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Discriminating the brightness stability of cellulosic pulp in relation to the final bleaching stage

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ABSTRACT

The reasons for the improved brightness stability of pulp bleached in the final stage with hydrogen peroxide than with chlorine dioxide have been studied. UV–vis Diffuse Reflectance and UV Resonance Raman micro-spectroscopy @ 325 nm were employed to evaluate the chromophores formation/degradation in fully bleached eucalypt kraft pulp while applying a final chlorine dioxide or a hydrogen peroxide bleaching stages. Spectroscopic data were coupled to wet chemistry and mass spectrometry analyses of degradation products arisen during hydrothermal ageing of bleached pulps. The complementary analyses have revealed the important role of partially oxidised carbohydrates and of the residual xylan–lignin complex in ageing reactions. The leaching of degradation products from pulp during the final bleaching stage, rather than specific oxidation patterns of pulp polysaccharides with the bleaching agent was suggested to be a crucial factor predetermining the extent of brightness reversion of pulp.

1. Introduction

The bleached cellulosic fibres (pulps) are the basic raw material for the production of high grade papers. Among diverse properties, the level of brightness and its stability are of primary importance (Dence & Reeve, 1996; Suess, 2010). The brightness of bleached pulp can markedly drop under drying, transportation, storage and the conditions of use. In particular, a detrimental combination of temperature and humidity and, to a lesser degree, of light affects the pulp brightness. Cellulosic pulps with a low residual lignin content (chemical pulps) are produced from wood mainly by the kraft cooking process followed by a sequential treatment with different delignification/bleaching reagents that will shape the final properties of the bleached pulp and, specifically, the brightness reversion (or yellowing) (Dence & Reeve, 1996; Suess, 2010). In laboratory the brightness reversion is assessed via accelerated ageing tests under controlled dry or wet thermal conditions.

The bleached chemical pulps are composed mainly by cellulose (80–95%) and hemicelluloses (5–20%) though a small proportion of residual lignin (0.1–0.5%) is always present (Dence & Reeve, 1996). The brightness reversion of bleached chemical pulps has been earlier assigned to chromophore formation from almost all aforementioned pulp constituents (Rollinson, 1954). Presently, the ageing reactions of either residual lignin or carbohydrates are the main debatable causes for the reversion (Jaaskelainen, Toikka, Lahdetie, Liitia, & Vuorinen, 2009). The pulp yellowing has been also related to the amount of hydrolysable substances in bleached pulps arisen upon acidic pre-treatment (Beyer, Koch, & Fischer, 2006). Conversely, a great part of coloured matter produced during ageing could be extracted by methanol (Beyer, Koch & Fischer, 2006) or even by water (Granstrom, Gellerstedt, & Eriksson, 2002). Such products are result of thermal decay of polysaccharide chains which contain hydrolytically labile partially oxidised structural units containing carbonyl and carboxyl groups (Beyer et al., 2006).

The enhancement of chromophores formation upon ageing has been previously evidenced employing models of oxidised carbohydrates or their conversion products, such as 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (furfural), over different cellulosic pulps (Forsskahl, Tylli, & Olkkonen, 2000; Kawae & Uchida, 2005; Logenius, Friman, & Agnemo, 2008; Theander & Nelson, 1988). In addition, the effect of transition metals to the colour forming reactions upon ageing has been also confirmed (Beyer, Lind, Koch, & Fischer, 1999; Granstrom, Eriksson,

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Gellerstedt, Roost, & Larsson, 2001; Granstrom et al., 2002; Kawae & Uchida, 2005; Logenius et al., 2008).

The phenomena of brightness reversion is rather complex and some contradictory findings can be related to the artificial ageing conditions applied and to the different origin and process history of bleached pulps. For example, although hexeneuronic acids (HexA) content has been shown to correlate with thermal yellowing of bleached pulps (Sevastyanova, Li, & Gellerstedt, 2006), in many other studies this fact was not confirmed (Eiras, Colodette, Silva, & Barbosa, 2008; Loureiro, Fernandes, Carvalho, & Evtuguin, 2010; Süss, Schmidt, & Hopf, 2004). One of the reasons for this long-standing issue is related to difficulties in the assessment of residual chromophores due to their low abundance (ppm or even ppb range) in fully bleached pulps (Lachenal, Pipon, & Chirat, 2009; Rosenau, Potthast, Kosma, Suess, & Nimmerfroh, 2007). Bleaching chemistry of the final bleaching stages and its relationship with the gain and the stability of brightness are insufficiently studied.

The analysis of chromophores that have emerged during ageing is essential for understanding the mechanisms of brightness reversion and find technical solutions to overcome it. The analysis of chromophores in bleached pulps after ageing may involve their previous extraction and chemical characterisation or, alternatively, be assessed in situ. Just recently the residual chromophores from bleached chemical pulps were isolated and characterised thus allowing the identification of the important chromophore structures in bleached eucalypt pulps (Rosenau et al., 2007). Non invasive techniques, such as UV-Resonance Raman (UV-RR) spectroscopy, allow an in situ assessment of residual chromophores in bleached pulps present in minor amounts (ppm or even ppb). Rather particular chromophore structures can be assessed by Raman scattering while applying an appropriate UV excitation wavelength fulfilling the resonance conditions (Halttunen et al., 2001; Jaaskelainen et al., 2009; Loureiro et al., 2010; Loureiro, Fernandes, Furtado, Carvalho, & Evtuguin, 2011; Saariaho, Jaaskelainen, Nuopponen, & Vuorinen, 2003). On the other hand, unlike to the narrow spectral envelope used for the ISO brightness measurement at 457 nm, UV–vis Diffuse Reflectance (UV–vis DR) spectroscopy provides complementary information on chromophores across the entire UV–vis spectral window (Schmidt & Heitner, 1999).

