



Formation of carbonyl groups on cellulose during ozone treatment of pulp: Consequences for pulp bleaching



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ABSTRACT

The formation of carbonyl groups during the ozone treatment (Z) of eucalyptus (*Eucalyptus grandis* and *Eucalyptus urophylla* hybrid) kraft pulps and their behaviors during subsequent alkaline stages were investigated by the CCOA method with carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)-ethoxy] amide (CCOA) as the carbonyl-selective fluorescence label. Several pulp samples with or without lignin and hexenuronic acids (hexA) were used to elucidate the effects of these components when present in unbleached kraft pulp. Both hexA and lignin increased the formation of carbonyl groups on cellulose and hemicellulose during ozonation. It was concluded that radicals are likely formed when ozone reacts with either lignin or hexA. These carbonyl groups were involved in cellulose depolymerization during subsequent alkaline extraction stages with sodium hydroxide (E) and alkaline hydrogen peroxide (P, in ZEP or ZP). Their numbers decreased after E but increased during P when H₂O₂ was not stabilized enough. Several ways to minimize the occurrence of carbonyl group formation are suggested.

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1. Introduction

Around 130 million tons of cellulose are extracted from wood every year to make paper and other cellulosic products. The main extraction process is the kraft process, as it produces 95% of the cellulose. During this process, carried out under alkaline conditions and at high temperature (160 °C), lignin is cleaved into phenolic fragments and is subsequently solubilized. However, after the kraft process, the cellulose still contains some residual lignin, which has a brown color due to new chromophores formed during the process. Some residual hemicelluloses, xylans and glucomannans, are also present. The alkaline conditions of the kraft process induce the formation of hexenuronic acid groups (hexA) at xylans (Teleman et al., 1995). The hexA groups enhance pulp yellowing (Buchert, Bergnor, Lindblad, Viikari, & Ek, 1997; Rosenau et al., 2012). They were also shown to play an important role in brightness development of chemical pulps during bleaching (Shatalov & Pereira, 2009).

For many applications, pulp has to be bleached. Bleaching is generally performed by chlorine dioxide after some complementary delignification with oxygen in an elemental chlorine-free (ECF) process. Chlorine dioxide selectively oxidizes the residual lignin, which eventually renders it soluble. However, some chlorinated phenolics are formed. Bleaching without chlorine dioxide is possible, using oxygen (O), ozone (Z), and peroxide (P) applied sequentially in a totally chlorine-free (TCF) process. In fact, ozone can be used as a substitute for chlorine dioxide and is applied either to minimize the charge of chlorine dioxide in ECF sequences or to get rid of all chlorinated chemicals in a totally chlorine-free bleaching process. Today more than 20 bleaching lines including an ozone stage are operating worldwide (Métais, Germer, & Hostachy, 2011).

In spite of potential environmental and economic benefits, the application of ozone leads to drawbacks, the most critical being the degradation of cellulose below a DP, which affects the mechanical properties of the final product (Kang, Zhang, Ni, & Van Heiningen, 1995; Ragnar, Eriksson, & Reitberger, 1999; Rautonen, Rantanen, Toikkanen, & Malinen, 1996). Although it is well documented that pulp ozonation generates radicals, which degrade cellulose (Gierer & Zhang, 1993; Magara, Ikeda, Tomimura, & Hosoya, 1996; Ragnar, Dahllöf, & Lundgren, 2005), it is admitted that another cause of cellulose depolymerization is the generation of carbonyl groups during the Z stage, which are responsible for cellulose chain cleavage (β -elimination) in subsequent alkaline stages, such as in the

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alkaline extraction (E stages) or the peroxide (P) stages and their combinations (Fuhrmann, Li, & Rautonen, 1996). Those groups might also induce some yellowing (Chirat & De la Chapelle, 1999; Sjöström & Eriksson, 1968). Finally, it has to be noted that the DP determination by viscosity measurements does not reflect the real DP since under the alkaline conditions prevailing during the procedure oxidized cellulose may undergo β -elimination.

It is known that, under the conditions of ozone bleaching, carbonyl groups are created on pulp carbohydrates (Chandra & Gratzl, 1985; Godsay & Pearce, 1984). Whether these groups are formed by a direct reaction of ozone on the carbohydrates or by radicals formed during the ozone treatment has been a matter of discussion (Chirat & Lachenal, 1997). The formation of hydroxyl radicals may have several causes. One cause could be the decomposition of ozone in water, which is known to generate radicals. However this reaction, which increases with the pH, would be slow at the pH applied in pulp ozonation (2.5) (Hoigné & Bader, 1976). One other cause of hydroxyl radical generation was found. It has been demonstrated that hydroxyl radicals are produced when ozone reacts with lignin (Ragnar et al., 1999). Although these radicals are certainly the main cause of cellulose depolymerization, their contribution to the formation of carbonyl groups is unclear. According to Gierer (1997), OH radicals form carbonyl groups on carbohydrates at C2 and C3 positions, explaining the oxidative cleavage under alkaline conditions. More recently this finding was challenged based on computational methods showing that carbonyl formation at C2, C3 and C6 positions is energetically unfavorable under alkaline conditions (Guay et al., 2001). However under ozonation conditions (i.e., at acidic pH), Kishimoto and Nakatsubo (1998) claimed that the oxidation of hydroxyl groups at C2, C3 and C6 positions into carbonyls was mainly caused by radical species. Finally, it has also been shown that carbonyl groups could be introduced on industrial fully bleached pulps during an ozone treatment while there is no lignin, most probably by a direct reaction of ozone on the carbohydrates (Chirat & De la Chapelle, 1999).

