV-Vis spectrophotometer and UVProbe 2.32 software. All washings were done with Milli-Q purified water (Millipore Corporation, resistivity 18.2 MΩcm)
2.2. Oxidation of bleached birch pulp

TEMPO was mixed with ClO$_2$ water solution in a closed vessel. Despite its low water solubility, TEMPO was dissolved (observed as a color change from red to black) while the radical TEMPO was converted to the nitrosonium ion. The pulp was mixed with water (pulp consistency 1-4 %) and transferred to the Büchi reactor (continuous mixing, temperature 25-50 °C, volume of pulp suspension 1-1.2 dm$^3$). Then, the activated TEMPO solution and NaOCl were added to the reactor. The pH level was adjusted to 8 by 1 M NaOH with an automatic titrator after a rapid pH decrease during the beginning of the oxidation. The oxidation rate was followed by iodometric titration until all HOCl had been consumed. The pulp was washed through a wire cloth. The carboxylate content (SCAN-CM 65:02) and the CED-viscosity (SCAN-CM 15:99) were analyzed from the washed pulp samples.

2.3. Conversion of residual aldehydes to carboxylates by HClO$_2$

The suspension of the oxidized pulp (1-4 % pulp consistency) was acidified with 1 M HCl to pH 2. NaClO$_2$ (10 mM initial concentration) was added to the solution and the conversion was executed in a Büchi reactor (2-3 hours, 25-50 °C). The washing and the analysis of the pulp was done by the same procedure described in the previous chapter.

2.4. Oxidation tests with model compounds

n-Propanol and NaClO were mixed with water in the Büchi reactor at 25 °C. When NaBr was applied, it was added to the reactor right in the beginning. When ClO$_2$ was applied, it was added after a delay to the mixture. The pH level ascended to 11 after the NaOCl addition and decreased rapidly when the oxidation reaction started. The pH level was adjusted to 10 with 1 M NaOH and an automatic
titrator after the rapid decrease of pH. The oxidation rate was followed by iodometric titration until all HOCl was consumed.

2.5. Active chlorine titration

10 ml of KI solution (80 g/l) and 20 ml of 1 M sulphuric acid were added to an Erlenmeyer flask. A known amount of the sample (unfiltered sample solution from reactor) was added to Erlenmeyer bottle. NaOCl was titrated with iodometric titration.

The stoichiometry between chlorine (Cl$_2$) and the measured hypochlorite (NaOCl) is 1:1. The stoichiometry between chlorine (Cl$_2$) and the measured chlorite (NaClO$_2$) is 1:2. The stoichiometry between chlorine (Cl$_2$) and the measured chlorite (ClO$_2$) is 1:2.5.

2.6. Oxidation of TEMPO with ClO$_2$

Solutions of 1 mM TEMPO and 1 mM ClO$_2$ were prepared with pure water. The solutions were mixed in 1:1 ratio and monitored for their absorption spectra with a Shimadzu 2550 UV-Vis spectrophotometer.

3. Results

3.1. The relationship between the dynamics of TEMPO activation and NaBr addition

The role of NaBr in converting TEMPO radical to nitrosonium ion was explored in oxidation of n-propanol with hypochlorite (Figure 1). When the concentration of the added NaBr was low enough, the oxidation of the alcohol did not start immediately but an induction period was observed. The length of
the induction period was inversely related with the amount of added NaBr. The oxidation of the alcohol proceeded fast after the induction period and the oxidation rate depended little on the concentration of NaBr. Clearly, the bromide accelerated the initial formation of the nitrosonium ion, probably through the formation of HOBr. The insignificance of bromide after the activation could be explained by a fast reoxidation of the hydroxylamine by HOCl (Bragd, et al., 2000; Pääkkönen, et al., 2015). Thus, the key for a bromine-free oxidation by hypochlorite is to apply another activator for the initial conversion of the TEMPO radical.

Fig. 1. Consumption of hypochlorite (57 mM) in TEMPO (0.09 mM) mediated oxidation of n-propanol (100 mM) at pH 10 at 25 °C. Three different concentrations of NaBr were applied: 2, 6 and 16 mM.

3.2. Activation of TEMPO by ClO$_2$ studied by UV-Vis absorption spectroscopy

The TEMPO radical reacted rapidly with ClO$_2$ at RT (Figure 2A). The yellow color of the ClO$_2$ disappeared immediately when ClO$_2$ and TEMPO solutions are mixed. The pseudo-first-order rate
constant for the reaction between ClO$_2$ and 0.01 M TEMPO is 3.7 x 10$^5$ s$^{-1}$ according to Ganiev (Ganiev, et al., 2001).

