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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-aminooxethoxy)-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 H_2O_2 was not stabilized enough. Several ways to minimize the occurrence of carbonyl group formation are suggested.

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 (Röhrling, Potthast, Rosenau, Lange, Borgards, et al., 2002; Röhrling, 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 μequiv./g; hemicelluloses 23%; pentosanes 20%. Fully bleached: Kappa number ≤1; DPv 1110; hexA content ≤7 μequiv./g; hemicelluloses 22%; pentosanes 18%. Lignin-free: Kappa number 5.0; DPv 1630; hexA content 48.2 μequiv./g; hemicelluloses 20%; pentosanes 17%. Lignin- and hexA-free: Kappa number ≤1; DPv 1420, hexA ≤7 μequiv./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% H_2O_2) and P_{Mg} stages (70 °C, 2 h, 2% NaOH & 2% H_2O_2, 0.5% $MgSO_4{\cdot}7H_2O$), Na_2S stages (70 °C, 2 h, 2% Na_2S), B stages (20 °C, 30 min, 1% $NaBH_4$), A stages (90 °C, 3 h, pH adjusted at 3 with H_2SO_4) and Long A stages (same conditions, 7 h). Those stages where 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), H_2O_2 solution (Roth, at a concentration of 35%),

$MgSO_4$ (Janssen Chimica, 99.5% minimum purity), 2 M H_2SO_4 solution (prepared from commercial Carlo Erba product, 96% minimum purity), Na_2S (Roth, 60% purity), $NaBH_4$ (Fisher Scientific). Ozone was produced in a laboratory ozone generator (LN 103, Ozonia) from pure oxygen at a concentration of 50–60 mg/L.

2.3. Carbonyl group determination

Both the formation of carbonyl groups and the distribution of cellulose molecular weight were assessed by the CCOA method, with carbazole-9-carboxylic acid [2-(2-aminooxethoxy)-ethoxy] amide (CCOA) as the carbonyl-selective fluorescence label (Röhrling, Potthast, Rosenau, Lange, Borgards, et al., 2002; Röhrling, Potthast, Rosenau, Lange, Ebner, et al., 2002). A 25-mg pulp sample was used in each experiment. After labeling of the samples, dissolution in *N,N*-dimethylacetamide/lithium chloride 9% (w/v) (DMAc/LiCl) was achieved via solvent exchange at room temperature. Measurements were performed by gel permeation chromatography (GPC). The GPC system consists of a fluorescence detector (TSP FL2000) for monitoring the CCOA label, a multiple-angle laser light-scattering detector (MALLS) [Wyatt Dawn DSP with argon ion laser (λ_0 = 488 nm)], and a refractive index detector (Shodex RI-71). Four GPC columns (Variant/Agilent™, PL gel mixed-ALS, 20 μm, 7.5 mm × 300 mm) were used as the stationary phase. A degasser (Dionex DG-2410), autosampler (HP 1100), pulse damper, pump (Kontron pump 420), and column oven (Gynkotek STH 585) were also part of the system. The operating conditions of the GPC were 1.00 mL/min flow rate, 100 μL injection volume, 45 min run time, λ_{ex} = 290 nm, and λ_{em} = 340 nm. DMAc/LiCl (0.9%, w/v), filtered through a 0.02-μm filter, was used as the eluant.

The system yields a molecular weight distribution, in addition to the amount and profile of carbonyl groups relative to the molecular weight. The carbonyl value is obtained through calibration with a set of pulp standards calibrated against pure CCOA. Data evaluation was performed with the standard Chromeleon 4, Astra 4.73, and GRAMS/32 software packages. The protocol allows a good approximation of the carbonyl content of the cellulose and hemicellulose fractions, as it is possible to attribute the carbonyl groups to specific molecular-weight regions. The typical molecular distribution curve shows a small peak corresponding to the low molecular fraction of the pulp carbohydrates. This fraction essentially contains the hemicelluloses. Some low molecular cellulose chains may be also present. Profiles of this functional group can be generated, giving figures with both carbonyl group content (μmol/g) and differential weight fractions plotted as functions of the molecular weight. The amount of carbonyls ("Carbonyl groups", "Carbonyls on hemicelluloses", "Carbonyls on cellulose") is always given per gram of pulp. The accuracy of the CO values is estimated to be ±1 μmol/g.

