ECF BLEACHING WITH A FINAL HYDROGEN PEROXIDE STAGE: IMPACT ON THE CHEMICAL COMPOSITION OF *Eucalyptus globulus* KRAFT PULPS

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Two industrial elemental chlorine free (ECF) bleaching sequences, D_0(EOP)D_1(EP)D_2 and OQ(PO)DP, are compared with respect to the bulk content of lignin, carboxyl, hexeneuronic acids (HexA), and reducing groups after each bleaching stage. HexA groups contribute significantly to the total content of carboxyl groups, and their degradation during chlorine dioxide bleaching is reflected by a decrease of the carboxyl content. The higher degradation using an enhanced use of oxygen-based bleaching chemicals is associated with a higher fiber charge reduction, mainly due to xylan depletion. Additionally, the effect of process variables of a laboratory final hydrogen peroxide stage on the chemical composition of the fully bleached pulp (D_0(EOP)D_1P and OQ(PO)DP) is studied. The ability of final peroxide bleaching to raise the content of carboxyl groups is dependent on the operating conditions and pulp bleaching history. A balance between carbohydrate oxidation and dissolution of oxidized groups determines the effect on fiber charge. The effect of hydrogen peroxide stabilizers added into the final stage on the content of carboxyl groups is also reported.

Keywords: Oxidation; Carboxyl groups; Carbonyl groups; Hexeneuronic acids; Intrinsic viscosity; Bleaching history

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INTRODUCTION

Elemental chlorine free (ECF) bleaching sequences are presently the most used technology in wood pulp bleaching. The consolidation of this multistage pulp bleaching technique still needs better coordination between bleaching stages and target brightness, enhanced flexibility, and higher washing efficiency, within the so-called concept of a minimum impact mill (Annergren 2005). Regarding eucalyptus bleached pulps, there is an ever-increasing market demand, mainly for printing and writing paper grades (Colodette et al. 2008). These specific products require pulps with high quality standards in terms of strength and optical properties. In the case of market bleached fiber, the final bleaching stage has a crucial role in adding value to the end product.

A number of studies have shown the benefits of using a final hydrogen peroxide stage (P) in the ECF bleaching of eucalypt kraft pulps instead of the conventional chlorine dioxide final stage (D). In addition to chlorine dioxide savings (McDonough et al. 2001; Suss et al. 2000), a boost in brightness (Senior et al. 1998; Suss et al. 2000), lower brightness reversion (Carvalho et al. 2008; Eiras and Colodette 2005; McDonough et al. 2001; Seco et al. 2008; Suss et al. 2000), higher beatability (Carvalho et al. 2008; Parthasarathy and Colodette 2007; Seco et al. 2008), and improved paper-making properties, most notably tensile strength (Carvalho et al. 2008; Loureiro et al. 2009b; Seco et al. 2008), of the fully bleached pulps have been claimed. The final alkaline P stage enables an electrolytic fiber swelling caused by a greater amount of carboxyl groups and by a higher osmotic pressure inside the fiber wall thus promoting pulp beatability and inter-fiber bonding potential (fibers more flexible and conformable) (Loureiro et al. 2009b). The effect of fiber charge (generated by the COOH groups) is of great importance for the improvement of different strength properties of the bleached pulp (Dang et al. 2007a; Laine and Stenius 1997).

Oxidation of cellulosic compounds comprising random fragmentation within the polymeric chains is, however, detrimental from the viewpoint of fiber strength. A reduction in fiber strength affects in different ways the strength properties of the bleached pulps and in particular is detrimental for tear strength (Page 1994). In this context, optimized operating conditions are essential in the final bleaching stages.

There is a high demand for high quality eucalypt bleached pulp with a high degree of strength, brightness and brightness stability. Given the relationship between the oxidation degree and the papermaking properties of the bleached pulps, this study focuses on analyzing the profiles of oxidized groups (CHO, COOH, and hexeneuronic acids) along two industrial elemental chlorine free (ECF) bleaching sequences. Accordingly, a conventional ECF sequence and an ECF-light sequence are compared, D_0(EOP)D_1(EP)D_2 and OQ(PO)DP, respectively, where Q stands for a chelating stage, E corresponds to an alkaline Extraction stage, and (PO) means a Peroxide stage pressurized with Oxygen). In addition, the impact of a final P stage, applied to either a DED or OQ(PO)D partially bleached pulp, on the chemical composition of the fully bleached pulps is addressed. The effect of the corresponding operating conditions (time, temperature, chemical charges, and hydrogen peroxide stabilizers) on the content of oxidized groups of the fully bleached pulps is reported. The stabilizers utilized were magnesium and chelants with the intent of minimizing hydrogen peroxide decomposition in the final P stage and hence improving pulp bleachability and bleaching selectivity.