The complete reaction of ClO$_2$ was verified by the lack of its absorption maximum at 360 nm right after the mixing of ClO$_2$ and TEMPO. The spectrum of the 1:1 mixture is similar to the spectrum of the nitrosonium ion (Pääkkönen, et al., 2015). The difference spectrum of the reaction mixture and the TEMPO solution had a maximum at 290 nm and a minimum at 245 nm (Figure 2B). According to Israeli (Goldstein, Merenity, Russo, & Samuni, 2003, Israeli, et al., 2005) the change in the absorption at 290 nm can be applied to detect the formation of the oxidized TEMPO while the change in the absorption at 245 nm is related with the decay of the TEMPO radical.
3.3. ClO₂ as an activator in TEMPO-catalyzed oxidation of 1-propanol

Without using any added NaBr or ClO₂ the catalytic oxidation of 1-propanol was not initiated (Figure 3). After adding an equimolar or higher amount of ClO₂ relative to TEMPO the system was activated immediately without any induction phenomenon, and the oxidation proceeded at a high rate and consumed 1.8 equivalents of hypochlorite and 0.84 equivalents of sodium hydroxide at pH 10, corresponding to conversion of 1-propanol mostly to propionic acid. 2-Propanol reacted only slowly under similar conditions.

**Fig. 3.** Consumption of hypochlorite (60 mM) in TEMPO (0.8 mM) mediated oxidation of 2-propanol (25 mM) and mixture of 2-propanol and 1-propanol (25 mM + 25 mM) at pH 10 at 25 °C. No NaBr was used but ClO₂ (1.3 mM) was added at reaction time of 16 min.

The consumption of NaOCl by 1-propanol depended on pH of the reaction medium (Figure 4). When the ClO₂ activated TEMPO was added in the beginning of the reaction without any delay, one equivalent of NaOCl was consumed in a very short time. At pH 10 the second equivalent of the oxidant was also
consumed rapidly while the further oxidation was slow at pH 7 and non-existent at pH 5. Thus, the oxidation rate of the aldehyde intermediate (propanal) to the acid (propionic acid) depended strongly on pH of the reaction medium.

Fig. 4. Effect of pH on the consumption of hypochlorite (60 mM) in TEMPO (0.8 mM) mediated oxidation of 1-propanol (30 mM) at 25 °C. No NaBr was used but TEMPO was activated by final addition of ClO₂ (1.3 mM) that initiated the reaction.

3.4. ClO₂ activated TEMPO-mediated oxidation of bleached birch pulp

When TEMPO was first activated with equimolar amount of ClO₂ and then mixed with the pulp suspension and hypochlorite, the oxidation started immediately (Figure 5). The initial rate of the reaction was equal to that of the bromide ion assisted catalytic oxidation. After NaOCl consumption of ~2 mmol/g pulp the reaction slowed down and continued at ~1/40 of the initial rate (pH 10, 25 °C, 4 % pulp consistency, NaOCl 5 mmol/g, TEMPO 0.05 mmol/g). At the same conversion, the rate of the bromide ion (0.3 mmol/g) assisted oxidation decreased to 1/3 of the initial rate. Obviously the
accessible hydroxymethyl groups were initially oxidized by the nitrosonium ion while an additional oxidation of secondary alcohols with HOBr took place afterwards. In the end of the ClO$_2$ activated and NaBr assisted oxidations the carboxylate contents of the washed pulps were 1.03 (1.14) and 1.10 (1.34) mmol/g, respectively (values in parentheses were measured after conversion of residual aldehydes to carboxylates by HClO$_2$). The higher carboxylate content after the NaBr assisted oxidation probably resulted from the formation of cellulose dialdehydes (oxidation at C-2 and C-3) and their further oxidation into the corresponding carboxylates (Kuramae, Saito, & Isogai, 2014).

To further illustrate the role of HOBr in the secondary oxidation a small amount of NaBr (2 mM) was added in ClO$_2$ activated TEMPO catalyzed oxidation (pH 10, 25 ℃, 1 % pulp consistency, NaOCl 4.5 mmol/g, TEMPO 0.08 mmol/g) after NaOCl consumption of 2 mmol/g (Figure 6). The addition immediately increased the secondary oxidation rate significantly thus verifying the role of HOBr. In the end of the reaction the carboxylate content of the washed pulp was 1.02 mmol/g.