3. Generation of carbonyl groups with ozone on various pulps

The effect of ozone on a kraft pulp is globally known. The main reaction is the oxidative opening of the aromatic rings in lignin which increases its hydrophilicity and leads to its dissolution in water (Gierer, 1997). However, the pH being acidic (2.5), some of the oxidized lignin fragments are not readily soluble. This explains why an alkaline extraction stage usually follows the ozone stage. Some hydrogen peroxide may be added in the extraction stage to complement the oxidation of the lignin and increase the delignification rate. During the whole process cellulose is partly depolymerized and oxidized. Carbonyl and carboxyl groups are formed (Godsay & Pearce, 1984). These reactions may be caused by molecular ozone. However ozone is far more reactive with lignin than with carbohydrates (hemicelluloses and cellulose).

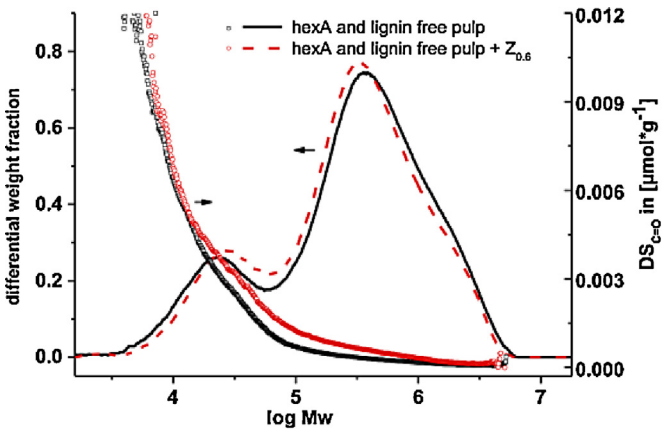

Fig. 1. Carbonyl group profile (DS_{CO}) and molecular weight distribution plots obtained for a hexA- and lignin-free pulp before and after ozone treatment (0.6%).

Consequently, it is generally admitted that cellulose oxidation and depolymerization is due to radicals generated during the ozone treatment. More precisely, the oxidizing species would be the OH radicals formed when ozone reacts with the phenolic rings in lignin (Kang et al., 1995; Ragnar et al., 1999). Kraft pulps also contain hexenuronic acid groups (hexA) (Teleman et al., 1995). These groups are located on the xylans. Since they possess an aliphatic carbon–carbon double bond, their reactivity with ozone is high. It has been shown that the oxidation and elimination of the hexA groups takes place very early during the ozone stage (Pouyet, Das, Lachenal, & Chirat, 2013).

During the ozone treatment of pulp the carbonyl groups created on the carbohydrates may be located on the xylans (by oxidation of the hexA), or at other places on the hemicelluloses, and on cellulose. The distribution of the carbonyls between hemicelluloses and cellulose has never been investigated. Only their total number has been measured (Chandra & Gratzl, 1985; Chirat & De la Chapelle, 1999; Godsay & Pearce, 1984). Knowing the extent of carbonyl formation on cellulose is of high interest since only these particular carbonyls may induce a severe depolymerization of the carbohydrates under alkaline conditions.

Finally, while the degradation of pulp carbohydrates during ozonation is known to be increased by the presence of lignin, as mentioned above, nothing is known about the effect of lignin and hexA on the formation of carbonyl groups on cellulose.

3.1. Effect of ozone on lignin- and hexA-free pulp

The results given in Fig. 1 and Table 1 were obtained with a hexA- and lignin-free raw material, containing only cellulose and hemicelluloses. This new material was obtained according to the method described above (long A stage followed by chlorite treatment) and analyzed as such, and after two ozone treatments with 0.3% or 0.6%, respectively, of ozone on pulp. Fig. 1 shows the type of curves obtained by the CCOA method coupled with GPC, and gives both the carbonyl content and the molecular weight distribution of the sample. The starting sample yields a typical distribution of carbonyl groups relative to molecular weight. The number of carbonyls increases with decreasing chain lengths due to the increasing influence of the reducing aldehyde groups, which are a significant part of the total number of carbonyl groups. Upon ozonation, the carbonyl content value does not change much for those samples. Only a slight increase of the total amount is observed. This slight increase in carbonyl groups after the ozone treatment is visible in the whole range of the MWD (cf. Fig. 1). The calculated values and the average M_w are given in Table 1.