EXPERIMENTAL

Pulps

Eucalyptus globulus kraft pulps were provided by two distinct Portuguese pulp mills operating with different ECF bleaching sequences. These were a conventional D_0(EOP)D_1(EP)D_2 sequence and an ECF-light OQ(PO)DP sequence. The pulps were collected after cooking and then after each stage of the bleaching plant. A greater amount of D_0(EOP)D_1 and OQ(PO)D pulps was collected in order to study, in the laboratory, a final hydrogen peroxide bleaching stage under several operating conditions. All industrial pulps were thoroughly washed with distilled water in the laboratory and then conditioned in a dark and cold room.

Analysis of Pulps

The kappa number of the unbleached and pre-delignified pulps was measured according to ISO 302 standard procedure. The amount of carbonyl groups content (as aldehyde groups) was measured spectrophotometrically according to the procedure described elsewhere (Obolenskaya et al. 1991) based in the 2,3,5-triphenyltetrazolium chloride (TTC; Sigma-Aldrich) reaction. The selectivity of the TTC reaction with reducing carbonyl groups was confirmed by Strlic and Pihlar (1997) for a number of model compounds. The quantification of carboxyl groups was determined according to TAPPI T 237 method, while the hexenuronic acid (HexA) content was quantified according to the procedure described by Chai et al. (2001) (adopted as the official procedure TAPPI T 282), adapted to eucalypt pulps by Pedroso and Carvalho (2003). The contribution of HexA to the pulp kappa number was estimated using the empirical equation developed by Pedroso and Carvalho (2003),

$$\text{KN} \approx \text{Lignin KN} + \text{HexA KN} = 5.3\ \text{TL} + 0.09\ C_{\text{HexA}} \tag{1}$$

where TL is the total lignin content (% odp) and C_{HexA} is the HexA content (mmol / kg odp). This equation was used even though some points deviated slightly from the specified range of $7.5 \leq \text{KN} \leq 69$, $1.2 \leq \text{TL} \leq 12$, and $18 \leq C_{\text{HexA}} \leq 61$.

The aromatic residual lignin content of a number of samples of fully bleached pulps was measured spectrophotometrically at 280 nm after dissolution of the pulps in a cadoxen solution as described by Evtuguin et al. (2002). The monosaccharide analysis of the bleached pulps was determined after Saeman hydrolysis of the pulp samples (treatment with H_2SO_4 72% for 3 h at 25ºC, followed by hydrolysis with H_2SO_4 1M during 2.5 h at 100ºC), followed by gas chromatography analysis of the alditol acetate derivatives (Selvendran et al. 1979).

Hydrogen Peroxide Final Bleaching

The operating conditions of the final P stage were the same as those published elsewhere regarding bleaching kinetics (Loureiro et al. 2009a), where all components were pre-heated to the desired temperature. Hydrogen peroxide charge (0.5 to 2.0% odp – oven dried pulp) and sodium hydroxide charge (0.6 to 0.9% odp), temperature (70 to 90ºC) and reaction time (0 to 180 min) were manipulated. The effect of additives, acting as hydrogen peroxide stabilizers, was also studied, using magnesium sulfate and the sodium salts of ethylenediaminetetracetate (EDTA) and diethylenetriaminepentaacetate (DTPA). Every laboratory final P stage was run in sealed polyethylene bags immersed in a reciprocal shaking water bath with temperature control and using 20 g odp at 10% consistency.

RESULTS AND DISCUSSION

Industrial ECF Bleaching Comparison: Kappa Number and HexA, COOH, and CHO Contents

The kappa number (KN) and the hexeneuronic acid (HexA) content determined experimentally, as well as the KN fractions from lignin and HexA calculated by Eq.1, are presented in Table 1 for the unbleached and pre-delignified kraft pulps from the two studied fibrelines (after the D_0 or O stage). Although possessing the same kappa number, both unbleached pulps had different HexA content. This confirms the dependence of HexA content with kraft pulping conditions of *E. globulus* wood (Daniel et al. 2003; Pedroso and Carvalho 2003).

The impact of non-lignin oxidizable structures, mainly HexA, in the kappa number test is well established (Li et al. 2002a; Li and Gellerstedt 1997; Li et al. 2002b). In addition, oxidized lignin structures, such as quinones and muconic acids, also consume permanganate in the kappa number test (Brogdon 2001), besides the smaller interference of other oxidizable structures, including carbohydrate derivatives (Li et al. 2002b).