**Fig. 5.** Consumption of hypochlorite in TEMPO (2 mM) mediated oxidation of a birch kraft pulp (40 g pulp/dm$^3$) at pH 10 at 25 ℃. TEMPO was activated by ClO$_2$ prior to mixing with NaOCl or the catalysis was assisted by NaBr.
Fig. 6. Consumption of hypochlorite in TEMPO (0.8 mM) mediated oxidation of a birch kraft pulp (10 g pulp/dm³) at pH 10 or pH 7 at 25 °C. TEMPO was activated by ClO₂ prior to addition of NaOCl. In one experiment (pH 10, 45 mM NaOCl) NaBr (2 mM) was added at reaction time of 95 min.

The selectivity of the fast initial reaction was studied at low NaOCl charge (pH 10, 25 °C, 1 % pulp consistency, NaOCl 2.0 mmol/g, TEMPO 0.08 mmol/g). In this case the fast NaOCl consumption equaled to 1.0 mmol/g (Figure 6). The aldehyde content of the pulp suspension equaled to 0.20 mmol/g while the carboxylate content of the washed pulp was 0.57 mmol/g (value measured after conversion of residual aldehydes to carboxylates by HClO₂). The untreated pulp had a carboxylate content of 0.06 mmol/g and thus the calculated selectivity of the initial oxidation was estimated to be ~80 % (ΔCHO 0.20 mmol/g, ΔCOOH 0.31 mmol/g, ΔNaOCl -1.0 mmol/g). At pH 7 the proportion of the rapidly reacting fraction of NaOCl was somewhat smaller (0.6 mmol/g).

The effect of the dosage of NaOCl on the carboxylate and aldehyde contents were studied at pH 8 at 25 °C (2-4 % pulp consistency, 2-2.5 mM TEMPO) (Figure 7A) (details of these and additional
experiments at higher temperatures are summarized in Table S1). The carboxylate content of the oxidized pulp increased as a function NaOCl dosage until reaching a maximum level of ~1.0 mmol/g. The aldehyde content of the pulps was in average ~0.15 mmol/g and was little affected by the amount of NaOCl used. At NaOCl dosages < 3 mmol/g ~65 % of the spent oxidant was consumed in production of aldehyde and carboxylate groups in the pulp (Figure 7B). The effect of NaOCl dosage on the carboxylate formation was also demonstrated by FTIR spectroscopy (Figure S1). The lowest carboxylate content to convert the oxidized pulp into NFC gel by a single pass through a fluidizer was 0.7 mmol/g (without post-oxidation with HClO₂) corresponding to NaOCl charge of 2.2 mmol/g (25 °C, pH 9, 4 % pulp consistency, TEMPO 0.05 mmol/g, reaction time of 80 min). Excessive use of NaOCl (5 mmol/g) led to oxidation of secondary alcohol groups of xylan, C2-C3 bond cleavage of anhydroxylopyranosyl units and formation of the corresponding ‘dicarboxylate xylan’ as shown by 13C NMR spectroscopy of the solubilized material (Fig. S2).
**Fig. 7.** (a) Effect of the dosage of NaOCl on the carboxylate and aldehyde contents of pulps oxidized using ClO₂ activated TEMPO as a catalyst. Conditions: pH 8, 25 °C, pulp consistency 2-4 %, 2-2.5 mM TEMPO. (b) Effect of the dosage of NaOCl on its consumption in formation of carboxylate (ΔCOOH) and aldehyde (ΔCHO) groups in pulp during its ClO₂ activated TEMPO-mediated oxidation. Conditions: pH 8, 25 °C, pulp consistency 3-4 %, 2 mM TEMPO. The dotted line denotes the theoretical 100 % selectivity. (c) Effect of the dosage of NaOCl on depolymerization of cellulose, quantified by the increase in 1/DP, in pulps oxidized using ClO₂ activated TEMPO as a catalyst. Conditions: pH 8, 25 °C, pulp consistency 2-4 %, 2-2.5 mM TEMPO. (d) Effect of the dosage of NaOCl on yield of cellulose. Conditions: pH 8, 25 °C, pulp consistency 4 %, 2.5 mM TEMPO.
The extent of depolymerization of cellulose, characterized by change in 1/DP, was nearly linearly related with the dosage of NaOCl when it was < 3 mmol/g (Figure 7C). Overdosing of NaOCl led to a rapid decrease in the selectivity and the yield of the oxidation (Figure 7D). The measured yields with the dosage of NaOCl < 3 mmol/g are comparable with the yields (yield > 90 %) at corresponding NaOCl dosages reported with NaBr/TEMPO/NaOCl oxidations of pulp (Isogai, A, Saito, & Fukuzumi, 2011). The rate of depolymerization depended also on pH. Increasing pH from 8 to 9-10 doubled the depolymerization rate, probably due to the alkali-catalyzed β-elimination reaction of the aldehyde (or keto) structures. Due to the sensitivity of the oxidized pulp for β-elimination, the DP of cellulose was always calculated from CED viscosity values measured from pulps stabilized by a post-oxidation by HClO₂ that converts aldehydes to carboxylates. Thus the combination of low temperature and pH 8 were considered optimal conditions for production of NFC for applications, such as reinforcement, that require a combination of a high viscosity and a high carboxylate content.