Table 1
Carbonyl content (μmol/g) and average molecular weight of hexA- and lignin-free pulps before and after ozone treatment.

Pulp sample	Carbonyl groups [μmol/g]	Carbonyls on hemicelluloses [μmol/g]	Carbonyls on cellulose [μmol/g]	M_w [kg/mol]
HexA- and lignin-free	7.2	5.5	1.6	624
HexA- and lignin-free + $Z_{0.3}$	7.5	4.9	2.6	604
HexA- and lignin-free + $Z_{0.6}$	8.8	5.7	3.1	548

Table 2
Carbonyl content [μmol/g], DP_v, and hexA [μequiv./g] content of a lignin-free pulp before and after ozone treatment.

Pulp sample	Carbonyl groups [μmol/g]	Carbonyls on hemicelluloses [μmol/g]	Carbonyls on cellulose [μmol/g]	DP_v	M_w	HexA content [μequiv./g]
Lignin-free	4.6	<5	<5	1630	750	48
Lignin-free + $Z_{0.3}$	22.4	14.4	8.0	1240	620	<5
Lignin-free + $Z_{0.6}$	18.3	11.4	6.9	1145	570	<5

The measured increase is proportionally more significant on cellulose, considering the low starting level. The substantial depolymerization induced by the reaction of ozone on carbohydrates (visible at 0.6% ozone) cannot be held responsible for the slight increase of the carbonyl values on the cellulose chains. As a matter of fact, this depolymerization is not supposed to form new reducing ends that could have been labeled, but rather lactone-like structures from oxidized aldehydes groups (Pan, Chen, Gratzl, & Chang, 1995). One could then conclude that, even when 100% of the ozone is available for reaction with the polysaccharides (no other oxidizable components), few carbonyl groups are formed. As a consequence, the direct reaction of ozone with cellulose is unlikely to be the main reason for the oxidation (and subsequent degradation) of regular pulps during ozone-containing sequences at the ozone charges applied in this study.

3.2. Effect of ozone on a lignin-free pulp still containing hexA

During the ozone treatment of an unbleached hardwood kraft pulp, the hexA groups must readily react since, like lignin, they possess carbon–carbon double bonds. Removing the lignin by a chlorite treatment provides a bleached pulp that still contains a significant amount of hexA. It is then possible to isolate the effect of the hexA during the ozone treatment of carbohydrates.

The results obtained with the lignin-free pulp, still containing hexA, before and after ozone treatment (0.3% and 0.6% of ozone charge, cf. Table 2) clearly show a very substantial creation of carbonyl groups on the carbohydrates at the lower ozone charge. Most are formed on the hemicelluloses, which would be in line with the easy ozonolysis of the carbon–carbon double bonds of the hexA groups. The decrease in carbonyl groups (between 0.3% and 0.6% of ozone, Table 2) that is not seen in the case of the hexA- and lignin-free pulp could be explained by an oxidation of those groups to carboxyl functions by ozone (Vuorinen, Fagerström, Räsänen, & Vikkula, 1997; see Fig. 2).

In this experiment, the amount of hexA decreased from 48 μequiv./g to almost 0 μequiv./g, with only 0.3% ozone applied. Considering that 1 mol of ozone reacts with 1 mol of hexA, the amount of ozone that effectively reacted with the hexA only leaves a small amount of ozone left to react with other compounds (around 25%). However, the carbonyl group content of the cellulosic part also increased considerably after 0.3% ozone was applied. As there is no such increase of the carbonyl content of the cellulose part in a pulp containing only polysaccharides, the only plausible explanation is that the presence of hexA or its degradation products during an ozonation step induces the generation of carbonyls on the cellulose. In order for such a reaction to happen, an involvement of radical species is likely. The slight decrease observed after 0.6% ozone being applied may be attributed to some solubilization due to the severe depolymerization of the carbohydrates (measured by the average viscometric degree of polymerization, DP_v), or also to the oxidation of carbonyls to carboxyls, which may happen at the C1 position or C6 position (Lemeune, Jameel, Chang, & Kadla, 2004).

