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DISSERTATION

INTEGRATED MASTER IN CHEMICAL ENGINEERING

SUPERVISORS

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A thesis submitted to the FACULTY OF SCIENCES AND TECHNOLOGY of the UNIVERSITY OF COIMBRA in partial fulfilment of the requirements for the equivalence to the degree of Integrated Master in Chemical Engineering

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ABSTRACT

Brightness stability is a very important property of beached cellulosic pulps. The impact of the final bleaching stage is assessed in this study for the purpose of understanding the fundamental reasons behind the improved brightness stability of bleached eucalypt pulp when the conventional chlorine dioxide stage (D) is replaced by an alkaline hydrogen peroxide stage (P). Particular emphasis was devoted to the role of xylan because within the fibrous structure this component has higher accessibility to brightening agents.

Isolated xylans from partially (DED) and fully (DEDD/DEDP) bleached eucalypt kraft pulps were characterized using ^{1}H NMR, UV-Vis in cadoxen solutions, size exclusion chromatography and UV-Resonance Raman spectroscopy @ 325 nm. Comparative analysis was done for xylan isolated from partially bleached pulp (DED) and subjected to treatment either with chlorine dioxide or alkaline hydrogen peroxide under the same final bleaching conditions. Chlorine dioxide final stage induced new unsaturated moieties in xylan structure, while hydrogen peroxide was very effective in the removal of xylan-related chromophores. The role of xylan to the delay of brightness development in the final chlorine dioxide stage was highlighted.

UV-vis Diffuse Reflectance and UV Resonance Raman micro-spectroscopy were employed to evaluate the differences on chromophores formation/degradation in fully bleached eucalypt kraft pulp upon both final 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 oxidized carbohydrates and of the residual lignin structurally associated to xylan in ageing reactions. A part of the new formed chromophores was the result of iron complexes with ageing products. The leaching of degradation products from pulp in the alkaline peroxide stage was suggested to be a crucial factor that predetermined its lower brightness reversion over the pulp bleached under the weakly acidic chlorine dioxide stage.

RESUMO

A estabilidade da brancura é uma propriedade muito importante das pastas celulósicas branqueadas. O impacte do estágio final de branqueamento foi avaliado com o objectivo de entender as razões do ponto de vista fundamental que expliquem a superior estabilidade de brancura de pastas de eucalipto branqueadas quando o estágio convencional com dióxido de cloro (D) é substituído por um estágio alcalino de peróxido de hidrogénio (P). Foi dado um ênfase particular ao papel da xilana pois, inserida na estrutura fibrosa, é o componente com maior acessibilidade aos agentes de branqueamento.

Xilanas isoladas de pastas kraft de eucalipto parcialmente (DED) e totalmente branqueadas (DEDD/DEDP) foram caracterizadas por espectroscopia ^{1}H NMR, UV-vis em soluções de cadoxeno, cromatografia de exclusão molecular e espectroscopia de Raman no UV com efeito ressonante aos 325 nm. Uma análise comparativa foi realizada entre a xilana isolada da pasta parcialmente branqueada (DED) e posteriormente branqueada com dióxido de cloro ou com peróxido de hidrogénio alcalino com as mesmas condições utilizadas no branqueamento final das pastas. O dióxido de cloro como estágio final introduziu novas estruturas insaturadas na xilana, enquanto o peróxido de hidrogénio foi eficiente na remoção de estruturas cromóforas da xilana. O papel da xilana no retardamento do desenvolvimento de brancura no branqueamento final com dióxido de cloro foi evidenciado.

Espectroscopia UV-vis de reflectância difusa e de Raman no UV com efeito ressonante foram aplicadas na avaliação das diferenças na formação/degradação de cromóforos em pastas de eucalipto branqueadas após ambos os estágios finais. Estes dados foram complementados com análises de química húmida e de espectrometria de massa dos produtos de degradação obtidos durante o envelhecimento hidro-térmico das pastas branqueadas. Estas análises revelaram o papel importante dos hidratos de carbono e da lenhina residual associada estruturalmente à xilana nas reacções de envelhecimento. Parte dos novos cromóforos formados resultam da complexação de ferro com os produtos de degradação provenientes do envelhecimento. A lixiviação de produtos de degradação da pasta durante o estágio de peróxido de hidrogénio alcalino foi sugerida como um factor crucial que predeterminou a menor reversão de brancura comparativamente à pasta branqueada com dióxido de cloro.

CONTENTS

I. INTRODUCTION

The International Pulp Bleaching Conference (IPBC) held since 1955 can be considered as a mirror of the progress in pulp bleaching technology[1]. The latest IPBC was held on October 5-7, 2011, in Portland, OR, USA, succeeding to the joint TAPPI PEERS (Pulping, Engineering, Environmental, Recycling and Sustainability) Conference (October 2-5)[2]. In general, the presented studies confirmed that the advances in the pulp bleaching field have been more incremental than radically new over the last years. This steady-state scenario reflects the sound environmental performance of the prevailing elemental chlorine free (ECF) bleaching technology mainly based on chlorine dioxide[3]. In fact, the environmental regulations that served in the past (1985-1995) has the key driving forces to breakthrough innovations in the pulp bleaching process are no longer dictating research trends[3]. Besides the minimization of environmental impacts, new mills are also focused into the maximization of energy efficiency, improvement of product quality and optimization of capital and operating costs[4].

Although the pulp bleaching process is presently considered a mature technology, many unresolved questions remain. More in depth studies towards the use of much fewer stages and/or new designs and concepts along with less energy, water and chemicals consumption are still needed as remaining challenges[3]. In fact, the mainstream topic in pulp and paper research has been directed into the biorefinery concept and hence a considerable amount of effort was displaced from more conventional research areas as pulp bleaching. However, like most developments in pulp and paper production, the introduction of the biorefinery concept should be conceived in an integrated way. Not surprisingly, one new topic in the last IPBC program was dedicated to "Bleaching and the Biorefinery"[2]. Nonetheless, the published results comprising this integrated biorefinery-pulping/bleaching perspective have rendered new opportunities in pulp bleaching research.

One recognized finding in this new research context was that the pre-hydrolysed chips were easier to delignify and to bleach by chorine dioxide[5-7]. This positive impact on pulp bleachability of the fully bleached pulp was linked to the extraction of hemicelluloses prior to the pulping process, within the so-called pre-hydrolysis step. The improvement in the bleachability of pre-hydrolysed pulps was proposed to be due to a lower molecular weight of lignin and/or to a lesser amount of lignin-carbohydrate linkages as a result of the extensive

removal of hemicelluloses during pre-hydrolysis and subsequent pulping[7]. In the case of eucalypt pulps similar results were attained with the additional finding of a decrease in brightness reversion[5,6].

One topic that is commonly recognized to be poorly understood is the role of lignin-carbohydrate complexes (LCCs). This is a remaining issue to be better investigated towards technical advances in different stages of bleached pulp production. These knowledge gaps entail problems with the separation/fractionation of pulp components not only within these new biorefining processes[8] but also considering the existing pulping and bleaching technologies[9,10]. In fact, almost all lignin was shown to be covalently linked either to glucomannan or to xylan in wood[9] and kraft pulp[11,12]. In the case of eucalypt pulps, which are presently the most important source of bleached market pulp in the world[13], the main hemicellulose is xylan and therefore special attention should be devoted to this component and its association with lignin[14]. In fact, these xylan-lignin condensed structures can survive the whole bleaching process thereby contributing to the delay of brightness development (chromophores removal) and also to a decreased brightness stability of the bleached pulp[14,15]. Besides the known alkaline stability of benzyl ether bonds between lignin and carbohydrates, there is the additional formation of lignin-carbohydrate linkages during the alkaline pulping process[10,16].