4. Discussion

TEMPO itself is unreactive towards alcohols and therefore its conversion to the nitronium ion is needed to initiate the catalytic oxidation. In conventional TEMPO catalyzed oxidation this activation is brought about by HOBr (NaBr + NaOCl). Relatively high NaBr addition is needed to accomplish the activation in a short time. ClO₂ oxidizes TEMPO immediately and a stoichiometric amount of the oxidant is enough to complete the reaction.

The TEMPO-mediated oxidation of cellulosic pulps occurs in two phases of different kinetics. In the first stage up to ~2 mmol/g of NaOCl is consumed and < 1 mmol/g of the hydroxymethyl groups of
cellulose are oxidized to aldehyde and carboxylate groups. This fraction is < 20 % of all hydroxymethyl
groups of cellulose (~5 mmol/g) in a typical kraft pulp. The magnitude of the fraction is characteristic
for the pulp and does not depend on the activation method of the catalyst.

The slower secondary stage may consume lots of NaOCl without significantly increasing the
content of oxidized groups in the pulp. Obviously these slower reactions occur mainly in the dissolved
material or lead to additional dissolution of hemicelluloses or cellulose. It was recently reported that
in the NaBr assisted TEMPO catalyzed oxidation of hardwood pulps the dissolved xylan is almost
completely oxidized through cleavage of the C2-C3 bond leading to 2 equivalents of carboxylates per
monomer (Kuramae, Saito, & Isogai, 2014). In our bromide-free oxidations the same phenomenon was
observed, even though to a smaller extent (Scheme 1).

Our results indicate that HOBr is the main oxidant of the secondary alcohols in the conventional
oxidation method. When NaBr is not applied, secondary oxidation by HOCl becomes important at pH
7-8. This is the pH range where the pH inside the cell wall is optimal for the reaction of polysaccharides
with HOCl.

The aldehyde content of cellulose stays at a relatively high, constant level throughout the catalytic
oxidation. Alkali-catalyzed β-elimination is possibly a reason for why cellulose is depolymerized more
extensively when the oxidation is carried out at pH > 8. The stability of the oxidized pulp could be
increased with a post-oxidation by HClO₂ that selectively converts the residual aldehydes to the
corresponding carboxylates. The oxidation kinetics of 1-propanol led us to expect that a higher pH in
the catalytic oxidation should lead to a lower residual aldehyde content. Such an effect was, however,
not observed and thus the aldehyde formation still remains partly unresolved.
Scheme 1. The proposed and known reaction routes in TEMPO-mediated oxidation of cellulose (R = CH$_2$OH) and xylan (R = H) by HOCl and HOBr. a) Oxidation of hydroxymethyl group by TEMPO$^+$ to aldehyde and further to carboxylate groups (Isogai, A, Saito, & Fukuzumi, 2011). b) Oxidation of 2,3-diols to dicarboxylates by hypohalides (Whistler & Schweiger, 1957; Kuramae, Saito, & Isogai, 2014). c) Conversion of TEMPO to TEMPO$^+$ by ClO$_2$ or HOBr (Pääkkönen, et al., 2015) and reoxidation of TEMPOH to TEMPO$^+$ by HOCl or HOBr.
5. Conclusions

Activation of the catalyst is a key step in TEMPO-catalyzed oxidation of cellulose, or primary alcohols in general, by hypochlorite. In the conventional oxidation method, the activation is realized through the addition of NaBr. Alternatively, a stoichiometric amount of ClO$_2$ can be applied for immediate, *in situ* activation of TEMPO. This approach could be attractive for oxidative modification of cellulosic pulps in mills that use ClO$_2$ in their bleaching processes. The selectivity of the oxidation remains high up to carboxylate content of 0.8-1.0 mol/kg which enables easy mechanical disintegration of the oxidized pulps to produce gels of fibrillated cellulose.