It is commonly accepted that the bleaching history, and especially the final bleaching stages, affects seriously the brightness stability of pulps (Eiras et al., 2008; El-Sakhawy, 2005). In fact, the introduction of a final alkaline hydrogen peroxide treatment (P stage) instead of chlorine dioxide stage (D stage) in the elemental chlorine free (ECF) bleaching improves the brightness stability of fully bleached eucalypt kraft pulps, despite the higher amount of HexA residues in their composition (Loureiro et al., 2010). These rather significant differences in brightness stability of pulps bleached by final chlorine dioxide and hydrogen peroxide are not well understood and were the main goal of this study focused on a comparative analysis of chromophore and chromogen groups in those pulps and degradation products derived from oxidised structures of polysaccharides upon accelerated ageing. Accordingly, partially (DED) and fully bleached (DEDD and DEDP) pulps were submitted to a solid-state analysis by UV-RR and UV–vis DR spectroscopy and the ageing degradation products extracted by aqueous ethanol were assessed by mass spectrometry analyses.

2. Experimental

2.1. Pulps

A partially $D_0(EOP)D_1$ pre-bleached *Eucalyptus globulus* kraft pulp was collected in a Portuguese pulp mill (EOP designates the alkaline extraction stage reinforced with oxygen and hydrogen peroxide). This semi-bleached pulp will be referred further as DED pulp. In the laboratory, the DED pulp was thoroughly washed with distilled water and conditioned in the dark at 4 °C. The DED pulp possessed an ISO brightness of 87.3% and was bleached either with a final D or P stage reaching 91 ± 0.5% of ISO brightness measured according to ISO 2470. In order to induce significant structural changes in pulps, rather harsh conditions were applied in the final D stage (8.0% ClO_2 odp, as active Cl_2, 70 °C, 180 min) and in the final P stage (8.0% H_2O_2 odp, 1.1% NaOH odp, 0.2% DTPA odp, 90 °C, 60 min). A chelating agent (DTPA) with a good chemical stability was selected with the purpose of minimising transition metal-induced decomposition of hydrogen peroxide (Ramo & Sillanpaa, 2001; Sillanpaa & Ramo, 2001). It was previously shown that with the use of these harsher operating conditions the differences obtained in terms of intrinsic viscosity and brightness reversion were of the same order as those found in DEDD and DEDP bleached pulps using more conventional bleaching conditions (Loureiro et al., 2010). The DEDD and DEDP bleached pulps were characterised in terms of intrinsic viscosity (ISO 5351 procedure), brightness reversion (TAPPI T 260 procedure) and HexA (TAPPI T 282 procedure).

2.2. Artificial wet-thermal ageing of bleached pulps

In this study, the DED, DEDD and DEDP bleached pulps were adjusted to pH 5 at 1% consistency with the addition of H_2SO_4 and then filtered off. 5 g (odp) of each wet pulp (30% humidity) were then artificially aged under wet-thermal conditions in double sealed polyethylene bags immersed in a water bath at 70 °C for 5 days in dark. The reversion results were assessed via the Post Colour (PC) number as determined by the k/s difference (Kubelka–Munk theory) before and after the ageing: $PC = 100(k/s_{\text{aged}} - k/s_{\text{init}})$. After ageing the pulps were suspended in an ethanol–water (1:1) solution (liquid to pulp ratio of 5) for 12 h and then filtered off.

2.3. Solid-state analysis

The bleached pulp samples set to the pH 5 were pressed into 11 mm-diameter pellets using 100 mg of pulp. The same amount of pulp was sampled after the ageing treatment and subsequently air-dried in dark at room temperature. For comparative reasons all pulps were conditioned at 50 °C for 1 h before pressing into pellets that were kept over P_2O_5.

UV–vis Diffuse Reflectance (UV–vis DR) spectra were recorded at room temperature on a JASCO V-560 spectrophotometer equipped with a JASCO ISV-469 integrating sphere and using $BaSO_4$ standard as background reference. The reflectance spectra were converted into k/s spectra using known Kubelka–Munk equation.

UV-Resonance Raman (UV-RR) spectra were recorded using a Jobin Yvon (Horiba) LabRam HR 800 micro-Raman spectrometer @ 325 nm (He–Cd UV laser, Kimmon IK Series) under backscattering configuration using a 40× NUV objective. The spectral range was 750–1800 cm^{-1} in order to cover chromophores and carbohydrate related bands and the spectra were collected during 30 s of acquisition time to avoid photodegradation. For each pulp sample at least 3 points were analysed in order to obtain an average spectra. The spectral data was subjected to background correction (linear luminescence – fluorescence) and normalised to the ca. 1375 cm^{-1} band as performed in previously published studies for the fully bleached pulps with negligible amounts of residual lignin (Loureiro et al., 2010, 2011).

2.4. Analysis of extracts from aged pulps

Three extracts from the aged DED, DEDD and DEDP bleached pulps were analysed for pH (Hanna Instruments pH-meter), UV–vis

Table 1
Effect of the final **D** and **P** bleaching stages applied to the industrial DED pulp on the ageing behaviour of the fully bleached pulps.