The aforementioned pre-hydrolysis step is similar to the inclusion of an acidolytic stage in chemical pulp bleaching as proposed very recently[17]. This acidolytic treatment at 110 ºC was suggested to cleave benzyl sugar ethers thus enabling a boost in final brightness[17]. On the other hand, this is in good agreement with the previously identified role of xylan as a source of chromophores at the final stages of eucalypt pulp bleaching[14]. Using UV-Resonance Raman (UV-RR) spectroscopy, these remaining chromophore structures were specifically identified as polyunsaturated structures belonging to the xylan-lignin complex[14,15]. Conversely, although using a milder temperature of 95 ºC in a more extended (180 min) acidic washing stage (A), D_0(EOP)D_1AP bleached eucalypt pulps possessed a remarkable brightness stability[18]. This was assigned to the probable hydrolysis of the remaining hexeneuronic acid (HexA) residues in xylan and mostly other unsaturated chromogen structures present in pulps of low degradation rate[18].

In this study it is grasped this opened opportunity to further understand the role of xylan in the final bleaching of Portuguese *Eucalyptus globulus* kraft pulps. At the final stages of the bleaching process cellulose and hemicelluloses are especially vulnerable to oxidation with bleaching reagents. Therefore, the brightness gain and reversion are also expected to be

sensitive to the oxidation patterns of carbohydrates with these chemicals. Owing to the conspicuous differences in brightness reversion between $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps, without correlating to their HexA content[14], these eucalypt pulps were selected as a final bleaching case-study.

This thesis is divided into one introduction section covering a short description of bleaching nomenclature and final bleaching trends which is then followed by some fundamentals on the wood chemical composition and focusing on the chemistry of polysaccharides and lignin-carbohydrate complexes. The subsequent chapter is devoted to the description of all experimental procedures that were utilized. The third chapter gathers all results obtained with their ensuing discussion. Finally, the main conclusions are given in the last chapter before the list of references that support this work.

Part of the results presented in this thesis has been published in the journal Carbohydrate Polymers:

- Loureiro PEG, Domingues MRM, Fernandes AJS, Carvalho MGVS, Evtuguin DV. Discriminating the brightness stability of cellulosic pulp in relation to the final bleaching stage. Carbohydrate Polymers 88(2): 726-733 (2012); doi:10.1016/j.carbpol.2012.01.024.

II. EUCALYPT PULP BLEACHING AND CHEMISTRY

The pulp bleaching process is a multi-stage technology for the purpose of increasing the reflectance of visible light from the wood pulp. Following the wood pulping process (mainly kraft cooking) and using more selective chemicals, it promotes the removal of residual lignin in the first stages (delignifying stages) and then continues with the degradation of the residual chromophores at the final stages (brightening stages)[19,20].

Each stage of the pulp bleaching process has an assigned notation in accordance with a standard protocol such as the TAPPI Technical Information Sheet (TIPS) TIP 0606-21 "Recommended pulp bleaching stage designation method"[19]. In Table I it is presented the description of the main reagents utilized in wood pulp bleaching along with their stage-designations.

Table I. Description of typical pulp bleaching reagents and their corresponding stage-designations (adapted from[19-21]).

BLEACHING REAGENT	CHLORINE CONTAINING			CHLORINE FREE			
	Chlorine Cl_2	**Chlorine dioxide** ClO_2	**Hypochlorite** NaOCl	**Hydrogen peroxide** H_2O_2	**Peracetic acid** CH_3COOOH	**Oxygen** O_2	**Ozone** O_3
Stage designation	C	D	H	P	Paa	O	Z
Type of reaction	electrophilic		nucleophilic		electrophilic		
pH	acid		alkaline		acid	alkaline	acid
No. of e^- transferred (e^- mol^{-1})	2	5	2	2	2	4	6
reaction sites	olefinic; aromatic; HexA	free phenolic; double bonds; HexA	carbonyl groups; conjugated double bonds		olefinic; aromatic; HexA	free phenolic; double bonds	olefinic; aromatic; HexA

II.1. Final bleaching

Although the chemistry and technology of the final bleaching stages is of paramount importance for the quality standards of the bleached pulp (e.g., strength and optical properties), it is one of the less investigated areas in bleached pulp production. This can be explained by the difficulties in the assessment of the nature of the remaining chromophores at the last stages of the bleaching process and thus the absence of a clear and defined strategy to get rid of the residual chromophores. Considering the widespread utilization of ECF bleaching, chlorine dioxide is very often the only available solution. However, in spite of the extraordinary performance of this chemical in terms of bleaching selectivity, it may not be the best final bleaching option[22]. Only recently, the importance of optimizing the final D-stage regarding the relationship between bleaching pH and brightness gain has been recognized[23,24]. The near-neutral final chlorine dioxide brightening process, under buffered conditions, was claimed to be most effective than the more conventional acidic D-stage[23,25].

As a different alternative to chlorine based chemicals, the utilization of alkaline hydrogen peroxide bleaching (P stage) is now established as an efficient final bleaching option mainly in terms of chromophores removal[14,26]. In particular, eucalypt kraft pulps ECF bleached with a final P stage exhibit much higher brightness stability, when compared to pulps bleached with a conventional D stage[14,26-29]. Moreover, the bleached pulp has improved refinability and higher tensile strength[28,29]. Consequently, sequences as A/D(EOP)DP and D_{HT}(EOP)DP are now established in eucalyptus pulp bleaching being the A(EOP)DP sequence the best from the standpoint of chlorine dioxide consumption[30].

Besides DD and DP, other final bleaching strategies recently studied comprise PaaP, ZP[31,32], D/Paa[33,34] and (PO)Paa[33] stages. In the bleaching of a softwood kraft pulp Z/P final stages produced the best results regarding high brightness with low reversion followed by D/P and then Paa/P[32]. In general the final Paa stage in the ECF bleaching of eucalypt pulps exhibited a boost in final brightness with no significant effect on brightness reversion and a slight viscosity drop[33].

II.2. Cellulose and Xylan

The woods used in the industrial production of cellulosic pulp can be classified as hardwoods or softwoods, either derived from gymnosperm or angiosperm trees, respectively[35]. Among hardwoods, the *Eucalyptus globulus* is the main wood utilized in the Iberian Peninsula for the production of pulp and paper products. Compared to other hardwood species, including within the genus *Eucalyptus*, the *E. globulus* wood is recognized to possess a superior technical performance during kraft pulping[36,37] and in pulp bleaching[36] processes. These differences in response among species are known to be affected by morphology, density and chemical composition of the wood[38] and thus are intimately related to the structural features of the biopolymers that compose this raw material[36,39].

The proportions of the main chemical constituents of softwoods and hardwoods vary in the approximate ranges presented in Table I, where it is also shown the corresponding values for *E. globulus*[35]. In fact, it is observed that the latter has a relative low content of lignin and a high content of cellulose compared to most species, though chemical composition within the same species is also variable.

Table II. Approximate ranges of the contents of the main chemical constituents of softwoods and hardwoods and of *Eucalyptus globulus* (values as % of the dry wood weight)[35].

