

Chemical characteristics and stability of eucalyptus kraft pulps bleached with tertiary amine catalyzed hypochlorous acid

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Abstract We recently found that subsequent treatments of hardwood kraft pulps with a tertiary amine (DABCO; 1,4-diazabicyclo[2.2.2]octane) catalyzed hypochlorous acid (H_{cat}), ozone (Z) and hydrogen peroxide (P) may provide full brightness with low chemical dosages in a short overall reaction time. Here we report chemical characteristics and stability of H_{cat} -Z-P bleached eucalyptus kraft pulps. In comparison with a normal ECF (elementary chlorine free) bleached pulp the H_{cat} -Z-P bleached pulps had low carbonyl group content while the degree of polymerization of cellulose remained at high level. However, the brightness of the H_{cat} -Z-P bleached pulps was reversed more easily under humid ageing conditions in comparison with the ECF bleached pulp. The discoloration was accompanied by an increase in Raman emission at 1560 cm^{-1} which is indicative of formation of highly conjugated chromophores. The brightness reversion did not correlate with the carbonyl

content that is often considered to be the main origin of the brightness loss under humid conditions. In contrast, the brightness instability of the catalytically bleached pulps possibly resulted from the relatively high organochlorine content.

Keywords Catalytic bleaching · Carbonyl content · Organochlorine content · Degree of polymerization · Brightness reversion

Introduction

A main target of bleaching is to increase the brightness of the pulp. Although the brownish color of unbleached chemical pulps originates mainly from lignin, other chemical components may contribute to the stability of the color of the brightened pulps during transportation or storage through the combined effect of humidity and heat over longer periods of time (Cardona-Barrau et al. 2003). High contents of the uncolored xylan-bound hexenuronic acid (HexA), especially, can potentially lead to yellowing of bleached kraft pulps (Costa and Colodette 2007). Therefore, achieving a high brightness and brightness stability, characteristic for market pulps (Jullander and Brune 1957), translates into effective removal of the residual lignin and HexA from the pulp.

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Chemical pulp bleaching is a multistep process, which consists of sequential treatments with oxidants like chlorine dioxide (ClO_2), ozone (O_3) and hydrogen peroxide (H_2O_2), in combination with acids and alkali. It is a common practice to begin the bleaching with ClO_2 (D stage) which, oxidizes specifically phenolic lignin structures and forms simultaneously hypochlorous (HOCl) and chlorous acids (HClO_2) (Tarvo et al. 2010). HOCl is electrophilic in an acidic solution because of the equilibrated generation of chlorine molecule and cation that leads to oxidize both phenolic and non-phenolic lignin structures and HexA. Part of the reaction products are chlorinated. HOCl can also oxidize secondary and primary alcohol groups after oxidation of these groups to a carboxylic acid in cellulose and hemicelluloses into keto and aldehyde groups, respectively (Zhou et al. 2011). On the other hand, HClO_2 may convert the aldehydes further into carboxylic acid groups.

As a strong electrophile, O_3 oxidizes both lignin and HexA when applied in pulp bleaching (Z stage). The somewhat low selectivity of Z stage, resulting from the in situ formed reactive oxygen species, especially hydroxyl radical, has limited its wider industrial application. In Z stage, the typical side reactions include formation of carbonyl groups (aldehydes and ketones) and further oxidation product, a carboxylic acid, especially in an aqueous solution in hemicelluloses and cellulose and its subsequent depolymerization.

H_2O_2 is a nucleophile that is commonly applied for increasing the brightness of pulps especially in the end of bleaching sequences. H_2O_2 reacts specifically with unconjugated and conjugated aldehydes and ketones, such as hydroxyquinones formed in other bleaching sequences (Kuitunen et al. 2011). In peroxide bleaching (P stage) traces of transition metals may catalyze the decomposition of H_2O_2 and formation of hydroxyl radicals that may lead to oxidation and depolymerization of hemicelluloses and cellulose similar to Z stage. (Zeronian and Inglesby 1995).