Pulp	ISO brightness (%)	HexA (mmol/kg)	Brightness reversion[a] PC number	Loss of intrinsic viscosity after ageing and extraction (dm^3/kg)
DED	87.3	3.2	4.3	−241
DED**D**	91.0	1.9	6.5	−254
DED**P**	91.5	2.9	3.7	−68

[a] Measured at 457 nm according to the *k*/*s* spectra in Fig. 1 (not related to the ISO brightness values presented).

absorption (using JASCO V-560 spectrophotometer), solids content after drying at 105 °C, metals content (Fe, Cu, Mn, Na, Mg, Ca) by atomic absorption spectroscopy (TAPPI T 266 standard procedure; Perkin Elmer Atomic Absorption Spectrometer 3300), sulphate ions by ionic chromatography (Waters Action Analyser Millipore).

The extracts were dried under vacuum and analysed as trimethylsilyl (TMS) derivatives on a gas chromatograph (Trace Gas Chromatograph 2000 series), equipped with a mass spectrometer (Thermo Scientific DSQII) (GC–MS). The dried samples were silylated with 300 μL BSTFA and 50 μL TMSCl in pyridine (500 μL) at room temperature for 12 h in dark. The DEDP extract was set to pH 5 before drying. The conditions of GC analysis were as follows: column capillary DB-1 J&W (30 m × 0.32 mm *i.d.* 0.25 μm); initial temperature of the column – 80 °C; gradient of temperature – 4 °C/min; final temperature – 270 °C; injector temperature – 240 °C; detector temperature – 250 °C.

Electrospray ionisation-mass spectrometry (ESI-MS; Micromass Q-TOF2 hybrid tandem mass spectrometer) was carried out in a negative mode after extract dilution (10%) in a mixture (1:1) of water and acidic methanol (0.1% formic acid). The samples were introduced at a flow rate of 10 μL/min into the electrospray source. In MS and MS/MS experiments TOF resolution was set to approximately 9000. The cone voltage was set to 30 V, and capillary voltage was maintained at 3 kV. Source temperature was at 80 °C and desolvation temperature at 150 °C. Tandem mass spectra were obtained using Ar as the collision gas and the collision energy was set between 25 and 45 V. The data was processed using MassLynx software (version 4.0).

3. Results and discussion

3.1. Brightness reversion of pulps bleached by ClO_2 and H_2O_2

The industrial pre-bleached DED eucalypt kraft pulp with 87.3% ISO brightness was submitted to bleaching either with chlorine dioxide (DEDD pulp) or with hydrogen peroxide (DEDP pulp) under laboratory conditions reaching 91 ± 0.5% ISO brightness. The analysis of brightness reversion of the two fully bleached pulps clearly indicated their distinct behaviour upon hydrothermal ageing at 70 °C, 30% pulp humidity for 5 days (Table 1). Although the degree of brightness reversion with these ageing conditions was much higher when compared to the conditions previously studied according to the TAPPI T 280 procedure (100 °C, 100% R.H., 1 h) (Loureiro et al., 2010), the differences between the DEDD and DEDP pulps are maintained. The final chlorine dioxide stage (DEDD) revealed almost twice the brightness reversion when compared to that obtained after a final hydrogen peroxide stage (DEDP).

As the brightness reversion did not correlate with the HexA content in pulps (Table 1), the contribution of other chromogen structures to the formation of chromophores in pulps during ageing may be anticipated. The different nature and the amount of oxidised structures induced by final bleaching with ClO_2 and H_2O_2 in pulps would be expected to predetermine their different response to ageing. Accordingly, a discrimination of the origin and the amount of degradation structures have been studied employing UV–vis DR and UV-RR spectroscopy in the solid-state and by the assessment of low-molecular weight products released from aged pulps by extraction with ethanol–water (1:1, v/v).

3.2. Analysis of pulps by UV–vis DR and UV-RR spectroscopy

The UV–vis DR and UV-RR spectra @ 325 nm of the DED, DEDD and DEDP bleached pulps before and after wet-thermal ageing (30% pulp humidity at 70 °C for 5 days) followed by extraction with ethanol–water (1:1) solution are presented in Figs. 1 and 2, respectively. As follows from the data presented in Fig. 1, the unsaturated structures in bleached pulps absorbing at ca. 225–325 nm are degraded upon ageing giving rise to new chromophores absorbing at higher wavelengths (ca. 350–600 nm) thus contributing to brightness reversion (yellowing). Consequently, the lower level of unsaturated structures absorbing at 225–325 nm in DEDP than in DEDD pulp pre-determines the higher brightness stability of the former. Due to the rather low amounts of HexA in DEDD and DEDP bleached pulps (Table 1) this structure unlikely contributes significantly to the absorption at 250–300 nm. Hence, trace amounts of residual oxidised lignin and of oxidised structures of polysaccharide origin remaining in pulp are expected to be responsible for brightness reversion.