Wood species	Lignin	Cellulose	Glucomannan	Glucuronoxylan	Other polysaccharides	Extractives
Softwood	27-32	33-42	14-20	5-11	3-9	2-5
Hardwood	21-31	38-51	1-4	14-30	2-4	1-5
E. globulus	21.9	51.3	1.4	19.9	3.9	1.3

The main structural component of the wood is cellulose (Fig. 1), a linear homopolysaccharide composed of D-glucopyranose units linked together by β-(1→4) glycosidic bonds. Hemicelluloses are the second most abundant polysaccharide and, in general, are branched heteropolysacharides. Their monomer constituents may consist of hexoses, such as D-glucose, D-mannose and D-galactose and/or pentoses, such as D-xylose and L-arabinose, in addition to acidic residues, such as 4-*O*-methyl-D-glucuronic acid and D-galacturonic acid, and small

amounts of deoxyhexoses (L-rhamnose and L-fucose)[35,40].

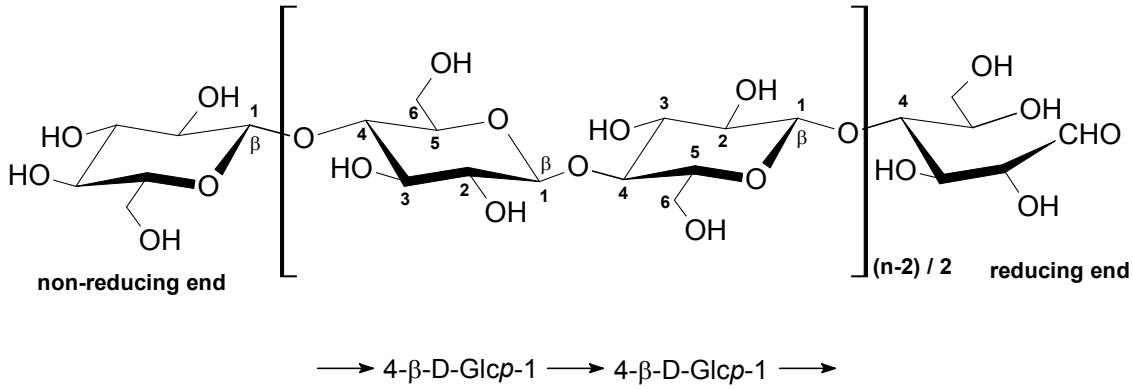

Figure 1. Structure of cellulose. The repetition unit (cellobiose) is composed of two β-D-glucopyranose (Glc*p*) units with the corresponding abbreviated formula below.

As D-xylose is the main sugar residue of hardwood hemicelluloses, they are named xylans. Xylans possess a (1→4)-linked β-D-xylopyranosyl backbone usually substituted with sugar residues and *O*-acetyl groups. Hardwood xylans are composed of (1→4)-linked β-D-xylopyranosyl backbone with the main side group being 4-*O*-methyl-D-glucuronic acid (glucuronic acid). Although there are structural differences in terms of type and proportions of side groups, the main component is the *O*-acetyl-4-*O*-methylglucurono-β-D-xylan and hence hardwood xylan is classified as glucuronoxylan (Fig. 2)[35,41].

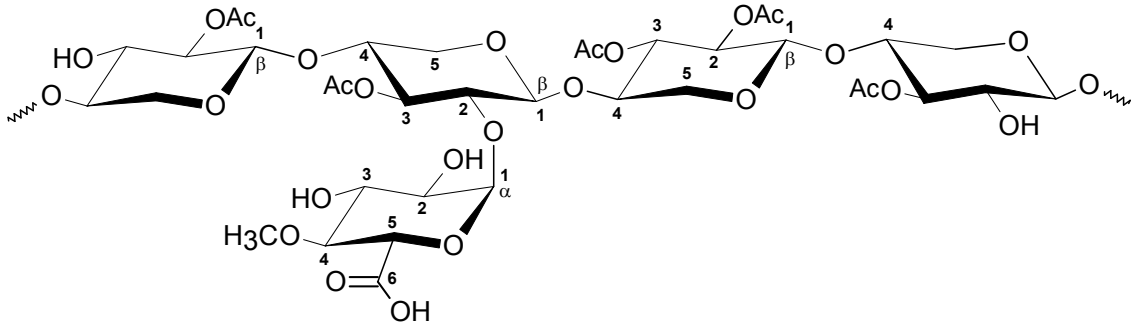

Figure 2. Principal structure of glucuronoxylan bearing the main units: β-D-xylopyranose (Xyl*p*); 4-*O*-methyl-α-D-glucopyranosyluronic acid (Glc*p*A); Ac is the acetyl group (CH_3CO).

The typical proportion of *O*-acetyl groups at C-2 or C-3 positions of the xylopyranosyl ring is of 70% of the xylosyl residues[35,42]. However, these groups are easily cleaved under alkaline

conditions[35,43]. As for the (1→2)-linked 4-*O*-methyl-α-D-glucuronic acid residues the average value is of 10% side groups along the xylopyranosyl backbone. The 1,2 linkage between the uronic acid side group and the xylose unit is very resistant whereas the xylosidic ether linkages are easily hydrolyzed under acidic conditions[35].

The heteroxylan of *Eucalyptus globulus* grown in Portugal reveals a peculiar chemical composition (Fig. 3). This hemicellulose is a (2-*O*-α-D-galactopyranosyl-4-*O*-methyl-α-D-glucurono)-D-xylan. The (1→4)-linked β-D-xylopyranosyl backbone is branched by (1→2)-linked side chains composed of 4-*O*-methyl-α-D-glucuronic acid, either terminal or substituted at O-2 with α-D-galactose. About 30% of the 4-*O*-methyl-α-D-glucuronopyranosyl residues exhibit this substitution[44]. Practically 50% of the β-D-xylopyranosyl residues are acetylated at O-3 (34%), O-2 (15%) or O-2,3 (6%). The 10% β-D-xylopyranosyl residues with terminal (1→2)-linked 4-*O*-methyl-α-D-glucuronic acid were acetylated at O-3[43].

In addition, the more intact *E. globulus* xylan, isolated with Me_2SO (DMSO), contained about 70% of the D-glucopyranosyluronic residues substituted by (1→2)-linked galatopyranosyl (Gal*p*) units and about 30% by glucopyranosyl (Glc*p*) units. It was also revealed a terminal structural fragment, in the same proportion as the non-reducing end-groups, composed of [→3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*A-(1→4)-β-D-Xyl*p*][43], similar to previous findings in birch xylan[35].

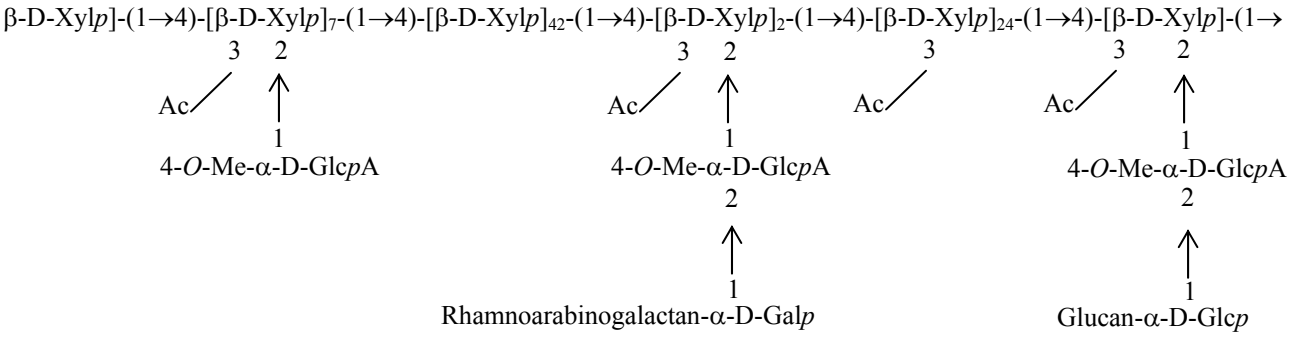

Figure 3. Abbreviated formula of the glucuronoxylan from *E. globulus* wood[43].