The presence of carbonyl groups in cellulose leads ultimately to its partial depolymerization and deterioration of the strength (Beyer et al. 2006). In addition, the carbonyl groups in cellulose and hemicelluloses are often mainly responsible for the brightness reversion of fully bleached chemical pulps (Röhring et al. 2002; Sevastyanova et al. 2006; Jullander and Brune 1957; Lewis and Epstein 1962; Zhou et al. 2011;

Perrin et al. 2014). The structure and origin of the carbohydrate derived chromophores have been studied in details (Sevastyanova et al. 2006; Forsskahl et al. 2009; Theander and Nelson 1988; Potthast et al. 2005). Some chromophores may also form during the bleaching process and contribute to so-called brightness ceiling that makes it difficult to achieve the highest brightness (Knill and Kennedy 2003; Vikkula et al. 2006). However, the pulp chromophores, such as hydroxyquinones, are difficult to characterize due to their presence in trace amounts (Schedl et al. 2017).

Moving from the use elemental chlorine and hypochlorite as the main bleaching chemicals to chlorine dioxide based elemental chlorine free (ECF) bleaching technology has dramatically reduced the emission of toxic organochlorine substances (Juuti et al. 1996). However, ECF bleaching does not totally avoid the formation of organochlorine compounds because HOCl is always formed as an intermediate in the reactions of ClO_2 with lignin (Gunnarsson and Ljunggren 1996; Lehtimaa et al. 2010). The residual organochlorine in pulps (OX) is a concern in certain end uses, such as food packaging, of the pulp. In addition, OX may lower the brightness stability of bleached pulps (Owens et al. 1994). Regular ECF pulps have OX content of 100–200 ppm (g/odt) while so-called ECF-light pulps contain less than 30 ppm OX.

Recently, in searching ways to control the reactions of the in situ formed HOCl we found that certain tertiary amines (R_3N), such as 1,4-diazabicyclo[2.2.2]octane (DABCO), efficiently catalyzed its reactions with HexA and lignin over a wide range of pH (Chenna et al. 2013). The reactive species of the catalytic system is a chloroammonium cation ($\text{R}_3\text{N}^+\text{-Cl}$) that is a non-nucleophile (unlike HOCl) and a much stronger electrophile than HOCl (Chenna et al. 2016). Combining the initial catalytic treatment (H_{cat} stage) with subsequent treatments with ozone and alkaline peroxide led to very low residual lignin and HexA contents and high brightness (Afsahi et al. 2015). Surprisingly, the viscosity of the pulp remained at a high level proposing that cellulose remained almost unreacted during the whole bleaching sequence ($\text{H}_{\text{cat}}\text{-Z-P}$).

In this study, we wanted to confirm the observation on the selectivity studying the development of carbonyl group content, molar mass distribution and OX during the course of the sequence. Additionally,

the fully bleached pulps were analyzed for their brightness stability and characterized with time-gated Raman spectroscopy (Kostamovaara et al. 2013; Rojalín et al. 2016) to possibly get some understanding on the residual chromophore structures.

Experimental

Materials

Oxygen-delignified eucalyptus kraft pulp was obtained from a Brazilian pulp mill with kappa number 11.4, ISO brightness 57% and viscosity 1130 mL/g. The industrial ECF bleached eucalyptus kraft pulp used as a reference pulp had kappa number 1.8 and ISO brightness 89%. An aqueous solution of NaOCl (3.5%), KI solution and 0.2 M Na₂S₂O₃ (99.9%) were purchased from VWR International (Leuven, Belgium). DABCO (98%) and 2 M HCl were bought from Sigma-Aldrich Chemie GmbH (St. Munich, Germany) and Merck KGaA (Darmstadt, Germany), respectively.