Since carbohydrate polymers possessing carbonyl groups may undergo β -elimination under the alkaline conditions prevailing in the extraction stages that usually follow ozone bleaching treatments, knowing whether these carbonyls are located on celluloses or hemicelluloses is of prime importance, since only cellulose depolymerization is supposed to affect the strength of the fibers. It has been observed that a substantial loss in the average depolymerization degree (DP_v) of the pulp takes place during the subsequent extraction stages with caustic soda, either with only alkali (E) or reinforced with hydrogen peroxide (P) (Roncero, Colom, & Vidal, 2003). This proves that some carbonyls are located along the cellulose chains, but does not say anything about their relative number on the cellulose part. This aspect has never been investigated, likely because of the lack of an appropriate experimental procedure.

Finally, lignin is not the only impurity prone to reacting with ozone during a Z stage. The carbon-carbon double bonds of the hexA groups are very readily oxidized by ozone (Ventorim, Colodette, de Fatima Gomes, & da Silva, 2008). The impact of their presence on the formation of carbonyl groups on cellulose is not known. This point is particularly relevant in the case of hardwood kraft pulps, which usually contain high levels of hexA groups. Moreover, carbonyl groups not only make carbohydrates sensitive to alkaline conditions (Lewin, 1997), but also promote their yellowing (Chirat & De la Chapelle, 1999).

The aim of this work was to investigate the formation and the location of the carbonyl groups on pulp carbohydrates during an ozone bleaching stage applied to a eucalyptus kraft pulp, and to follow them during subsequent alkaline stages. At the same time, the effects of these treatments on the molecular weight distribution of the pulp carbohydrates were studied. The distribution of carbonyl groups was determined according to the CCOA

(carbazole-9-carbonyl-oxy-amine) fluorescence labeling method, as described in the literature (Röhring, Potthast, Rosenau, Lange, Borgards, et al., 2002; Röhring, Potthast, Rosenau, Lange, Ebner, et al., 2002), followed by size exclusion chromatography (SEC). Finally, the relevance of these results for TCF bleaching is discussed.

2. Materials and methods

2.1. Pulps

Oxygen-delignified and fully bleached eucalyptus (hybrids between *Eucalyptus grandis* and *Eucalyptus urophylla*) kraft pulps referred to as kraft+O and fully bleached, respectively, were provided by a Brazilian pulp mill. Two other pulps were prepared from the oxygen-delignified pulp (kraft+O) by applying a chlorite treatment (Wise, Murphy, & D'Addieco, 1946), or a long acid stage (Long A) treatment followed by a chlorite treatment, respectively referred to as lignin-free pulp, and hexA- and lignin-free pulp in this paper. These pulps have been characterized by the following measurements:

Kraft+O: Kappa number 9.3; DPv 1630; HexA content 71.7 $\mu\text{equiv./g}$; hemicelluloses 23%; pentosanes 20%. Fully bleached: Kappa number ≤ 1 ; DPv 1110; hexA content $\leq 7 \mu\text{equiv./g}$; hemicelluloses 22%; pentosanes 18%. Lignin-free: Kappa number 5.0; DPv 1630; hexA content 48.2 $\mu\text{equiv./g}$; hemicelluloses 20%; pentosanes 17%. Lignin- and hexA-free: Kappa number ≤ 1 ; DPv 1420, hexA $\leq 7 \mu\text{equiv./g}$; hemicelluloses 19%; pentosanes 17%. The hemicelluloses values were obtained by integration of the GPC curves given below in the figures. The values also contain the small cellulose chains. The pentosane contents (Tappi T 223 cm-01 standard) include most of the hemicelluloses in the pulp (xylans). The hemicellulose and pentosane contents of the kraft+O pulp, which is the only one containing lignin, are given based on the total content in carbohydrates. The kappa number determination followed the ISO 302-1981 standard. The metal content of the kraft+O and Fully bleached pulps were measured by X ray fluorescence.

2.2. Pulp bleaching: operating conditions and pulp characterization

Various stages were carried out on the pulps, such as E stages (70 °C, 2 h, 2% NaOH), P stages (70 °C, 2 h, 2% NaOH & 2% H₂O₂) and P_{Mg} stages (70 °C, 2 h, 2% NaOH & 2% H₂O₂, 0.5% MgSO₄·7H₂O), Na₂S stages (70 °C, 2 h, 2% Na₂S), B stages (20 °C, 30 min, 1% NaBH₄), A stages (90 °C, 3 h, pH adjusted at 3 with H₂SO₄) and Long A stages (same conditions, 7 h). Those stages were carried out at a consistency of 10%. The reagents are given in weight on pulp (oven-dried basis).

The ozone stages (Z_X stages, with X% of ozone) were performed at 25 °C. Prior to the ozone treatment, the pulp was acidified to a pH of 2.5 with sulfuric acid, centrifuged to reach a consistency of 40%, and fluffed. Ozonation was then performed in a rotating spherical reactor. The quantity of ozone is expressed as a percentage of ozone charge on an oven-dried pulp basis. For the other stages, the temperature was controlled using a thermostated bath, with the reactions taking place in polyethylene bags. The following procedures were used for pulp characterization: Kappa number (ISO 302-1981), viscosity (ISO 5351/1-1981) given here in terms of DP_v (Sihtola, Kyrklund, Laamanen, & Palenius, 1963), and brightness (ISO 3688-1977). Hexenuronic acid content was measured according to the procedure described by Chai, Zhu, and Li (2001).

The main chemicals used in the study are: NaOH (Roth, 99% minimum purity), H₂O₂ solution (Roth, at a concentration of 35%),

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