II.3. Lignin-carbohydrate bonds

The other major macromolecular component in wood is lignin. This is a highly heterogeneous branched polymer made of phenylpropane units. Besides variations in the content of lignin according to the type of wood (Table II), the chemical composition and the main types of linkages between their building blocks also depend on the wood species. In general, for softwood lignins the main monomer is coniferyl alcohol while hardwood lignins are comprised of both coniferyl alcohol and sinapyl alcohol. Aromatic rings having one methoxyl group (OCH_3) on C-3 position are usually referred as guaiacyl units, whereas syringyl units are those having two methoxyl groups at C-3 and C-5 positions (Fig. 4). The linkages between the sub-units are carbon-carbon (e.g. 5-5, β-5, β-1 and β-β) and mainly ether (e.g., β-*O*-4, α-*O*-4 and 4-O-5) bonds[35,45-47].

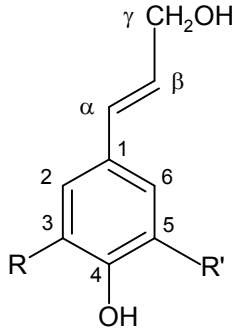

Figure 4. Basic building block of lignin. I) R = R' = H, *p*-coumaryl alcohol (compression wood); II) R = H, R' = OCH_3, coniferyl alcohol (hardwoods and softwoods); III) R = R' = OCH_3, sinapyl alcohol (hardwoods).

The existence of lignin-carbohydrate covalent bonds or the so-called lignin-carbohydrate complex (LCC), as first referred by Bjorkman[48], has been studied continuously but with uncertainties regarding the type, frequency and amount of these bonded aggregates in woods and pulps[9,35,49]. The LCCs that have been reported are mainly covalently bonded aggregates of lignin and hemicelluloses (glucomannan and xylan). As reviewed by Watanabe[50,51], several types of lignin-carbohydrate bonds have been proposed, including:

- benzyl ether type between the α-hydroxyl group of a phenylpropane unit of lignin and a hydroxyl group of a carbohydrate unit;
- benzyl ester type between the α-hydroxyl group of a phenylpropane unit of lignin and the carboxyl group of a glucuronic acid residue;
- glycoside type between a alcoholic or phenolic hydroxyl group of a phenylpropane unit of lignin and a reducing end group of carbohydrates;
- acetal type between two hydroxyl groups from carbohydrates and the side-chain α-carbonyl group of a phenylpropane unit of lignin.

However, it was recently found uronic acid residues attached to the γ-position of the side chain, forming γ-ester LCC bonds instead of benzyl ester type[8,52]. Among the lignin-carbohydrate bonds referred in the literature, those of benzyl ester and ether types (Fig. 5) are often considered the most frequent type of linkages in the cell walls, which in turn are closely related to the biosynthesis of lignin. However, benzyl esters are labile under the alkaline pulping conditions and thus are easily cleaved[9,50,51,53,54]. In contrast, benzyl ether type linkages of LCCs with a *p*-etherified aryl group (non-phenolic units) remain after kraft pulping and are considered the key-responsible for the decrease of the degradation rate of lignin in the final stage of delignification (Fig. 6)[50].

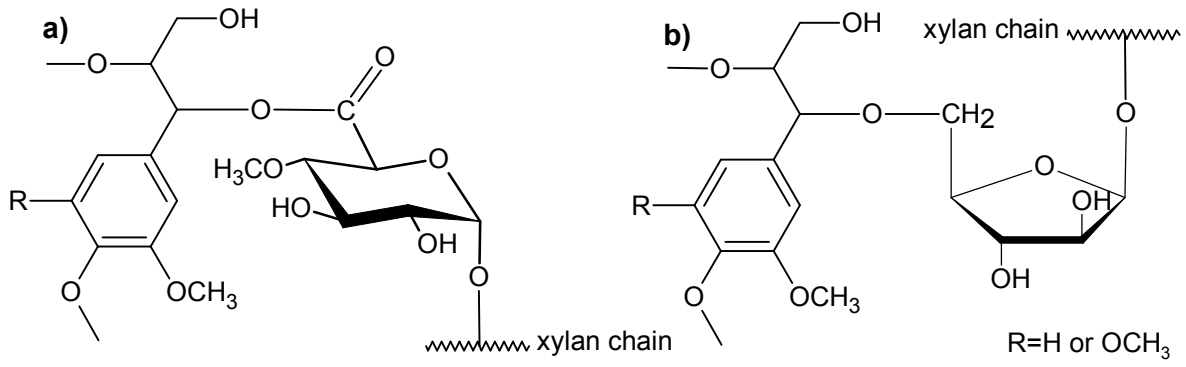

Figure 5. Proposed structures of lignin-carbohydrate complexes: **a)** benzyl ester type and **b)** benzyl ether type (adapted[35,55]).

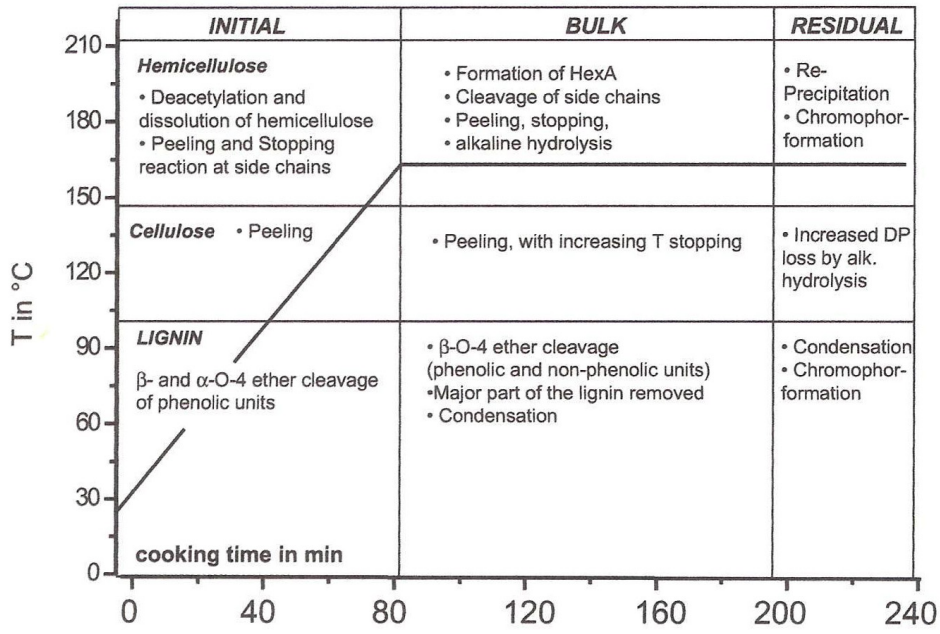

Figure 6. Overview of reactions during kraft pulping[56].