The UV-RR spectra @ 325 nm (Fig. 2) shows an increased intensity signal at ca. 1600 cm^{-1} upon ageing assigned to polyunsaturated conjugated chromophore structures (Loureiro et al., 2010, 2011). This band at ca 1600 cm^{-1} is assigned to oxidised structures possessing carbonyl groups conjugated with unsaturated C=C moieties or with aromatic ring (Loureiro et al., 2011). Simultaneously, the signal intensity at 1093 and 1120 cm^{-1} in aged DEDD and DEDP pulps was decreased (Fig. 2). The last bands correlate with OCO groups, which are increased in oxidised polysaccharides due to the presence of hydrated carbonyl and carboxyl moieties (Loureiro et al., 2010) and indicate the decay of the corresponding structures upon ageing. Hence, the hydrothermal degradation of oxidised structures (chromogens) led to the formation of polyconjugated chromophore structures in pulps. Among other chromogen structures, the participation of intermediate furan-type structures derived from carbohydrate thermal degradation in the chromophore formation during pulp ageing is expected (Forsskahl et al., 2000; Kawae & Uchida, 2005; Theander & Nelson, 1988). In addition, the contribution of furan derivatives to the delay in brightness development during final chlorine dioxide bleaching has been also suggested (Loureiro et al., 2011).

Most part of the coloured matter could be removed from aged pulps by extraction with ethanol–water solution (Fig. 1), being in agreement with the results of previously published studies on aged pulp extraction by water (Granstrom et al., 2002) or methanol (Beyer et al., 2006). The UV-RR spectra revealed that the level of chromophores bearing conjugated carbonyl groups in aged pulp after extraction was restored to that observed before the wet-thermal treatment (Fig. 2).

It is noteworthy that the intensity of band at 1600 cm^{-1} in UV-RR spectra @ 325 nm of pulps was proportional to *k*/*s* at 325 nm in UV–vis DR spectra (Loureiro et al., 2011). The absorption at 325 nm in the UV–vis DR spectra always increased upon accelerating ageing when using the standard procedure with dry pulps (100 °C, 100% R.H.) (Loureiro et al., 2011). However, in the present study, dealing with the extraction of aged products, the ageing procedure was carried out with wet pulp (30% humidity and 70 °C) and, despite all precautions, led to some uncontrolled leaching of degraded matter. This was a reason for a small decrease of *k*/*s* at 325 nm in UV–vis DR spectra of aged DED pulp. This fact does not

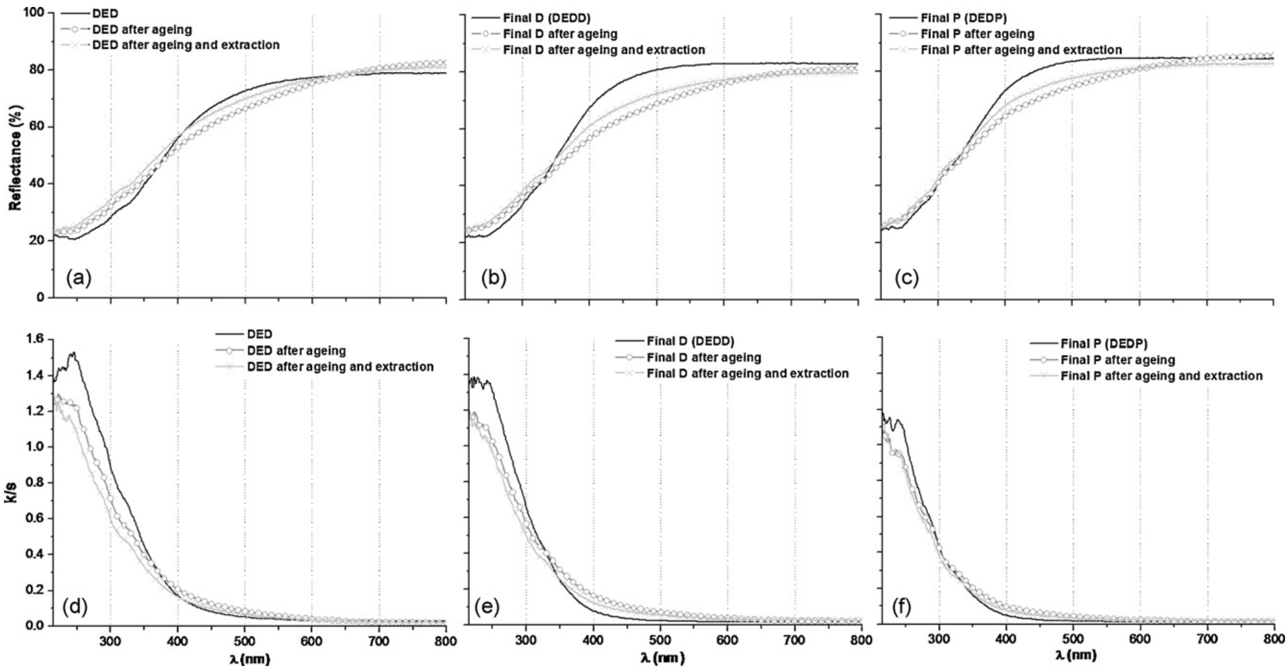

Fig. 1. UV–vis DR and corresponding *k*/*s* spectra of DED (a, d), DEDD (b, e) and DEDP (c, f) bleached pulps before and after the ageing and extraction with ethanol:water solution (1:1, v/v).