Therefore, lignin KN in Table 1 (calculated as KN-0.09C_{HexA}) comprises both unbleached lignin and oxidized lignin. Since quinones introduce deviations in the lignin/kappa number ratio (Brogdon 2001), the assessment of residual lignin content (% odp) in pre-delignified pulps (after first bleaching stage) may be not accurate using Eq. 1, which was developed for unbleached *E. globulus* kraft pulps (Pedroso and Carvalho 2003). This is more relevant after D_0, especially if high ClO_2 charges are used, because the amount of quinones was found to increase upon chlorine dioxide delignification (Brogdon et al. 2004; Zawadzki 1999), though oxygen delignification also produces quinone structures but to a lesser extent (Zawadzki 1999).

In hardwood pulps, such as *E. globulus* pulps used in this study, the major contributions for the kappa number come from lignin and hexenuronic acid (Li et al. 2002a). A high amount of HexA leads to the overestimation of lignin content given by the kappa number test if the HexA contribution is not accounted for. In fact, as confirmed in Table 1, the kappa number fraction assigned to HexA can reach 45% after oxygen delignification. It can also be concluded that HexA is not affected much by oxygen delignification, unlike chlorine dioxide delignification, which is in accordance with HexA reactivity (Buchert et al. 1995; Jiang et al. 2000). Therefore, the D_0 stage produces a consistent drop in kappa number due to lignin and HexA removal of nearly 70%. On the other hand, with oxygen delignification the drop in uncorrected kappa number (as measured) and lignin kappa number is around 35% vs. 45%, respectively. The slight reduction in HexA content after the O stage reflects the dissolution of xylan fragments in the alkaline medium.

Table 1. Kappa Number (KN) and HexA Content of Unbleached and Pre-Delignified Eucalypt Kraft Pulps (after D_0 or O stage of the two industrial bleaching sequences)

Pulp ID	KN as measured	HexA as measured (mmol / kg odp)	Lignin KN*	HexA KN*
Unbleached	15.4	48.0	11.1	4.3 (28% KN)
D_0	5.1	18.9	3.4	1.7 (34% KN)
Unbleached	15.4	54.6	10.5	4.9 (32% KN)
O	10.2	50.6	5.6	4.6 (45% KN)

* - calculated by the correlation (Pedroso and Carvalho 2003): $KN = 5.3\ TL + 0.09\ C_{HexA}$ where $5.3\ TL \equiv$ *Lignin KN* and $0.09\ C_{HexA} \equiv$ *HexA KN*

Figure 1 presents the bulk content of carboxyl groups, HexA, and of carbonyl reducing groups after each stage of bleaching. Once again after each D stage the HexA content was greatly reduced. The observed slight increase in the alkaline (EOP) and P stages can be due to heterogeneous dissolution of hemicelluloses, to some variability in the industrial samples (retention time), or to interference from oxidized lignin structures affecting HexA quantification. As reviewed by Brogdon (2009), muconic acids possess much higher molar absorbtivity than HexA at 260 nm. Therefore, their contamination in the dissolved hydrolyzed pulp can lead to an overestimation of HexA content, because this TAPPI method only accounts for the interference of unbleached residual lignin. However, given the presented results, the unexpected deviations are not relevant for the purpose of HexA profiling along both bleaching sequences.

As depicted in Fig. 1, HexA contributes significantly to the content of carboxyl groups and hence to the bulk fiber charge. The parallel downward arrows depicted in the D stages of Fig. 1 indicate a concomitant reduction in HexA and bulk COOH contents. Given HexA non-reactivity in the beginning stages of the ECF-light sequence (OQ(PO)DP), this drop is notable after the D-stage (a very steep decrease corresponding to 95% of HexA removal). In the D_0(EOP)D_1(EP)D_2 sequence, the chlorine dioxide delignification stage (D_0) does not achieve such a high HexA removal, the causes of which were attributed by Torngren and Ragnar (2002) to the fact that HexA degradation is kinetically hindered in the first D-stage (D_0-stage), being a dominant reaction in the second D-stage (D_1-stage).