On the other hand, besides natural LCCs there are the regenerated LCCs during the pulping process. It was previously proposed the formation of LCC bonds by aldol condensation and benzylic acid rearrangement during the conditions of the kraft pulping process[16]. In fact, as previously introduced, almost all residual lignin (*ca.* 90%) in kraft pulp was found to be chemically linked to the polysaccharide component and for the most part with hemicelluloses[12]. Those remaining alkali-stable linkages in LCCs, also perceived as amphipathic substances, are thus considered to affect pulp bleachability and to be the main origin of the residual chromophores in kraft pulp[50]. Besides these xylan-lignin derived chromophores, there is the additional role of alkali-resistant heteroaromatic-derived chromophores in kraft pulp xylan which are formed under the severe pulping conditions[57].

In fact, the formation of chromophores during kraft delignification (Fig. 6) is well acknowledged seeing that the pulp specific absorption coefficient increases compared to that of the original wood sample. Proposed chromophores include a series of lignin derived chromophores (arylcoumarones, stilbene quinones, *o*-quinone structures, metal-catechol complexes etc.) and also originated from the polysaccharide component[35,56]. The recognized low reactivity of kraft pulp lignin has been associated with its condensed structure and crosslinking with polysaccharides[35].

During the kraft cooking process, lignin and hemicelluloses may re-precipitate with decreasing pH in the last phase of delignification due to alkali depletion (Fig. 6). Moreover,

the dissolved polysaccharides, particularly eucalypt glucuronoxylan, may precipitate or be adsorbed at the fibre surface and thus affecting the wood pulp yield and pulp quality. It is known that the xylan structure affects the extent of adsorption[56]. In the case of *E. globulus* xylan, owing to its peculiar structure and high molecular weight (30-36 kDa), it is retained to a higher degree compared to other industrially important wood species[58]. However, it was recently found that xylan retention in pulp at the last phase of kraft pulping is mainly determined by solid-liquid phase equilibrium affecting xylan diffusion instead of the individual effect of the liquor pH[59]. Ensuring a high alkalinity towards the end of the kraft cooking is also important from the viewpoint of preventing an increased formation of stable lignin–carbohydrate complexes. Hence, it is straightforward to assume that the presence of alkali-stable chromophores based on LCCs play an important role in post-bleaching efficiency.

II.4. Brightness stability of bleached pulp: relationship with hemicelluloses

As depicted in Figure 7, chromophores are artificially created at the very first chemical processing stage, the kraft pulping. Only through the use of more selective chemicals in the following bleaching process the residual lignin and chromophores can be effectively removed and degraded and thus leading to the desired brightness development. However, during post-bleaching conditions the brightness of the bleached pulp can decline seriously at the drying section and during the storage and transportation of pulp bales, which is more important in the case of market pulp[60,61]. This phenomenon is brightness reversion and the extent of which affects the bleached pulp is governed by several factors, including the intrinsic chemical composition of pulp and external variables such as the temperature, moisture and, to a lesser degree, the effect of light. To mention that even in a conventional bleaching stage there is the possibility of brightness reversion due to uncontrolled depletion of bleaching reagent part way in the tower, thus reverting brightening development along the stage[62].

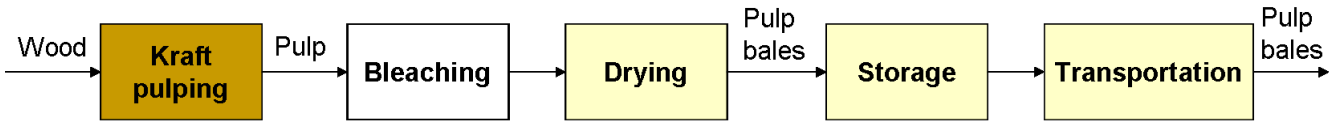

Figure 7. Simplified diagram of a kraft pulp fibreline representing stages where chromophores are created (yellowed blocks) and removed (bleaching).

The problem of brightness reversion of bleached chemical pulps has been earlier assigned to chromophore formation from almost all aforementioned pulp constituents[63]. Presently, the ageing reactions of either residual lignin or carbohydrates of bleached pulps are the main debatable causes for the reversion[64]. The pulp yellowing tendency has been also related to the amount of hydrolysable substances in bleached pulps arisen upon acidic pre-treatment[65]. Conversely, a great part of coloured matter produced during artificial ageing could be extracted by methanol[65] or even by water[66]. Such products resulted from the thermal decay of polysaccharide chains containing hydrolytically labile partially oxidized structural units containing carbonyl and carboxyl groups[65].

The enhancement of chromophores formation upon ageing has been previously evidenced by the deposition of models of oxidized carbohydrates or their conversion products, such as 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (furfural), over different cellulosic substrates[67-70] Moreover, the effect of transition metals in colour forming ageing reactions has been also confirmed[66,68,69,71,72].

The brightness reversion of bleached chemical puls is notoriously a rather complex subject and some contradictory findings can be related to the artificial ageing conditions applied (Fig. 8) and to the different origin and process history of bleached pulps. The desirable understanding and prediction of the ageing behaviour of materials has excited the interest of many research groups for a long-time. As regards bleached pulp brightness reversion a myriad of ageing procedures exists but no general method has been adopted by research groups[61,73]. In general, wet-thermal ageing is considered a more reliable method for measuring and predicting the brightness stability of kraft pulp, since both temperature and moisture have influence at the drying machine and shipment and storage of pulp bales where reversion mainly occurs (Fig. 7)[61]. In addition, one aspect poorly investigated regards the comparison between the bleached pulp behaviour under normal conditions of usage with the conditions of the accelerated ageing tests[74]. Because some ageing tests are performed at elevated

temperature and moisture contents it may not reflect the phenomena occurring during natural ageing[74,75].

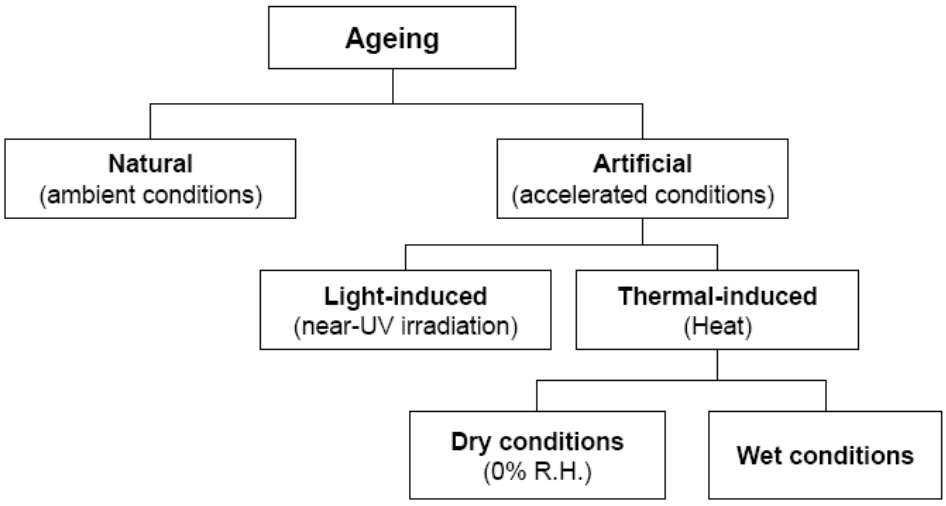

Figure 8. Overview of testing methodologies for the measurement of brightness reversion of bleached pulps (adapted from[60,74]).