detract from the major conclusions made based on UV–vis DR and UV-RR spectra but did not allow quantitative assumptions. Additionally, the pH and the dryness of bleached pulps can affect the intensity of bands at 1600 cm^{-1} and at 1093/1120 cm^{-1} in the UV-RR spectra due to possible effect of charge transfer complexes (CTC) from oxidised structures in pulp (Loureiro et al., 2010) and therefore should be controlled while performing a quantitative analysis. The pre-selected conditions for the samples preparation, before the Raman spectra acquisition, included the adjustment of pulp suspension to pH 5 and the conditioning of air dried pulps at 50 °C for 1 h. Apparently, both effects (pH and dryness of sample) are related to the extent of the interconversion of carbonyl groups (sp^2-hybridised carbon, detectable at ca. 1600 cm^{-1} if polyconjugated) into corresponding hydrated analogs presented in sp^3-hybridised form and detectable at 1093 cm^{-1} (Loureiro et al., 2010). This interconversion must influence the CTCs involving these groups. The importance of the equilibrium between carbonyls and their hydrated forms (hemiacetals/hemiketals) in the chromophore detection under Raman resonance conditions have been also previously highlighted (Loureiro et al., 2010; Potthast, Rosenau, Kosma, Saariaho, & Vuorinen, 2005).

3.3. *Analysis of extracts from aged pulps*

3.3.1. *GC–MS analysis*

Firstly, the analysis of extracts from the aged pulps was carried out using GC–MS. The identified products are depicted in Table 2 and their relative intensities shown in Fig. 3 for the purpose of a qualitative analysis. A wide range of monocarboxylic and dicarboxylic saturated/unsaturated hydroxy acids arisen from degradation of carbohydrates have been detected. Most of them can form complexes with transition metals (Abrahamson, Rezvani, & Brushmiller, 1994; Pierre, Elkordi, & Cauquis, 1986) which are present in the pulp and thereby partially contributing to pulp yellowing upon ageing.

The 2-furoic acid (FA, **3**) is only detected in DED and DEDP extracts due to eventual degradation of the remaining HexA residues (Teleman, Hausalo, Tenkanen, & Vuorinen, 1996), which were present in those non-aged pulps in higher amount than in the DEDD pulp (Table 1). The DED extract revealed increased relative amounts of products **1**–**3**, **8** and **16**, while in the DEDD extract oxalic (**4**), glyoxylic (**6**), glyceric (**10**) and malic (**12**) acids were the prominent products.

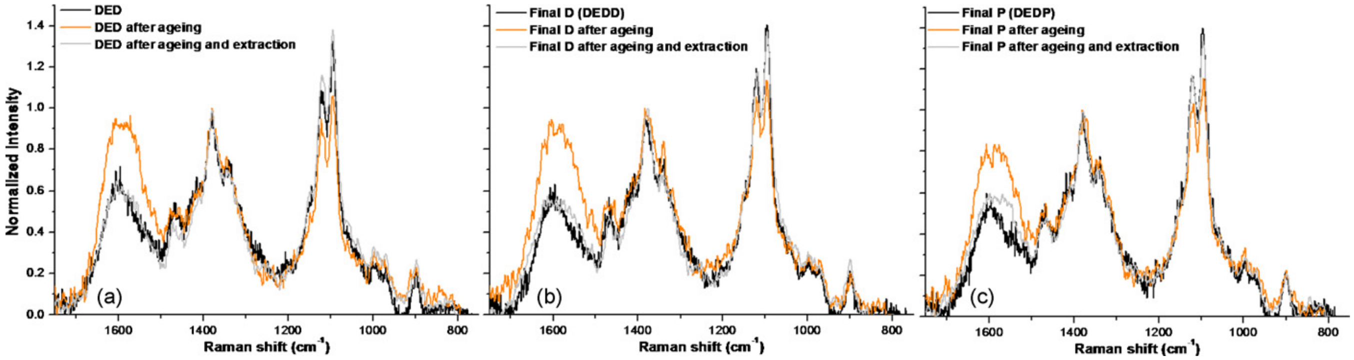

Fig. 2. UV-RR spectra of DED (a), DEDD (b) and DEDP (c) bleached pulps before and after the ageing and extraction with ethanol:water solution (1:1, v/v).