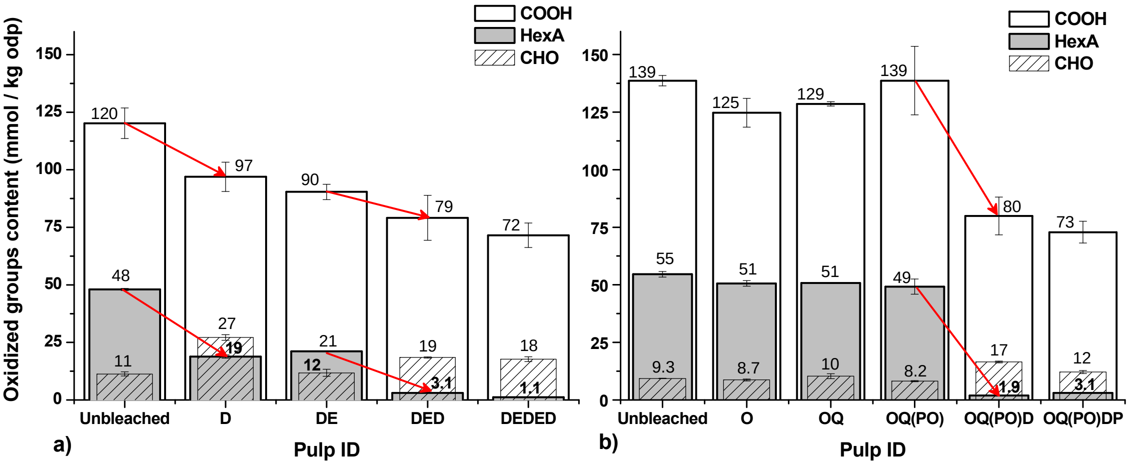

Fig. 1. Carboxyl, HexA and carbonyl groups profiles along two industrial ECF bleaching sequences: **a)** D_0(EOP)D_1(EP)D_2 and **b)** OQ(PO)DP

In unbleached pulps, residual lignin contributes to fiber charge, but xylan has the major contribution (Sjöström 1989) (from MeGlcA and HexA side groups). However, the content of carboxyl groups in xylan and consequently the fiber charge is strongly affected by the alkalinity of the kraft cooking process (Buchert et al. 1995). For an unbleached pine kraft pulp (KN of ca. 24), 52% of total COOH content was attributed to uronic acids, of which ca. 71% correspond to HexA, 13% to MeGlcA (methyl glucuronic acids), and 2% to MeIdoA (methyliduronic acid). The remaining carboxyl groups (48%) were assumed to be metasaccharinic acids (estimation of ca. 16%) and lignin bound acids (ca. 32%) (Buchert et al. 2001). The formation of carboxyl groups in residual kraft lignin has been reported upon chlorine dioxide bleaching (Sun and Argyropoulos 1996), alkaline extraction (Runge and Ragauskas 1999), and alkaline hydrogen peroxide bleaching (Gartner and Gellerstedt 2000). Therefore, the dissolution/removal of oxidized lignin (enriched in hydrophilic groups) and xylan side groups along bleaching contributes to the decrease of pulp carboxyl content. On the other hand, additional carboxyl structures are also introduced in polysaccharides by oxidative agents during the bleaching process (Sjöström 1993). This is most significant during the final stages, where cellulose becomes more vulnerable to oxidative attack. On the whole, it has been confirmed that a decrease of fiber charge occurs during the course of bleaching (Laine 1997), as depicted in Fig. 1, which is higher for the OQ(PO)DP sequence (47% compared to 40 % for the D_0(EOP)D_1(EP)D_2 sequence). The higher pulp degradation observed using the ECF-light sequence (Loureiro et al. 2010a) thus illustrates the importance of polysaccharide degradation/dissolution in charge reduction throughout bleaching. Fig. 2 clearly confirms this same tendency and also reveals some valuable insights in terms of carbohydrate oxidation pattern upon bleaching. Polysaccharide degradation occurs throughout the bleaching process, and the degradation is usually monitored by following pulp intrinsic viscosity. As depicted in Fig. 2, this trend is accompanied by a decrease in the content of carboxyl groups, mathematically described by a non-linear correlation for the D_0(EOP)D_1(EP)D_2 sequence, in contrast to the linearity found with the OQ(PO)DP sequence.