3.3. Effect of ozone on a regular oxygen-delignified kraft pulp

The results given in Fig. 3 and Table 3 were obtained from a kraft oxygen pulp (kraft + O) containing cellulose, hemicelluloses (including hexA), and lignin, treated with an increasing ozone charge of 0.6%, 1%, and 2%.

By looking at the values in Table 3, one can see that the global amount of carbonyl groups increases with ozone charge. The distribution of the carbonyl groups shows an increase of the carbonyl content in both hemicelluloses and cellulose.

The increase seen in the hemicellulose part can be explained once more by the oxidation of the double bonds in the hexA, and maybe also by the presence of carbonyl-containing shorter polysaccharide chains generated by the degradation of longer chains, as suggested by the severe decrease of M_w. The decrease of the generated carbonyls is not seen here even at a very high ozone charge. It could be that a substantial part of the ozone is actually consumed by lignin and lignin degradation products (Godsay & Pearce, 1984), and is not available for further carbonyl oxidation.

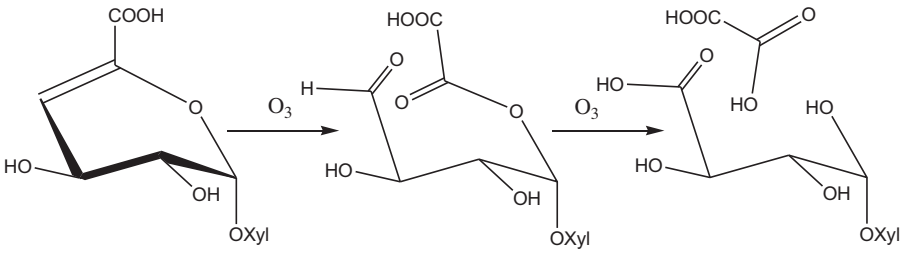

Fig. 2. Formation of carbonyl and carboxyl groups on hexA during ozone treatment.

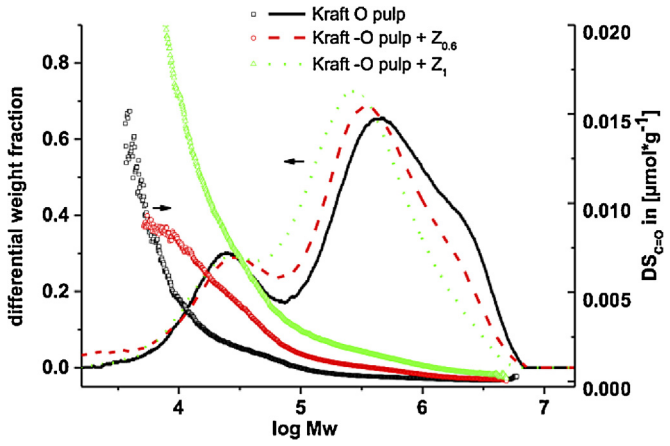

Fig. 3. Carbonyl degree of substitution (DS_{CO}) and molecular weight distribution plots obtained for a kraft + O pulp before and after ozone treatment (0.6% and 1%).

Table 4
Evolution of carbonyl groups during alkaline extraction carried out after Z.