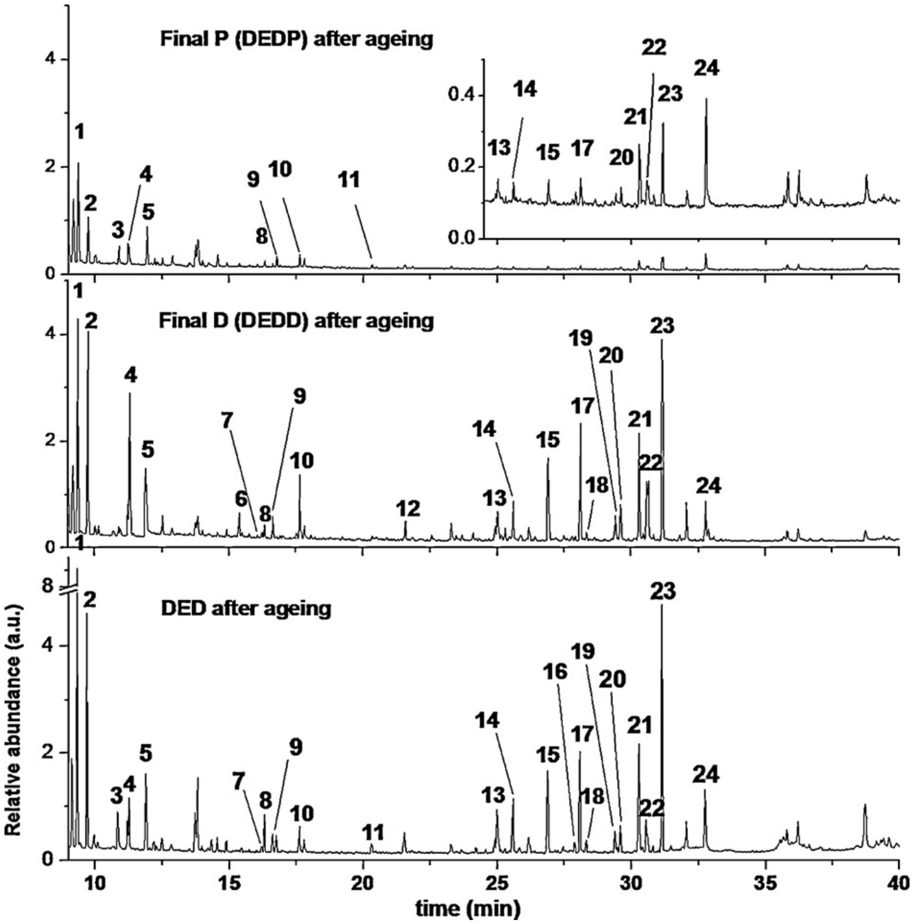

Fig. 3. Chromatograms of ethanol–water extractives (TMS-derivatives) from the aged DED, DEDD and DEDP bleached pulps.

3.3.2. *UV–vis absorbance, metal ions and molecular weight*

The DEDP extract had the lowest absorbance in its UV–vis spectrum (Fig. 4) and possessed the highest content of dry residue among all analysed extracts (Table 3). These features are mostly due to the increased amounts of inorganic salts (mainly sulphates) in the DEDP extract from the acidification with sulphuric acid for the pH adjustment before ageing. In fact, the DEDP bleached pulp showed an incomparably lower loss in intrinsic viscosity after both ageing and extraction steps when compared to the DED and DEDD bleached pulps (Table 1). This reflects a greater extent of oxidative reactions across the polysaccharides chains in final D (DEDD pulp) than in final P stage (DEDP pulps). Randomly oxidised polysac-

Table 2
Identified compounds in ethanol–water extracts from aged DED, DEDD and DEDP bleached pulps (analysed as TMS derivatives).

ID	Retention time (min)	Compound
1	9.35	2-Hydroxypropanoic acid (lactic acid)
2	9.72	2-Hydroxyethanoic acid (glycolic acid)
3	10.85	2-Furancarboxylic acid (furoic acid)
4	11.28	Ethanedioic acid (oxalic acid)
5	11.91	3-Hydroxypropanoic acid
6	15.37	Oxoethanoic (glyoxylic) acid
7	16.23	(*Z*)-Butenedioic acid (maleic acid)
8	16.32	Propan-1,2,3-triol (glycerol)
9	16.64	Butanedioic acid (succinic acid)
10	17.64	2,3-Dihydroxypropanoic acid (glyceric acid)
11	20.33	3,4-Dihydroxybutanoic acid
12	21.57	Hydroxybutanedioic acid (malic acid)
13	25.01	Arabinose
14	25.60	Arabinose
15	26.88	Xylose
16	27.90	Azelaic acid
17	28.11	Xylose
18	28.33	2-Keto-gluconic acid
19	29.37	Galactose
20	29.60	Galactose
21	30.30	Glucose
22	30.57	Glucose
23	31.16	Hexose
24	32.76	Hexadecanoic acid (palmitic acid)

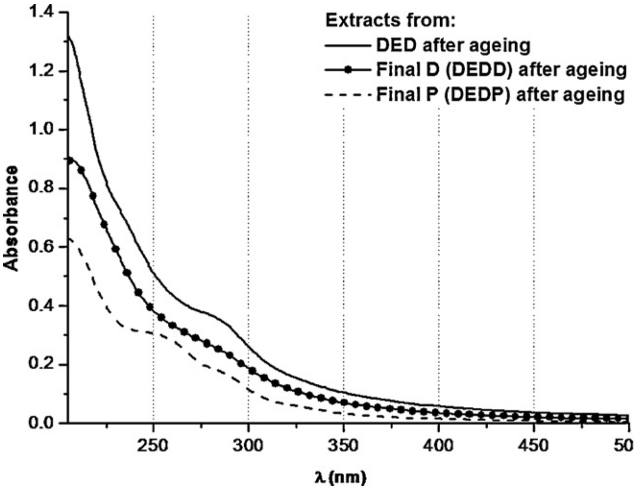

Fig. 4. UV–vis absorbance spectra of ethanol–water extracts from the aged DED, DEDD and DEDP bleached pulps.

Table 3
Results on metal ions and sulphates analyses in the extracts from aged DED, DEDD and DEDP bleached pulps.

Extract from aged pulp	Extract analysis							
	pH	Dry content (mg/L)	Metals (mg/L)[a]					SO_4^{2-} (mg/L)
			Fe	Cu	Na	Mg	Ca	
DED	5.0	120	0.23	0.54	7.96	0.24	0.60	7.81
DED**D**	3.7	170	0.26	0.31	6.29	0.12	0.40	61.01
DED**P**	2.5	720	0.24	0.20	9.51	0.22	0.94	547.81

[a] Manganese content below 0.015 mg/L.

charide chains in the D stage could suffer extensive cleavage of weakened glycosidic bonds promoted by acidic oxidation products (Krainz et al., 2009).