Methods

Bleaching conditions

The oxygen-delignified eucalyptus kraft pulp was bleached in laboratory in three stages with DABCO catalyzed hypochlorous acid (H_{cat}), ozone (Z) and hydrogen peroxide (P) as described elsewhere (Afsahi et al. 2015). The catalytic oxidation of the pulp was performed at room temperature at 3% consistency in a stirred Büchiglasuster batch reactor (2 L) made of borosilicate glass. DABCO (0.1% on pulp) was added to the pulp suspension (1 L) at pH 7 followed by NaOCl (1% on pulp) and the reaction was continued for 10 min.

The washed pulp from H_{cat} stage was acidified to pH 3 and centrifuged to ca. 30% dry matter content. The pulp was moved into a rotating glass reactor at room temperature and gas was flowed into the reactor from an ozone generator to reach a target O₃ dosage of 0.3, 0.4 or 0.5%.

After washing the pulp bleached with 0.5% O₃ dosage, the final brightening stage was conducted with hydrogen peroxide at 10% consistency in plastic bags placed in a water bath (85 °C). MgSO₄·7H₂O (0.2%)

was added to stabilize H₂O₂ (0.3 or 0.6%) and sodium hydroxide was added to reach pH 11.2. The bags were kept in the water bath for 1 h before washing with deionized water.

The H_{cat}-Z(0.5%)-P(0.6%) bleached pulp had a kappa number of 0.9, ISO brightness of 88%, HexA content of 1 mmol/kg and viscosity of 1080 mL/g. UV resonance Raman spectroscopic (UVR) analysis (Jääskeläinen et al. 2009) confirmed that the pulp contained very little residual lignin and HexA. The characteristics of all the bleached pulps can be found elsewhere (Afsahi et al. 2015).

Carbonyl group content and molar mass distribution

The widely applied carbonyl-selective fluorescence labeling with carbazole-9-carboxylic acid [2-(2-aminoethoxy)ethoxy]amide (CCOA) was applied to measure the content of carbonyl groups in the pulps (Röhrling et al. 2002). The CCOA method quantifies the total amount of keto and aldehyde groups in their free and masked (hydrate, hemiacetal/hemiketal) forms in cellulose (Potthast et al. 2005). The pulps were suspended in zinc acetate buffer (pH 4) with CCOA and agitated at 40 °C for 7 days in order to complete the labeling. After labeling, the pulps were dissolved in DMAc/LiCl (9% w/v) and then diluted to 0.9% w/v DMAc/LiCl. The sample solutions were analyzed by gel permeation chromatography (GPC) equipped with multiple-angle laser light scattering (MALLS), fluorescence and RI detectors (Potthast et al. 2003, 2005).

Organically bound chlorine in pulp (OX)

OX was measured with Trace Elemental Instruments Xplorer analyzer with the help of an auto sampler. Pulp samples from bleaching trials were treated according to the ISO 9562 method for the evaluation of OX. The relative error in OX measurements was 2%.

Brightness reversion test

Pulp hand sheets were prepared according to ISO 3688. The ISO brightness was measured (ISO 2470:2002) at 457 nm with an Elrepho 2000 Datacolor Reflectometer (Datacolor Inc., Lawrenceville, NJ). The aging under humid conditions was carried out

according to ISO 5630-3 (80 °C, 65% R.H. for 48 h). The brightness reversion was calculated both as the drop in brightness (ΔR) and as the post color number (PCN) calculated according to the equation defined originally by Giertz and McPherson (Zhou et al. 2011).

Time-gated Raman spectroscopy

The time-resolved Raman measurements were carried out using a Raman spectrometer (Timegate Instruments, Oulu, Finland) consisting of a 532 nm Nd:YVO microchip pulsed laser (pulse width < 100 ps, repetition rate 40–50 kHz, average output power ~ 20–30 mW) and a time-gated complementary metal-oxide semiconductor (CMOS) single-photon avalanche diode (SPAD) 128 × 8 matrix detector. The spectral resolution was ~ 10 cm⁻¹. The photo-bleaching effects were relieved using a sample enclosure equipped with a rotating plate wherein the sample was placed on a metal wafer and rotated using constant speed during the laser interrogation. A BAC100 Raman probe was used to deliver the laser beam onto the samples (B&W Tek, Newark, DE, USA). An electronic delay generator was applied in order to switch the gate in 50-ps steps for collecting the time-resolved Raman spectra datasets (Rojalin et al. 2016).