Pulp sample	Carbonyl groups [µmol/g]	Carbonyls on hemicelluloses [µmol/g]	Carbonyls on cellulose [µmol/g]
Kraft + O + $Z_{0.6}$	11.5	7.8	3.7
Kraft + O + $Z_{0.6}$E	8.2	6.3	1.9
Kraft + O + $Z_{0.6}$EP	11.1	n/a[a]	n/a[a]
Fully-bleached pulp + $Z_{0.6}$	14.5	9.5	5.0
Fully-bleached pulp + $Z_{0.6}$E	12.2	8.8	3.4
Fully-bleached pulp + $Z_{0.6}Na_2S$	10.2	6.5	3.7
Fully bleached + $Z_{0.6}$EP	10	n/a[a]	n/a[a]
Kraft + O + $Z_{0.6}$P	11.7	n/a[a]	n/a[a]
Kraft + O + $Z_{0.6}P_{Mg}$	10.5	n/a[a]	n/a[a]
Fully bleached + $Z_{0.6}$P	10.7	n/a[a]	n/a[a]
Fully bleached + $Z_{0.6}P_{Mg}$	9.3	n/a[a]	n/a[a]

[a] No values were given when P stages are involved, due to the degradation of the pulps leading to uncertainties in the determination of the contributions of hemicelluloses and cellulose.

The results also show an increase of the carbonyl content of the cellulose. The ozone reactivity with carbohydrates is lower than with the lignin and hexA (Godsay & Pearce, 1984; Pouyet et al., 2013). As a consequence, considering the presence of lignin and hexA, the amount of ozone left to react with the cellulose must be very low. Then, in principle, the direct action of ozone on cellulose should not create significant amounts of carbonyl groups. The formation of carbonyl groups cannot be explained by the depolymerization, either, since no new cellulose-reducing ends are supposed to be formed by oxidative chain cleavage (Pan et al., 1995). Again, the only explanation left is that radicals generated by the reaction of ozone with the other pulp components (lignin and hexA) oxidize the cellulose and form carbonyl groups, as described in the literature with model compounds (Kishimoto & Nakatsubo, 1998).

4. E and P stages effects related to carbonyl groups

4.1. E stage

Extraction stages (E) are generally implemented after oxidative stages in bleaching sequences. The purpose is to solubilize the lignin that has been oxidized during the previous stage. When E is applied after a Z stage, some degradation is observed. This degradation was observed with DP_v measured after Z and ZE. A reducing stage with sodium borohydride was performed before DP_v measurement to get rid of the influence of the carbonyl groups on the DP_v measurement (Fuhrmann et al., 1996). The results gave a DP_v of 1260 for $Z_{0.6}$, 1203 for $Z_{0.6}$E, 1335 for $Z_{0.6}$B, and a DP_v of 1250 for $Z_{0.6}$EB.

It is well accepted that this degradation is caused by the lability of the hydrogen located at the α position of the carbonyl group, followed by a subsequent β-elimination reaction (Sjöström, 1977; Lewin, 1997). According to the mechanism, if the carbonyl groups are mainly located at C6, a global increase of the carbonyl content should be seen. However, if the carbonyl groups are mainly located at C2 or C3, the content in carbonyl groups should not increase. In those cases, the primary carbonyl group (at the origin of chain cleavage) is now part of a dicarbonyl structure, which may rearrange in an alkaline medium to give a carboxylic compound (benzilic acid-type rearrangement), as seen in the peeling-stopping mechanism (Sjöström, 1977). This rearrangement easily explains why the global quantity of carbonyl groups can remain stable or even decrease, depending on the position of the primary carbonyl groups. Table 4 gives the evolution of the carbonyl content in pulp for the oxygen-delignified kraft pulp and the fully bleached pulp.

For both pulps (kraft + O and fully bleached), there is a decrease of the carbonyl content in both the hemicellulose and cellulose parts during the E stage following the $Z_{0.6}$ stage. The decrease in the hemicellulose part can be explained by the dissolution of some hemicelluloses containing carbonyls in the alkaline medium, in spite of a possible contribution from degraded longer chains. This explanation is in line with the higher solubilization of hemicelluloses during an alkaline stage in the case of high carbonyl content (Fuhrmann et al., 1996).

The decrease observed in the case of the cellulose fraction indicates that chain cleavage occurred, and that the carbonyl structures are decomposed and possibly rearranged in carboxyl groups. In the experiment with Na_2S, NaOH was entirely replaced by the same quantity of Na_2S (by weight), which means that the quantity of NaOH produced by the hydrolysis of Na_2S was actually half of that produced in E ($Na_2S + H_2O \rightarrow NaSH + NaOH$). Despite that, the removal of the carbonyl groups was greater in the hemicellulose fraction than during an E stage. The difference has to be linked to the higher nucleophilic power of the hydrogen sulfide anions. One hypothesis might be the addition of the hydrogen sulfide anion on the aldehyde groups of the hemicelluloses, as already described by Sjöström (1993).