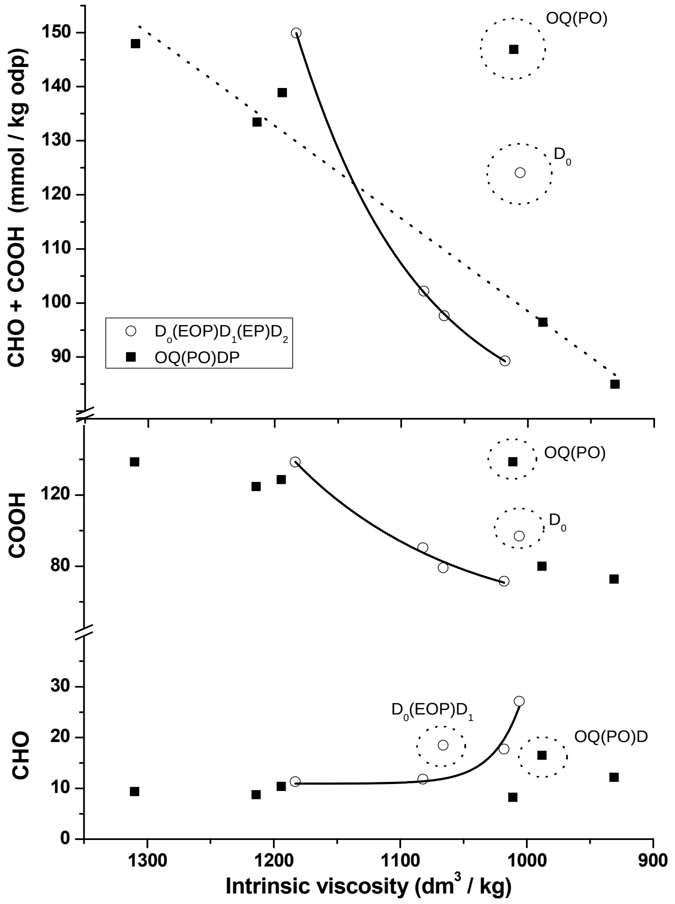

Fig. 2. Oxidized groups content as a function of pulp intrinsic viscosity along two industrial ECF bleaching sequences.

The highlighted points (dashed circles) belonging to the first D stage from the D_0(EOP)D_1(EP)D_2 sequence and to the PO stage from the OQ(PO)DP sequence further reveal some peculiarities. The D_0 stage produced a more heterogeneous pulp from a molecular weight point of view, having a higher amount of low molecular weight polysaccharides, evidenced by the highest amount of reducing carbonyl groups detected (Fig. 1). This therefore contributed to a down shifted value of pulp intrinsic viscosity as previously reported (Loureiro et al. 2010a). As regards PO bleaching, this stage produced the highest drop in pulp intrinsic viscosity and also a somewhat rise of fiber charge.

In terms of carbonyl reducing groups detected, their content increased due to the bleaching process, as depicted in Fig. 1. However, this increase was more pronounced with the D_0(EOP)D_1(EP)D_2 sequence compared to the OQ(PO)DP sequence, corresponding to an increase of ca. 64 % versus 29 %, respectively. Also it is notable that the higher intrinsic viscosity of the unbleached pulp that was ECF-light bleached is in line with the lower amount of reducing carbonyl groups detected, hence reflecting a greater preservation of the polysaccharide component during the cooking process. Although carbonyl groups conjugated to aromatic rings (e.g. acetophenone and benzophenone model compounds) did not react with TTC (Strlic and Pihlar 1997), other carbonyl-containing structures besides polysaccharides (e.g. oxidized lignin) cannot be fully disregarded.

The decrease in pulp intrinsic viscosity due to random cellulose (and hemicelluloses) depolymerisation is accompanied by a higher number of cellulosic chains, and thus of reducing end groups, which explains the profile obtained in Fig. 1, mostly in the case of the D_0(EOP)D_1(EP)D_2 sequence, and further demonstrated in Fig. 2. However, these terminal units are easily oxidized upon oxidative bleaching to the corresponding aldonic acids (Sjöström 1993). This can therefore mask the relationship between intrinsic viscosity and the content of reducing carbonyl groups. This is mainly the case of the OQ(PO)DP sequence, which also yielded the highest values for the amount of carboxyl groups. That is the reason why plotting the content of reducing groups, added to the content of carboxyl groups, improved the correlation notably.