It is commonly accepted that the bleaching history, and especially the final bleaching stages, affects seriously the brightness stability of pulps[76,77]. For example, although hexeneuronic acids (HexA) content has been shown to correlate with thermal yellowing of bleached pulps[78], in many other studies this fact was not confirmed[14,77,79]. 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[14].

In general, one main reason for this longstanding 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[26,80]. Bleaching chemistry of the final bleaching stages and its relationship with the gain and the stability of brightness are thus insufficiently studied.

The analysis of chromophores that have emerged during aging is essential for understanding the mechanisms of brightness reversion and to find technical solutions to overcome it. The analysis of chromophores in bleached pulps after ageing may involve their previous extraction and chemical characterization or, alternatively, be assessed in-situ. Just in recent times, the residual chromophores from bleached chemical pulps were isolated and characterized thus allowing the identification of the important chromophore structures in bleached eucalypt

pulps[26]. Particularly, an important structural moiety was identified in several residual chromophores, which was the 2-hydroxy-(1,4)benzoquinone. This structure exhibits a peculiar reactivity characterized by special stabilization by resonance and tautomerism as illustrated in Figure 9.

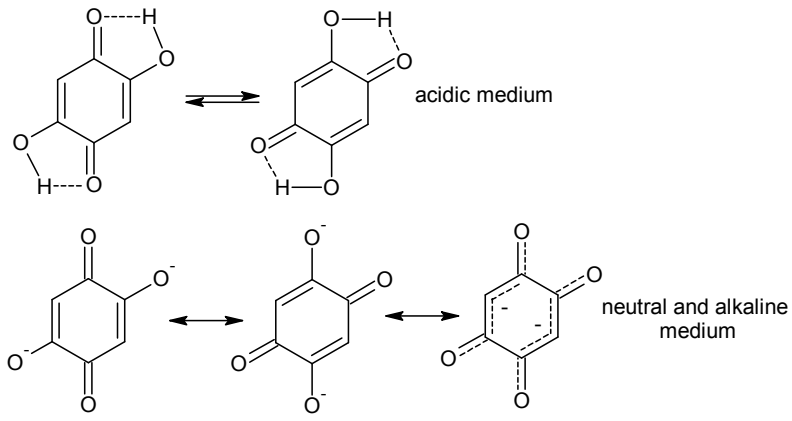

Figure 9. Stabilization of 2,5-dihydroxy-(1,4)benzoquinone.

The good brightening performance of DP final bleaching was explained by a synergistic effect of both stages through the removal of the special stabilization of 2-hydroxy-(1,4)benzoquinone structures. The D stage produces chloro-substituted derivatives without delocalized double bonds and thus become vulnerable to the final P stage[26].

The origin of 2-hydroxy-(1,4)benzoquinone structures was proposed to be from carbohydrates[26], similarly to Theander-type products[70,81]. These chromophores would be formed from oxidative degradation and re-condensation of degradation products of monosaccharides[26]. Just recently, the finding of the same compounds in lignin-free cotton linters confirmed their origin from (oxidized) carbohydrate structures rather than from lignin fragments[82]. However, in the case of wood pulps it is still not clear whether their main origin is cellulose or hemicelluloses[26,65].

In general, the role of hemicelluloses in the brightness reversion of bleached chemical pulps has been addressed in a number studies[65,83,84]. These previous efforts are not surprising seeing that this component contains the major part of oxidized groups in pulp, namely carboxyl groups, such as the native uronic acids and the artificially introduced hexeneuronic acids (HexA)[83,85]. In this context, the specific role of hexeneuronic acids on the brightness reversion of bleached pulps has been the subject of many studies and a positive correlation

between the amount of HexA and the extent of reversion have been obtained[78,86]. However, in other studies HexA content did not explain the differences in brightness reversion among ECF bleached pulps[14,27,79].

Hexeneuronic acid groups are formed during kraft pulping *via* demethylation of the native 4-*O*-methylglucuronic acid groups attached to the wood xylan backbone (Fig. 10). Their presence increases chlorine dioxide consumption in ECF bleaching and causes overestimation of the residual lignin in pulps by the kappa number test[87,88]. Because pulping temperature and alkaline profiles affect the HexA content (formation and degradation reactions), its variation in pulps can be significant, as demonstrated in *E. globulus* kraft pulps[89-91].

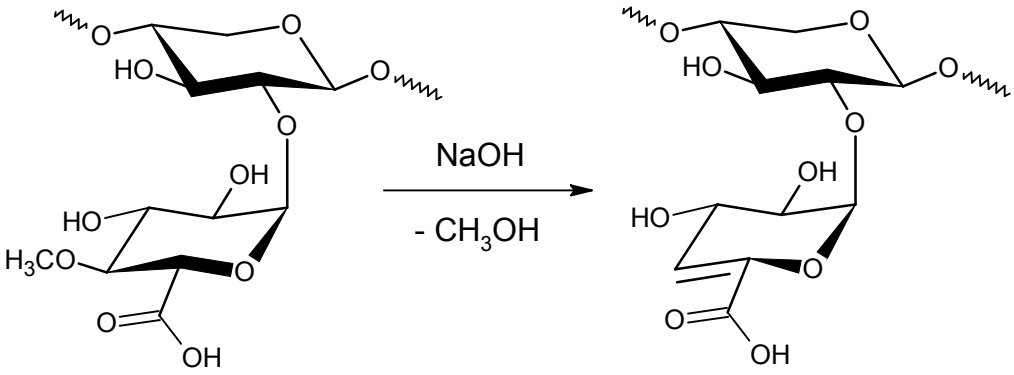

Figure 10. Alkali-catalysed reaction of 4-*O*-methylglucuronic acid group attached to xylan backbone resulting in the formation of 4-deoxy-L-*threo*-hex-4-enopyranosyluronic acid (HexA) group.

The role of either xylan or glucomannan in the brightness reversion of kraft pulps have been studied through the application of enzymatic treatments either with xylanase or mannase, respectively[83,84]. It was found a decreased of the content of carboxyl groups in pulps only in the case of hardwood pulps and xylanase treatment. The enzymatic removal of xylan had a superior effect on brightness stability (wet-thermal ageing) compared to that of glucomannan removal. Although the uronic acids were considered to participate in brightness reversion, at high brightness values and low uronic acids levels, their role was less obvious[83].

Considering the specific role of HexA, the beneficial use of a xylanase post-treatment in bleached hardwood kraft pulps on reducing brightness reversion was linked to the removal of HexA from the pulps[84]. Although only a part of HexA (about one third) could be accessible to the enzymatic degradation, the reduction of brightness reversion was significant. It was also suggested that the xylanase treatment on fully bleached pulps mainly removes HexA rather

than LCCs or re-precipitated xylan, which in turn could cause steric hindrance[84]. The corresponding proposed model for the improving effect of a xylanase treatment on the reduction of HexA-induced reversion of pulp is depicted in Figure 11.