Results and discussion

Wet chemical analyses of pulps

Carbonyl group content and molar mass distribution

The oxygen-delignified kraft pulp had a low carbonyl group content, which was only slightly increased in the DABCO catalyzed treatment with HOCl (Fig. 1). The subsequent ozonation more than doubled the amount of carbonyl groups depending on the ozone dosage. The final alkaline peroxide bleaching again lowered the carbonyl content to some extent to a level that was almost 50% less than the carbonyl content of industrial ECF bleached eucalyptus kraft pulp (Zhou et al. 2011). The increase in the carbonyl content during the ozonation and the decrease in the peroxide treatment are in consistence with the theory and published literature (Pouyet et al. 2014). In contrast, the negligible effect of the catalytic HOCl treatment on the

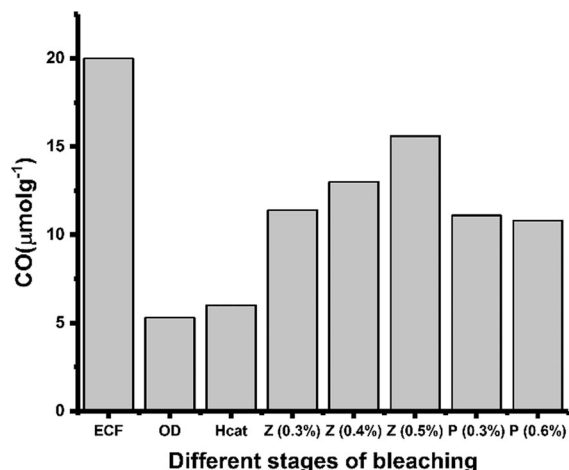


Fig. 1 Carbonyl group content of industrial ECF bleached pulp (ECF), industrial oxygen delignified pulp (OD), and the OD pulp bleached in laboratory subsequently with 0.1% DABCO and 1% active chlorine (H_{cat}), varying amounts (0.3–0.5%) ozone (Z) and hydrogen peroxide (0.3–0.6%) after the 0.5% ozone treatment (P)

carbonyl content is somewhat surprising and demonstrates the high selectivity of the chloroammonium cation towards electrophilic oxidation of HexA and lignin.

Visual observation of the molar mass distributions (MMD) of the pulps gave an impression that the catalytic treatment (H_{cat}) did not really depolymerize cellulose while the ozonation (Z) and peroxide treatment (P) led to some decrease in degree of polymerization (DP) of cellulose (Fig. 2). The molar mass of the H_{cat} -Z-P bleached pulp seemed to remain at similar or somewhat higher level in comparison with the industrial ECF bleached pulp.

The number and weight averaged molar mass values (M_n and M_w , respectively), together with the polydispersity indices ($D = M_w/M_n$) and molarity ($n = 1/M_n$) of the pulps are documented in Table 1. The molarity value refers to the amount of polysaccharide macromolecules in the pulps. The catalytic treatment of the OD pulp did not really affect its molarity, i.e. depolymerize it, within the experimental error of the method. On the contrary, the ozonation increased the molarity of the polysaccharides by ca. 6 mmol/kg in comparison with the ca. 10 mmol/kg increase in the carbonyl content. Thus, the formed carbonyl groups consisted partly of new reducing end groups formed through depolymerization of cellulose. Moreover, part of the carbonyl groups were formed