A further insight obtained from the analysis of Fig. 2 comes from the points belonging to the D_0(EOP)D_1 and OQ(PO)D partially bleached pulps. The chlorine dioxide stage (after (EOP) and PO stages) markedly raised the amount of reducing groups without leading to a loss in intrinsic viscosity. Bearing in mind that hypochlorous acid is generated in chlorine dioxide bleaching, owing to this strong oxidant, it is expected that carbonyl groups are generated in pulps (Adorjan et al. 2006). The carbonyl groups detected by the TTC reaction comprise both aldehyde and ketone groups, because the latter, due to isomerisation in the C-2 and C-3 positions of the pyranosyl residues, under basic conditions, are converted into aldehyde groups. As a result, the deviations detected in those particular points are assigned to the oxidation in the C-2 and C-3 positions upon chlorine dioxide bleaching. After final bleaching, while the total amount of reducing groups is reduced using a final P stage, after (EP)D_2 final bleaching it is maintained. In fact, it has been previously found that the carbonyl groups are the source for an elevated fiber charge after a hydrogen peroxide treatment (Dang et al. 2007b). Even so, the ability of peroxide bleaching to increase fiber charge seems to strongly depend on the operating bleaching conditions (chemical charges and temperature) (Dang et al. 2007b), thus encompassing dissolution/removal and formation of carboxyl groups in polysaccharides.

The chemical components contributing to the fiber charge of fully bleached pulps (Fig. 1: 70-75 mmol COOH / kg odp) should mainly consist of uronic acids and carboxylic acids from polysaccharide oxidation (including reducing ends) and a smaller contribution of oxidized lignin products. Although chlorine dioxide bleaching stages reduce the bulk content of carboxyl groups due to almost complete removal of HexA, a MeGlcA fraction will remain in the pulp (Sjostrom 2006). In fact, a previous study showed that a part of the MeGlcA groups are not converted to HexA during kraft pulping and remain stable during bleaching (Buchert et al. 1995).

Final P Stage: Effect of Hydrogen Peroxide Stabilizers on COOH Content

The effect of adding hydrogen peroxide stabilizers in the final P stage on the content of carboxyl groups of the fully bleached pulps is depicted in Fig. 3. Using the D_0(EOP)D_1 pulp, there was a decrease of the content of carboxyl groups, being even lesser with the addition of stabilizers in the final P stage. Regarding the OQ(PO)D pulp, an increase in the carboxyl content was obtained when no additives were introduced. Once more, this suggests the role of polysaccharide oxidation/degradation on fiber charge. It is thus realized that a balance between the introduction of charged groups and their dissolution determines the net increase of carboxyl groups after final bleaching with hydrogen peroxide.

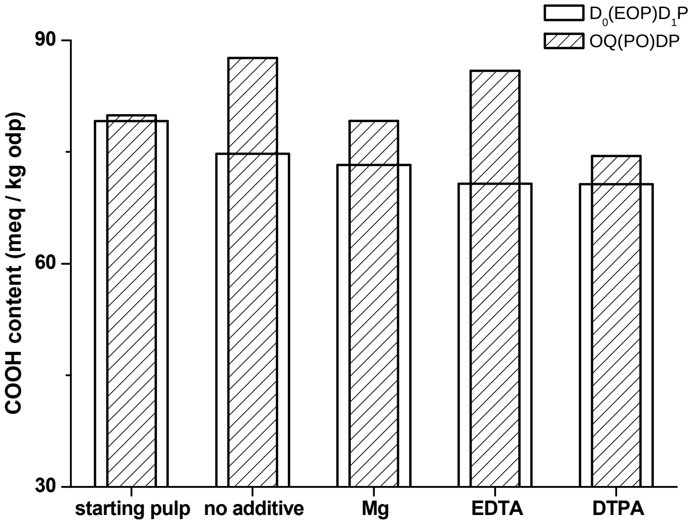

Fig. 3. Effect of hydrogen peroxide stabilizers added in a final P stage on the content of carboxyl groups of D_0(EOP)D_1P and OQ(PO)DP fully bleached pulps

While for the D_0(EOP)D_1 pulp the dissolution of charged moieties prevails (with or without stabilization), for the OQ(PO)D pulp, this balance can be shifted, resulting in an increase of charged groups. Besides the positive effect observed without additives, using the OQ(PO)D pulp, the addition of EDTA also increased the charge of the fully bleached pulp. This system has shown the lowest hydrogen peroxide consumption and a slight drop in intrinsic viscosity (Loureiro et al. 2009a). Therefore, the gain in the content of carboxyl groups should be related to a selective brightening action of the hydrogen peroxide anion, such as the elimination of quinone-type chromophores and conjugated carbonyl structures (Dence and Reeve 1996). In the extremely complex set of reactions present in hydrogen peroxide bleaching systems, the pathways of which are strongly dependent of metal-catalysed decomposition of hydrogen peroxide, the addition of stabilizers in the peroxide stage is a way to improve bleaching results (chemicals consumption and pulp properties).