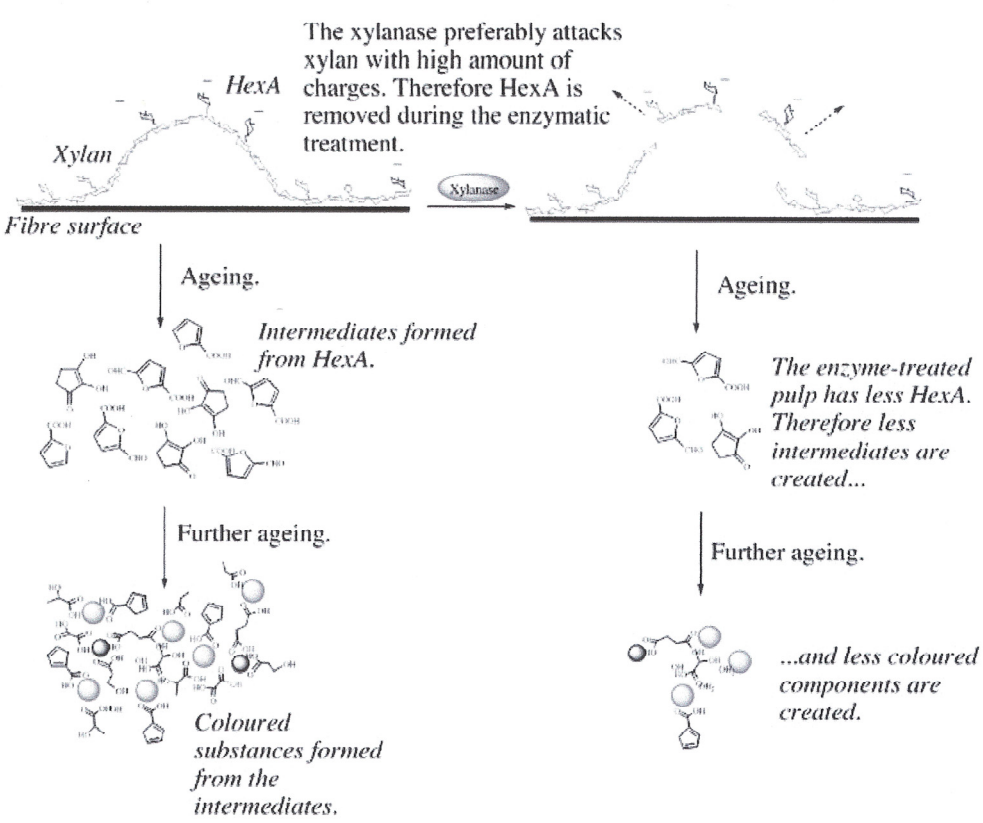

Figure 11. Proposed model for the improving effect of a xylanase treatment on the brightness stability of bleached pulp[84].

Although a xylanase post-treatment can be an interesting solution for the problem of brightness reversion, the cost of the enzyme, the potential yield loss and the eventual negative effect on the papermaking potential (due to xylan depletion) are factors to be considered[84]. The same type of compromise between costs and pulp quality stands for the adjustment of the bleaching sequence through the use of hot stages, powerful ozone bleaching or a final hydrogen peroxide stage[60,77].

The multi-factorial nature of pulp brightness reversion complicates the understanding of the phenomena and in finding solutions to tackle this puzzling problem. A schematic picture was proposed by Beyer et al.[71] showing some of the possible reaction pathways leading to brightness reversion of chemical pulps under wet-thermal conditions.

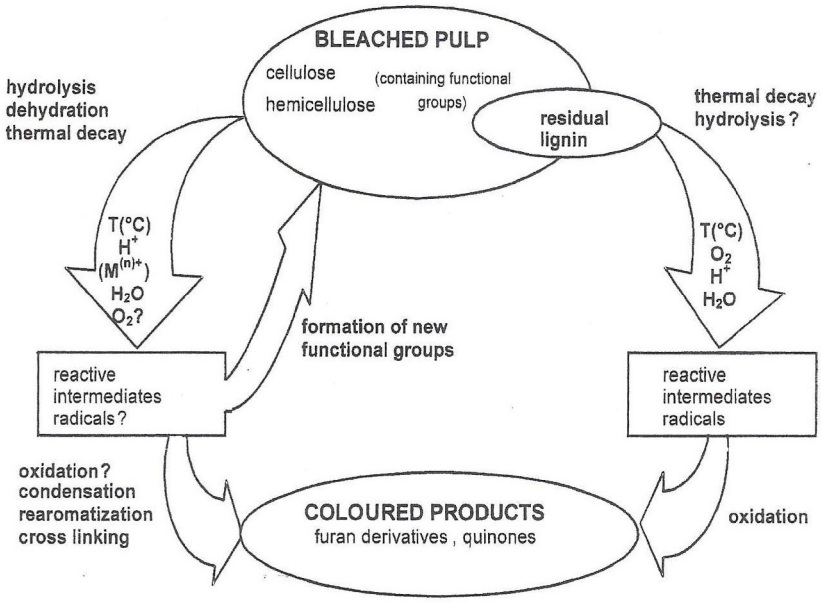

Figure 12. Proposed scheme of the reaction pathways in the wet-thermal reversion of TCF pulps[71].

Owing to the rather significant differences in brightness stability of pulps bleached by final chlorine dioxide and hydrogen peroxide which are not well understood, this final bleaching couple was selected as a case-study towards an improved understanding of this subject. Accordingly, the main goal of this study was focused on a comparative analysis of chromophore and chromogen groups in those pulps and, particularly, of the corresponding extracted xylans from pulps and bleached model-xylans. This was complemented with the analysis of the degradation products from bleached pulps submitted to wet-thermal ageing. Partially (DED) and fully bleached (DEDD and DEDP) pulps and xylans were submitted to a solid-state analysis by an advanced spectroscopic approach using UV-Resonance Raman (UV-RR) and UV-vis Diffuse Reflectance (UV-vis DR) spectroscopy and the ageing degradation products were extracted by aqueous ethanol and assessed by advanced mass spectrometry.

III. EXPERIMENTAL

III.1. Pulp bleaching

A partially $D_0(EOP)D_1$ bleached *Eucalyptus globulus* kraft pulp (87.3 % ISO brightness) was supplied by a Portuguese pulp mill. In the laboratory, the $D_0(EOP)D_1$ (also referred as DED) industrial pulp was bleached with either chlorine dioxide or hydrogen peroxide, yielding the DEDD and DEDP fully bleached pulps. Aiming at facilitating the identification of notable structural changes in the pulps upon final bleaching, excessive charge of reagents (up to 8.0% on a dry pulp basis) was applied (Table III).

Table III. Final bleaching data and pulp properties of the $D_0(EOP)D_1$, $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps[14]. Final D stage: 8.0% ClO_2 odp (oven dried pulp based and as active Cl_2), 70 ºC, 180 min; Final P stage: 8.0 % H_2O_2 odp, 1.1 % NaOH odp, 0.2% DTPA odp, 90 ºC, 60 min.

Bleaching data and pulp properties		**Pulp**		
		DED	**DEDD**	**DEDP**
H_2O_2 consumption (%)		---	---	92
NaOH consumption (%)		---	---	79
ClO_2 consumption as active Cl_2 (%)		---	94	---
Final pH		---	2.5	10.9
ISO brightness (%)		87.3	91.0	91.5
Intrinsic viscosity (dm^3/kg)		997	881	837
Brightness reversion	**(%)**	3.6	3.9	2.3
	PC number	0.67	0.52	0.26
CO (mmol/kg)		48.2	73.6	60.3
COOH (meq/kg)		78.1	77.8	83.3
HexA(mmol/kg)		3.2	1.9	2.9

These pulps were produced in another study[14] and their content of oxidized groups, intrinsic viscosity and optical properties are presented in Table III. The bleaching trials were run in sealed polyethylene bags immersed in a reciprocal shaking water bath with temperature control and using 20 g odp at 10% consistency. After bleaching, chemical consumptions were determined and the pulps were thoroughly washed with distilled water and finally conditioned in a dark room at 4 ºC.