Acknowledgements

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Supplementary data

Activation of TEMPO by ClO₂ for Oxidation of Cellulose by Hypochlorite - Fundamental and Practical Aspects of the Catalytic System

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Materials and methods

1. Oxidation on bleached birch pulps

TEMPO was activated with > equimolar amount of ClO₂. The pulp was mixed with water (pulp consistency 1-4 %) and transferred to a Büchi glass reactor (continuous mixing, temperature 25-50 °C, volume of pulp suspension 1-1.2 dm³). Then, the activated TEMPO solution and NaOCl were added to the reactor. The pH level was adjusted to 8 by 1 M NaOH with an automatic titrator after a rapid pH decrease during the beginning of the oxidation. The oxidation rate was followed by iodometric titration until all NaOCl had been consumed. The pulp was washed on a wire cloth. The carboxylate content (SCAN-CM 65:02) and CED viscosity (SCAN-CM 15:99) were analyzed from the washed pulp samples.

2. FTIR spectroscopy analysis

All pulp samples were washed with pure water and dried prior to FTIR analysis. FTIR spectra were collected in the mid-infrared region by using a Bio-Rad FTS 6000 spectrometer (Digilab, Randolph, MA, USA) equipped with a MTEC PAC300 photoacoustic detector. Win-IR Pro V3.4 software (Digilab, Randolph, MA, USA) was used to baseline correct the FTIR spectra. The spectra were normalized relative to the cellulose peak at 1161 cm⁻¹ (Kaitao, et al., 2016).
3. $^{13}$C NMR analysis

Solution state $^{13}$C NMR measurements were performed in D$_2$O at 27 °C on a Bruker Avance III spectrometer operating at 100.61 MHz for $^{13}$C. 1,3,5-Trioxane was used as an internal standard for chemical shift (93.1 ppm). The spectra were acquired with a spectral width of 240 ppm, a relaxation delay of 1.5 s, 64K data points, and 30K number of scans. The spectral data was processed using TopSpin 3.0 software.

Results

![FTIR spectra of birch kraft pulps oxidized with ClO$_2$ activated TEMPO and NaOCl (0.68, 1.37 and 3.2 mmol/g) under conditions similar to those presented in Figure 5. The spectrum of the unoxidized pulp is shown as a reference. The absorption band at 1604 cm$^{-1}$ represents the carboxylate functionality (Abidi, Cabrales & Haigler 2014).](image)

**Figure S1.** FTIR spectra of birch kraft pulps oxidized with ClO$_2$ activated TEMPO and NaOCl (0.68, 1.37 and 3.2 mmol/g) under conditions similar to those presented in Figure 5. The spectrum of the unoxidized pulp is shown as a reference. The absorption band at 1604 cm$^{-1}$ represents the carboxylate functionality (Abidi, Cabrales & Haigler 2014).
Figure S2. $^{13}$C NMR spectra of freeze-dried filtrates from oxidation of birch kraft pulp under conditions similar to those presented in Figure 5. ClO$_2$ activated TEMPO was used as the catalyst with NaOCl dosages of a) 5.0 mmol/g, b) 2.3 mmol/g, and c) 0 mmol/g. $^{13}$C shifts of xylan and dicarboxylate xylan were assigned according to (Kovacs & Hirsch, 1980) and (Kuramae, Saito, & Isogai, 2014), respectively.

Table S1. Summary of oxidations of birch kraft pulp by (A) ClO$_2$ activated TEMPO and NaOCl at pH 8 and (B) post-oxidation of these pulps by HClO$_2$ to convert the residual aldehydes to carboxylates.

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Pulp consistency</th>
<th>TEMPO (mM)</th>
<th>ClO$_2$ (mM)</th>
<th>NaOCl (mmol g$^{-1}$)</th>
<th>Carboxylates (mmol g$^{-1}$)</th>
<th>CED-viscosity (ml/g)</th>
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<td>2.3</td>
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