Nevertheless, the outcome of final peroxide bleaching, either in the absence or presence of additives, is dependent on the pulp bleaching history, more precisely on the type and content of the remaining metals (mainly transition metals and magnesium) (Loureiro et al. 2010a), on the nature of the last chromophores (Mateo et al. 2004; Rosenau et al. 2007; Rosenau et al. 2008) and also the evidenced degree of pulp degradation, which is further discussed.

Final P Stage: Chemical Composition of the Fully Bleached Pulps

The variation observed in terms of chemical composition during final bleaching with hydrogen peroxide is presented in Fig. 4, which illustrates the chemical composition of pulps in terms of reaction time (0 and 180 min) and temperature (70 and 90ºC) from previous kinetic studies (Loureiro et al. 2009a, 2010a). Additionally, the neutral monosaccharide composition of the pulps is presented in Table 2 only for the temperature of 90ºC with the intention of revealing the differences more clearly and assessably.

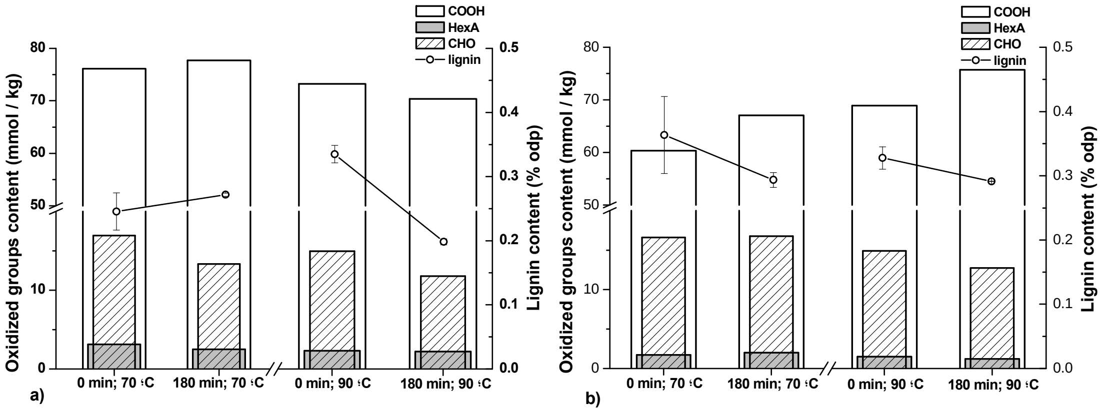

Fig. 4. Content of oxidized groups and of residual lignin during hydrogen peroxide final bleaching of **a)** D_0(EOP)D_1 and **b)** OQ(PO)D partially bleached pulps. Final P stage conditions: 2.0% odp H2O2; 0.6-0.9% odp NaOH; 0.05% DTPA; 70-90ºC; 0-180 min.

Table 2. Neutral Monosaccharide Composition (%, w/w) of the ECF Bleached Pulps Before and After a Final Hydrogen Peroxide Bleaching Stage (2.0 % odp H_2O_2; 0.8-0.9 % odp NaOH; 0.05% odp DTPA; 90ºC; 180 min). Errors reported as standard deviations

Pulp	Intrinsic viscosity (dm^3 / kg)	Rha	Ara	Xyl	Man	Gal	Glc
D_0(EOP)D_1	1048	0.4	0.1	24.5 ± 1.0	0.3	0.3	74.3 ± 1.0
D_0(EOP)D_1P	935	0.4	0.1	19.8 ± 0.2	0.3	0.3	79.2 ± 0.1
OQ(PO)D	958	0.3	0.1	19.4 ± 0.4	0.3	0.2	79.8 ± 0.4
OQ(PO)DP	797	0.3	0.1	19.0 ± 0.7	0.3	0.2	80.1 ± 0.7