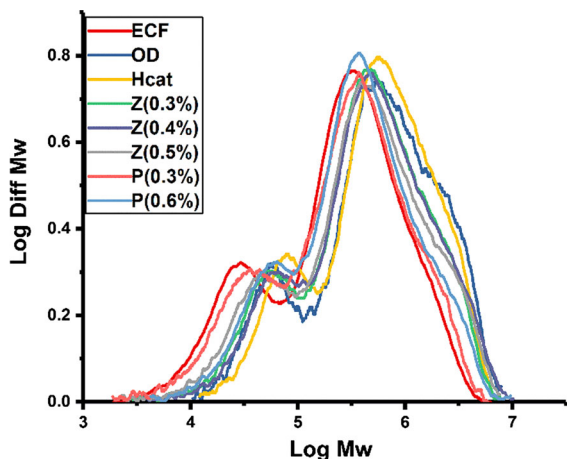


Fig. 2 Molar mass distributions of industrial ECF bleached pulp (ECF), industrial oxygen delignified pulp (OD), and the OD pulp bleached in laboratory subsequently with 0.1% DABCO and 1% active chlorine (H_{cat}), varying amounts (0.3–0.5%) ozone (Z) and hydrogen peroxide (0.3–0.6%) after the 0.5% ozone treatment (P)

without the polymer chain cleavage. The peroxide treatment again decreased the carbonyl content of the ozonated pulp by ca. 4 mmol/kg while the molarity of the polysaccharides remained unchanged. Thus, it looks like the peroxide treatment stabilized the ozonated pulp by oxidizing the labile carbonyl groups without depolymerizing cellulose. Without this stabilization the alkaline conditions applied should have resulted in chain cleavage at the sites of the carbonyl groups in non-terminal anhydrosugar units.

Table 1 Parameters calculated from molar mass distributions of industrial ECF bleached pulp (ECF), industrial oxygen delignified pulp (OD), and the OD pulp bleached in laboratory

Sample	M_w (kg/mol)	M_n (kg/mol)	D	n (mmol/kg)
ECF	485	68	7.2	14.7
OD	1052	185	5.7	5.4
H_{cat}	957	208	4.6	4.8
$H_{cat}Z$ (0.3%)	823	128	6.4	7.8
$H_{cat}Z$ (0.4%)	923	148	6.3	6.8
$H_{cat}Z$ (0.5%)	823	106	7.7	9.4
$H_{cat}Z$ (0.5%)P (0.3%)	612	89	6.9	11.2
$H_{cat}Z$ (0.5%)P (0.6%)	693	122	5.7	8.2

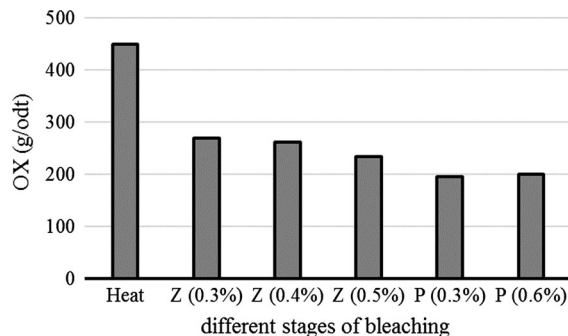


Fig. 3 OX levels of industrial oxygen delignified pulp bleached in laboratory subsequently with 0.1% DABCO and 1% active chlorine (H_{cat}), varying amounts (0.3–0.5%) ozone (Z) and hydrogen peroxide (0.3–0.6%) after the 0.5% ozone treatment (P)

Organically bound chlorine (OX)

The H_{cat} treatment introduced a significant amount of organically bound chlorine (OX) on the pulp (Fig. 3). The subsequent treatments with ozone and peroxide lowered the OX content to a level that corresponds to the upper OX limit of industrial ECF pulps. The OX content of H_{cat} –Z–P bleached pulp is high (ca. 200 mg/kg) in comparison with its low residual lignin content (Afsahi et al. 2015).