The carboxyl groups have a catalytic effect in ageing reactions (Beyer et al., 1999; Rosenau et al., 2008), as well as metal cations (Beyer et al., 1999; Granstrom et al., 2001, 2002; Logenius et al., 2008). It is worth noting the high relative content of released copper in DED and DEDD extracts (Table 3) that may either form coloured complexes with hydroxyl acids or catalyse the ageing reactions. On the other hand, the DEDD pulp could contain a certain proportion of degradation products from the preceding D stage (from DED pulps) that were not removed by washing.

The UV–vis spectra of aqueous ethanol extracts (Fig. 4) possessed typical patterns for dissolved lignin derivatives: characteristic maximum at ca. 280 nm, shoulder at ca. 245 nm and the intensive band at ca. 210 nm (Marques, Evtuguin, Magina, Amado, & Prates, 2009). However, no low molecular phenolic degradation products were detected by GC–MS and, therefore, the presence of some lignin oligomers in the extract may be anticipated. On the other hand, the random scission of polysaccharide chains upon ageing indicates the presence of oligomers among other reaction products. These assumptions were confirmed from the analysis of the extracts from aged pulps by ESI-MS (Fig. 5).

3.3.3. *ESI-MS analysis*

The ESI-MS spectra revealed a mixture of dissolved oligomers with molecular mass until 1500 Da in DED and DEDD extracts and till 700 Da in DEDP extract. The lowest abundance and diversity of oligomeric products were observed in extract from aged DEDP pulp. In terms of general patterns, ESI-MS spectra of DED and DEDD extracts were similar to that reported for the eucalypt lignin, whereas ESI-MS spectrum of DEDP extract was closer to the oligomers of carbohydrate origin (Marques et al., 2009). This may be explained, at least partially, by a more effective leaching of lignin-derived oligomeric compounds under the alkaline bleaching conditions of the final P stage than during the weakly acidic final D bleaching stage, thus explaining the lower abundance of oligomeric compounds in the extract from the aged DEDP bleached pulp. In this context, the removal of partially degraded thermally labile lignin-xylan complex during the alkaline P stage is predictable, thus explaining the much lower *k*/*s* decrease at ca. 225–325 nm in UV–vis DR spectra of the DEDP pulp than that of the DEDD pulp (Fig. 1). The extremely important contribution of xylan–lignin complex to the amount of chromogen/chromophore structures in eucalypt bleached pulps has been recently confirmed (Loureiro et al., 2010). This explains, to some extent, the significant diminishing of brightness reversion of eucalypt kraft pulp which was alkali-extracted before the final D stage (DEDED vs. DEDD) (Loureiro et al., 2011).

Unfortunately, the scarce knowledge on the structure of xylan–lignin complex did not allow some clear identification of corresponding oligomers in extracts from aged pulps. However, the signals at *m*/*z* 325, 375, 401, 875, and 1065 (among many others) in the negative mode ESI-MS spectra of DED and DEDD pulp extracts were previously found in kraft lignin-carbohydrate complex isolated from black liquor after eucalypt wood kraft pulping (Pinto, Evtuguin, Pascoal Neto, & Silvestre, 2002). The aforementioned signals were not detected in ESI-MS spectrum of the extract from DEDP pulp thus corroborating with the proposition about a more extensive removal of lignin-reach fraction from pulp during the final P stage.

Reliable assignments of several xylo-oligosaccharides (XOS) in extracts by ESI tandem mass-spectrometry (MS/MS) were possible based on previously reported database (Domingues & Evtuguin, 2001; Reis, Domingues, Domingues, Ferrer-Correia, & Coimbra, 2003). Thus, the series of acidic XOS were identified:

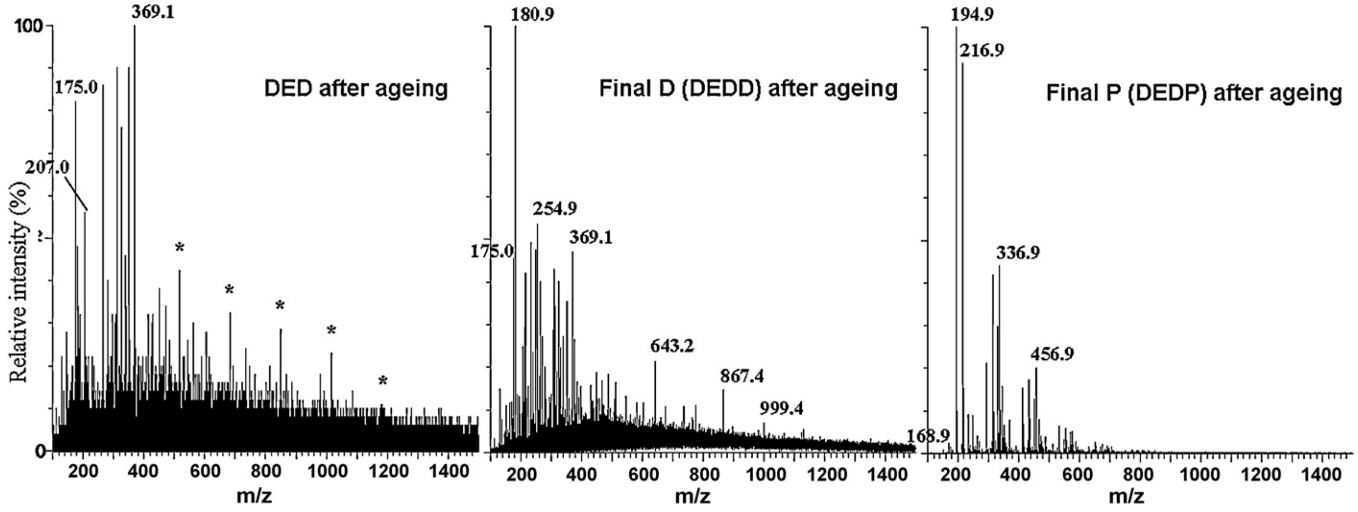

Fig. 5. Negative mode ESI-MS spectra of the ethanol–water extracts from the aged DED, DEDD and DEDP bleached pulps (*denotes contaminants).