Table 3
Carbonyl content [µmol/g] and weight average molecular weight [kg/mol] of a kraft + O pulp before and after ozone treatment.

Pulp sample	Carbonyl groups [µmol/g]	Carbonyls on hemicelluloses [µmol/g]	Carbonyls on cellulose [µmol/g]	M_w [kg/mol]
Kraft + O	5.4	4.1	1.3	751
Kraft + O + $Z_{0.6}$	11.5	7.8	3.7	569
Kraft + O + Z_1	24.4	14.4	10.0	460
Kraft + O + Z_2	35.4	18.4	17.1	454

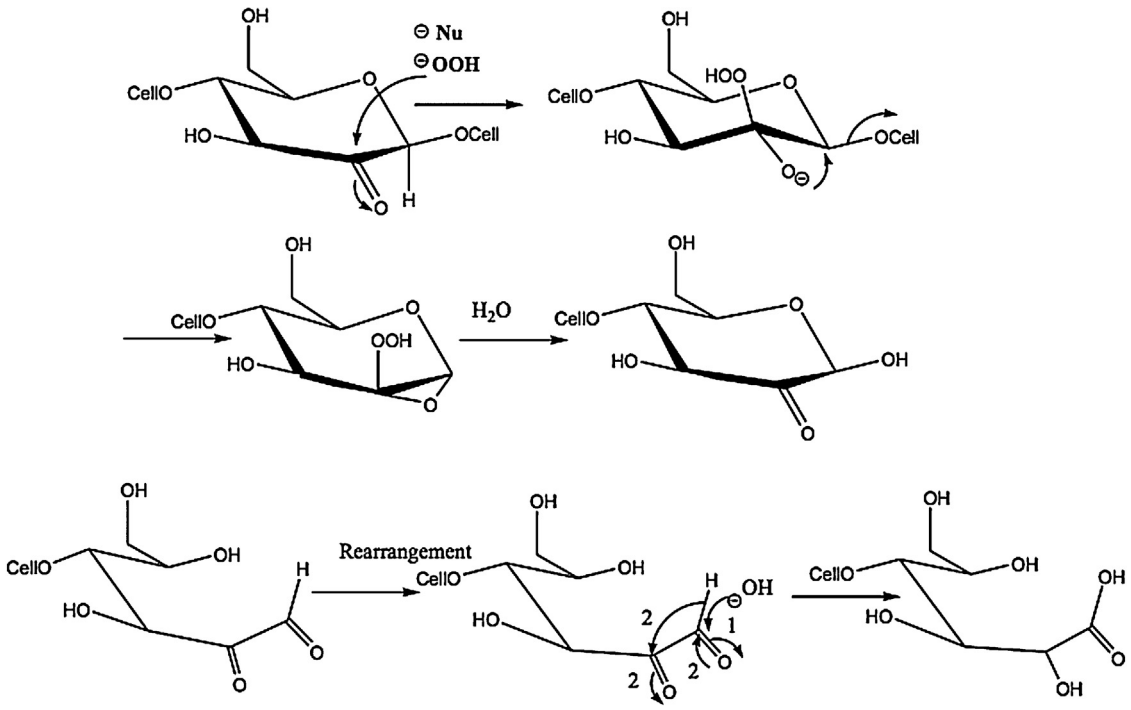

Fig. 4. Possible chain cleavage following a nucleophilic attack on the carbonyl group and alkaline rearrangement of the dicarbonyl structure.