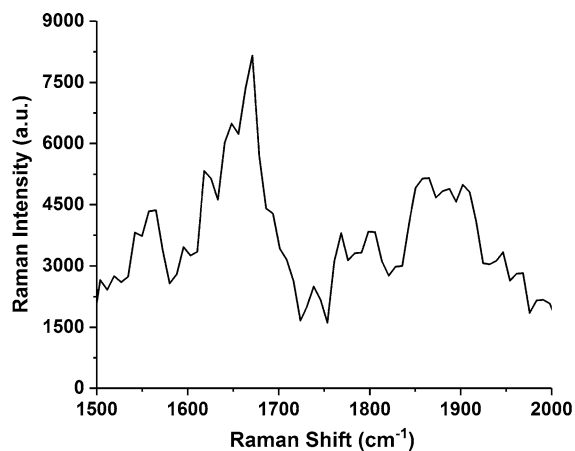
Brightness reversion

In this study, the humid aging method was applied because it simulates well the possible changes in warm and humid pulp bales during their storage and transportation. The brightness stability under the

subsequently with 0.1% DABCO and 1% active chlorine (H_{cat}), varying amounts (0.3–0.5%) ozone (Z) and hydrogen peroxide (0.3–0.6%) after the 0.5% ozone treatment (P)

Table 2 Brightness development of industrial ECF bleach pulp and laboratory bleached H_{cat}-Z-P pulps in humid conditions

Stage	ISO brightness (R) (%)		ΔR (%)	PC number
	Before aging	After aging		
ECF bleached pulp	89.2	86.2	3.0	0.44
H _{cat} /Z0.5%/P0.3%	86.1	80.0	6.1	1.23
H _{cat} /Z0.5%/P0.6%	88.1	80.5	7.6	1.56

**Fig. 4** Raman spectra of H_{cat}-Z-P bleached pulps representing the spectral changes before and after the ageing of the pulp under humid conditions

humid conditions typically shows correlation with chemical pulp characteristics such as contents of carbonyl groups, HexA and lignin (Zhou et al. 2011). Here, it was unexpectedly found that the H_{cat}-Z-P bleached pulps had stronger discoloration tendency in spite of their lower carbonyl group, HexA and lignin contents relative to the ECF pulp (Table 2). The observation could possibly be explained by the high OX level of the H_{cat}-Z-P bleached pulps as OX has been found to correlate with the yellowing tendency of cellulosic pulps (Owens et al. 1994).

We applied earlier time-resolved Kerr gate Raman spectroscopy for analyzing the chromophores in bleached thermomechanical pulps (Jääskeläinen et al. 2009). Here we used another type of time-resolved Raman spectroscopy for monitoring changes in the Raman spectra of the H_{cat}-Z-P bleached pulps during their aging (Rojalin et al. 2015). The difference spectra, representing changes caused by the aging, had a specific band at 1570 cm⁻¹ that is typical of highly conjugated unsaturated organic structures (Fig. 4).

Conclusions

The H_{cat}-Z-P bleaching removes the residual lignin and HexA from hardwood kraft pulps very selectively. In the catalytic stage cellulose remains almost unattacked while the subsequent ozone stage lowers moderately DP of cellulose and introduces some carbonyl groups in the pulp. The peroxide treatment reacts partly with the carbonyl groups without decreasing further DP of cellulose. In spite of their low lignin, HexA and carbonyl group contents, the H_{cat}-Z-P bleached pulps undergo thermal yellowing during the artificial aging test. The discoloration is accompanied by formation of highly conjugated unsaturated organic structures. The relatively high OX level of the H_{cat}-Z-P bleached pulps could possibly explain their aging tendency. However, further research is required to reveal the real origin of the phenomenon.

The possibility to reach full brightness with low chemical dosage and short bleaching time without degrading cellulose makes the H_{cat}-Z-P sequence attractive for bleaching of hardwood kraft pulps although means to control the OX level must be studied and developed.

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