4-methoxy glucuronic acid (MeGlcA, m/z 207.0), xylobiuronic acid (Xyl-MeGlcA, m/z 339.2) and its homologous series including Xyl_3-MeGlcA (m/z 603.2), Xyl_4-MeGlcA (m/z 735.3), Xyl_5-MeGlcA (m/z 867.4), and Xyl_6-MeGlcA (m/z 999.4). These findings are coherent with the known eucalypt heteroxylan structure that is basically O-acetyl-(4-*O*-methylglucurono)xylan (Evtuguin, Tomas, Silva, & Neto, 2003). The signals at m/z 111.1 and at m/z 175.0 were assigned to 2-furoic and HexA acids, respectively (Domingues & Evtuguin, 2001). The ESI-MS spectrum of the DEDP extract also exhibited abundant ions at m/z 216.9, 336.9 and 456.9. These ions were difficult to fragment in MS/MS experiments even at a very high collision energies (>40 V), but showed the losses of 120 Da from molecular ion, typical for the cross-ring fragmentation of pyranosyl ring (Reis et al., 2003). These signals were assigned to the carbohydrate-derived adducts with iron $[\text{M+Fe}-\text{H}]^-$. Thus the presence of transition metals in extracts complicated significantly the spectra patterns.

Regarding the eventual contribution of oxidised carbohydrates to the polyunsaturated chromophore structures detected in aged pulps (Figs. 1 and 2), different furan derivatives are produced under carbohydrate hydrothermal decay (Bikova, Belkova, & Treimanis, 2005; Popoff & Theander, 1972; Teleman et al., 1996; Theander & Nelson, 1988). Furans form linear or cyclic furan-derived oligomers via aldol condensation reaction and are typical chromophores (Beyer et al., 2006, 1999; Gandini & Belgacem, 1997). Hence the furan-derivatives should also contribute to oligomeric products detected in ESI-MS spectra. Among furan derivatives the furoic acid was the only unambiguously identified.

Reductic acid (2,3-dihydroxy-2-cyclopenten-1-one) is a recognised chromophore formed from uronic moieties and ketoglycosides under acidic treatment (Popoff & Theander, 1972) and has been also identified as an ageing product of bleached pulps (Beyer et al., 2006; Sevastyanova, Li & Gellerstedt, 2006). Reductic acid was not clearly identified by GC–MS among degradation products in extract as TMS derivative but its presence is suspected as an iron complex (m/z 168.9) and was detected in DEDP extract (Fig. 5). Reductic acid participates in condensation reactions with furan derivatives (Beyer et al., 2006) and, being complexed with iron, is a strong chromophore. Iron is also well known to be strongly bound to pulp in view of their persistence in pulps during bleaching and chelation stages (Sillanpaa & Ramo, 2001).

Low molecular weight degradation products formed during pulp ageing may suffer condensation reactions leading to the formation of aromatic structures (Popoff & Theander, 1972; Rosenau et al., 2007; Theander & Nelson, 1988). Dihydroxyacetophenone (Popoff & Theander, 1972) and hydroxybenzoquinone-type structures (Rosenau, Potthast, Kosma, Suess & Nimmerfroh, 2007) were detected among ageing products of bleached pulps and may be considered as strong chromophores. However, during this work these aromatic monomer structures were not clearly detected either by GS–MS or ESI-MS.

4. Conclusions

The significant difference in wet thermal brightness reversion between DED pulps bleached by a final hydrogen peroxide (DEDP) or chlorine dioxide (DEDD) stage is the result of a distinct amount of partially degraded polysaccharides and of xylan–lignin complex involved in the hydrothermal decay. This is reflected in the decrease of absorption in the UV–vis DR spectra of aged pulps at ca. 225–300 nm and the appearance of new chromophore structures absorbing at longer wavelengths including the visible region.

The content of partially oxidised structures was significantly higher in the DEDD than in the DEDP bleached pulp thus predetermining the worst brightness stability of the former. However, the amount of oxidised structures in pulp is not exclusively the result of a particular bleaching reagent (degree of induced oxidative degradation) but rather the consequence of retention of these degraded structures in pulp under specific bleaching conditions. Under the alkaline conditions of the final peroxide bleaching the major part of degraded oxidised compounds are leached from the pulp thus diminishing their contribution to the formation of chromophores during subsequent ageing. The low molecular weight products of carbohydrate origin arisen during pulp ageing (hydroxyacids, mono/dicarboxylic saturated/unsaturated acids, ketoacids, furan derivatives, etc.) are strong contributors to pulp yellowing, especially while complexing with transition metals (primarily ferrous salts). In this context the profile of metal ions in pulps is another important factor to consider.

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