The higher pulp degradation during the ECF-light bleaching sequence (Loureiro et al. 2010a), as mirrored in the lower intrinsic viscosity of the OQ(PO)D pulp (Table 2), is reflected in the relative content of xylose (0 min; Table 2) before the final P stage. Notwithstanding a higher proportion of xylose to glucose after D_0(EOP)D_1 bleaching, xylan was significantly lost in the alkaline conditions of final P stage after 180 min. This xylan removal is in line with the decrease in the carboxyl content in Fig. 4 under the same bleaching conditions, therefore confirming that xylan is an important bearer of carboxyl groups. Although the xylan yield upon the final P stage was lower for the D_0(EOP)D_1 based pulp, the decrease in intrinsic viscosity was less compared to the one observed with the OQ(PO)D pulp after the final P stage (Table 2). It is thus concluded that cellulose random depolymerisation is more pronounced using the OQ(PO)D pulp, but xylan is lost to a higher extent using the D_0(EOP)D_1 pulp. It seems that a more accessible xylan fraction was easily removed/dissolved in the final P stage of the D_0(EOP)D_1P sequence and that a more strongly bound portion remains more preserved to the action of the bleaching chemicals. In fact, using the more degraded OQ(PO)D pulp, only a slight drop in the xylose relative content occurs. Given this lesser amount of xylan removal, the charge balance could be shifted to a net increase of the carboxyl content for the case of the OQ(PO)DP sequence, as portrayed in Fig. 4. Using a milder temperature of 70 ºC at the final P stage, a slight increase in the content of carboxyl groups is attained with the

D_0(EOP)D_1P sequence. The more probable explanation is that xylan was more preserved at this temperature and as a result did not contribute as much to a reduction-shift of the carboxyl content.

The initial carboxyl contents at 70 and 90ºC (0 min; Fig. 4) were different because the pulps were pre-heated to the desired temperature with NaOH and DTPA at 13% consistency before the addition of hydrogen peroxide (Loureiro et al. 2009a). The effect of the pre-heating period was different between the two pulps. While the increase of temperature from 70 to 90ºC resulted in a reduction in the amount of carboxyl groups using the D_0(EOP)D_1 pulp, with the OQ(PO)D pulp the amount was raised. The reduction is fairly understood considering alkaline dissolution of charged moieties promoted by an increase of temperature. Conversely, the rise in carboxyl content for the OQ(PO)D pulp during the pre-heating period is explained by the alkaline hydrolysis of esters and/or lactones groups in the pulps as proposed by Katz et al. 1981 and highlighted by Pan 2004 using mechanical pulp. Using bleached chemical pulps, these groups are likely associated to hemicelluloses and cellulose components and also lignin-derived muconolactone products (Loureiro et al. 2010b).

At the end of the bleaching sequence the HexA contribution to the total charge content is very small, and the slight decrease observed after peroxide bleaching (Fig. 4) is attributed to xylan removal/dissolution.

In terms of the content of reducing groups, the general tendency depicted in Fig. 4 reveals a decrease during the course of time. The decrease in intrinsic viscosity is accompanied by an increase of reducing groups from the aldehyde end units but, given the presented results, these terminal units were likely oxidized to aldonic acids. The relationship between carbonyl and carboxyl groups reported by Dang et al. 2007b, who considered the former groups the source for elevated carboxyl content, is verified in most cases. It is not universal, as in some cases the hydrophilic enrichment due to carboxyl groups favour the alkaline dissolution of low molecular weight polysac-charides.

Figure 4 also compares the aromatic residual lignin content between the two studied pulps after peroxide bleaching. The spectroscopic measurements of aromatic lignin content (at 280 nm) from the pulp samples dissolved in a cadoxen solution reveals that the remaining aromatic lignin is further removed, but not to a high extent. Using the D_0(EOP)D_1 pulp, 90ºC enhances lignin removal (reaching less than 0.2% odp), while at 70ºC a lignin-retaining brightening action occurs. As for the OQ(PO)D pulp, the temperature impact is less obvious. Some interference in these values can be caused by the use of unbleached lignin absorption coefficient (Evtuguin et al. 2002) instead of the one corresponding to oxidized lignin which, in turn, should be dependent on the type of bleaching history. However, isolation of intact oxidized lignin is a rather difficult task.

CONCLUSIONS

1. The effects of the ECF bleaching sequence applied to *Eucalyptus globulus* kraft pulps on the bulk content of lignin, oxidized groups, and carbohydrate composition are rather diverse.
2. The more intense use of oxygen bleaching chemicals such as oxygen delignification and hydrogen peroxide bleaching stages renders a final bleached pulp more degraded, having a lower relative content of xylose, and with a higher decrease in carboxyl groups throughout bleaching.

3. The HexA contribution to fiber charge is highlighted in the unbleached pulps, while after chlorine dioxide stages HexA is readily removed, thus contributing to fiber charge reduction.
4. The advantage of using a final hydrogen peroxide stage to increase the content of carboxyl groups is dependent on the operating conditions, which can impact the balance between carbohydrate oxidation and charged moieties dissolution, especially in the case of xylan.
5. The outcome of using hydrogen peroxide stabilizers on carboxyl groups of fibers is also dependent on pulp bleaching history.

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