4.2. Effect of a P stage after ZE and Z stages

The degradation of the cellulose occurring during a P stage is a well-known fact (Zeronian & Inglesby, 1995). The degradation is generally believed to be due to metal ions in the pulp (Lapierre, Paleologou, Berry, & Bouchard, 1997). Those metals would turn peroxide into radicals, and those radicals would be the ones responsible for cellulose oxidation, which in alkaline media will result in depolymerization. In this study the kraft + O and the fully bleached pulps had the following metal content: Fe 20 ppm, Cu 5 ppm, Mn 20 ppm and Fe 5 ppm, Cu 1 ppm, Mn 5 ppm, respectively. After Z, another explanation could be linked to carbonyls, since the hydroperoxyl anion, which is a good nucleophile, may react with the carbonyl groups, as shown in Fig. 4. According to the proposed mechanism, depolymerization occurs. Globally, the number of carbonyl groups should ultimately decrease. As P stages are carried out under alkaline conditions, one idea to better apprehend the specific effect of peroxide is to analyze values obtained after a ZE stage (Table 4) to compare ZE and ZEP.

When a P stage is carried out after an E stage, there is a decrease of the molecular weight. The DP_v of the kraft + O + $Z_{0.6}$E goes from 670 kg/mol before P to 275 kg/mol after P, and goes from 390 kg/mol to 320 kg/mol in the case of the fully bleached pulp. This decrease can be explained by the role of metals, but might also be caused by the mechanism described in Fig. 4, though it is not possible to determine which effect has the highest impact. In the case of the fully bleached pulp, the amount of carbonyl groups decreases, as expected from the mechanism in Fig. 4. Similar results were obtained by Röhrling, Potthast, Rosenau, Lange, Borgards, et al. (2002). However this is not true for the unbleached pulp. In the latter case, one hypothesis could be that the amount of metal ions in the pulp is higher, which favors the decomposition of hydrogen peroxide into radicals. The latter may create new carbonyls.

Although the last values in Table 4 related to P and P_{Mg} (P stage with added magnesium) are even more difficult to analyze, as several effects may influence the data, the tendency is roughly the same as for ZEP; i.e., some carbonyl groups disappear on the bleached pulp during P, likely by oxidation involving the perhydroxyl anion. This is not observed on the unbleached pulp. On the contrary, more carbonyls are present after P. When Mg^{2+} cations are added, fewer carbonyl groups are formed, which is due to the better stability of hydrogen peroxide and the smaller quantity of radicals.

5. Conclusions

It has been shown in this study that ozone itself virtually does not form carbonyl groups on a purified (lignin- and hexA-free) cellulosic pulp when added in the usual quantities applied in pulp bleaching. However, when other compounds are present in the pulp, such as hexA alone or hexA plus lignin, carbonyl groups are formed on both hemicelluloses and cellulose. Most of the carbonyls introduced on hemicelluloses must be the result of hexA ozonolysis. Ozone alone cannot be directly responsible for the carbonyl generation on cellulose, as hexA and lignin react with most of it, and as very few carbonyl groups are created on the purified cellulose when directly submitted to ozone. It was concluded that the new carbonyl groups on cellulose are formed by some radicals produced when hexA and lignin react with ozone. During the alkaline extraction (E) that follows the ozone stage (Z), some carbonyl groups are removed from both hemicelluloses and cellulose. The decrease of carbonyl groups on cellulose can only be explained if depolymerization takes place via a β-elimination mechanism, which is observed, and if, at the same time, the dicarbonyl group that is formed undergoes a rearrangement into a carboxylic structure (benzylic acid-type rearrangement). Although this mechanism would also occur on the hemicelluloses, one cannot exclude the possible removal of carbonyl groups by the solubilization of some hemicellulose fragments in the alkaline medium.

Finally, a hydrogen peroxide stage (P) carried out after Z or ZE is supposed to destroy some of the carbonyl groups by oxidation. However, this is not seen when the starting pulp is an unbleached

pulp. On the contrary, some new carbonyl groups are generated very likely as a result of radical formation by peroxide decomposition.

Globally, carbonyl groups are created on cellulose during a TCF sequence like ZP or ZEP. Minimizing this phenomenon would imply getting rid of most of the hexA before the application of the Z stage (roughly 50% is removed in an industrial acidolysis stage (A)) or applying ozone later in the sequence. Another positive action would be eliminating the metal ions as much as possible, or stablizing H_2O_2 to avoid the production of radicals in P.

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