III.2. Xylan isolation

The air dried pulps ($D_0(EOP)D_1$, $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps) were manually disintegrated and then subjected to a soft mechanical treatment by ball milling during 35 min. Sixty mL of DMSO were added to 2 g of ball milled pulp (odp basis) in a sealed erlenmeyer flask. Xylan was dissolved at 60ºC for 12 h under stirring and temperature control. Afterwards, the pulp slurry was vacuum filtered and the filtrate was kept at room temperature in the dark. The filtered pulp cake was then inserted into the same erlenmeyer flask and the procedure was repeated with fresh solvent (more 60 mL of DMSO). The pulp cake was then washed with 40 mL of water in three consecutive steps and the filtrates were collected into the same flask. The dissolved xylan was precipitated by adding into a mixture of 400 ml ethanol and 350 mL methanol under vigorous stirring and acidified with 10 mL of formic acid to reach a pH around 3. The suspension was then centrifuged and washed with anhydrous methanol in five consecutive times and then dried in vacuum at room temperature. The partially xylan-depleted pulp was oven dried at 60 ºC.

III.3. Xylan bleaching

Fifty mg of DED xylan (previously isolated from the DED pulp) were dissolved in distilled water at room temperature during 3 days under stirring. The dissolved xylan was then bleached with 10% ClO_2 (as active chlorine on a dry xylan basis) at 0.5% consistency under stirring and temperature control (70 ºC) in a glass screw-top tube during 1 h (solution initial pH: 3.6).

As for hydrogen peroxide bleaching, xylan was dissolved during 1 h at room temperature with distilled water previously set to pH 11.9 with the addition of NaOH (xylan addition reduces

the solution pH) and under stirring. Hydrogen peroxide was then added: chemical charge of 10% H_2O_2 (on a dry xylan basis) at 0.5% consistency and during 1 h at 90ºC.

After bleaching the produced DED-D and DED-P bleached xylans were again precipitated in methanol-ethanol solution, and then consecutively and repeatedly centrifuged and washed with methanol and finally dried in vacuum under room temperature - the same purification procedure used for the isolated xylans.

III.4. Artificial wet-thermal ageing

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. Five 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 (*k* is the specific absorption coefficient and *s* is the specific scattering coefficient):

$$PC = 100\left[\left(k/s\right)_{aged} - \left(k/s\right)_{initial}\right] \quad \text{(Eq. 1)}$$

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.

III.5. Wet-chemistry characterization

III.5.1. UV-vis spectroscopy

Three mg of xylan were dissolved in 15 mL cadoxen under stirring. The solutions were then dissolved with 15 mL water and the UV-vis spectra were recorded on a JASCO V-560 spectrophotometer. The scanning speed was 200 nm/min and the bandwidth was 2 nm and using a cadoxen-water solution (1:1) as blank reference.

III.5.2. ^{1}H NMR spectroscopy

The xylans were dissolved in D_2O and using sodium 3-(trimethylsilyl)-propionate-d_4 as internal standard. The ^{1}H NMR spectra were recorded at ambient temperature on a Bruker AMX 300 spectrometer operating at 300.1 MHz. A relaxation delay of 12 s and r.f. angle of 90º was used and 1000 scans were collected.

III.5.3. Molecular weight distribution by size exclusion chromatography (SEC)

Three mg of xylan were dissolved in 100 µL of 8% LiCl/N,N-dimethylacetamide (DMAc) solution at 105 ºC during 1 h and then further diluted with 600 µL DMAc. The SEC was carried out on two PLgel 10 µm MIXED B 300×7.5 mm columns protected by a PLgel 10 µm pre-column (Polymer Laboratories, UK) using a PLGPC 110 system (Polymer Laboratories). The columns, injector system and the detector (RI) were maintained at 70 °C during the analysis. The eluent (0.1 M LiCl in DMAC) was pumped at a flow rate of 0.9 mL/min. The analytical columns were calibrated with pullulan standards (Polymer Laboratories).

III.5.4. Electrospray ionisation-mass spectrometry (ESI-MS)

Electrospray ionisation-mass spectrometry (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 ºC and desolvation temperature at 150 ºC. 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).

III.6. Solid-state characterization

Non invasive techniques, such as UV-Resonance Raman (UV-RR) spectroscopy, allow an in-situ assessment of residual chromophores in bleached pulps present in trace amounts. Rather particular chromophore structures can be assessed by Raman scattering while applying an appropriate UV excitation wavelength fulfilling the resonance conditions[14,15,64,92,93]. 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[94].

III.6.1. UV-vis Diffuse Reflectance (UV-vis DR) spectroscopy

Diffuse reflectance spectra were recorded at room temperature on a JASCO V-560 spectrophotometer equipped with a JASCO ISV-469 integrating sphere and using BaSO4 standard as background reference. The pulp samples were pressed into 100 mg pellets. The studied range was 200-800 nm with a scanning speed of 200 nm/min and a bandwidth of 5 mm. The reflectance (R as the reflectance of the opaque sample) spectra were converted into *k/s* spectra using known Kubelka-Munk equation (Eq. 2):

$$\frac{k}{s} = \frac{(1-R)^2}{2R} \qquad \text{(Eq. 2)}$$

A constant scattering coefficient among the studied samples was assumed for a comparative quantitative analysis of the changes in chromophores among the studied pulps.

As shown in Figure 13, there is excellent agreement between reflectance measurements at 457 nm using the integrating sphere and the ISO brightness measurement following ISO standards

(ISO 2470). Handsheets for optical properties determination were prepared using the standard procedure described in ISO 3688.

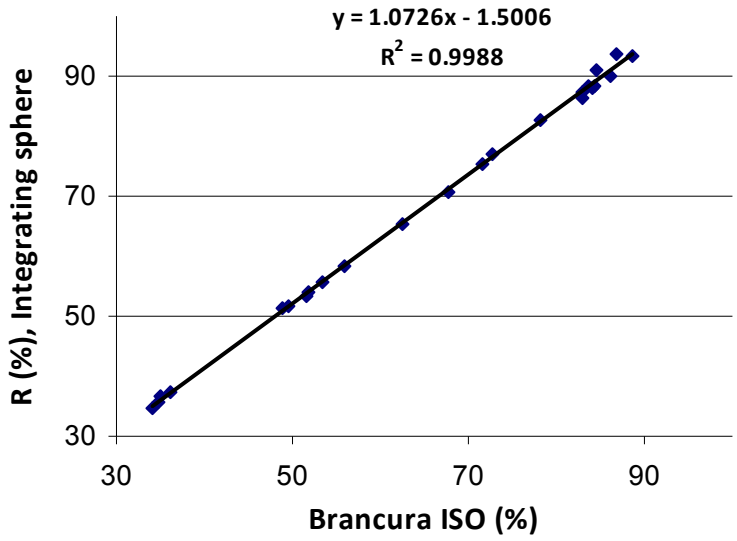

Figure 13. Diffuse reflectance at 457 nm using integrating sphere vs. ISO brightness of several pre-bleached pulps across $D_0(EOP)D_1E_2D_2$ and OQ(PO)DP bleaching sequences before and after wet-thermal ageing according to TAPPI T 260 (100 ºC and 100 % R.H.).

III.6.2. UV-Resonance Raman (UV-RR) spectroscopy

Micro-Raman spectra were recorded using a Jobin Yvon (Horiba) LabRam HR 800 micro-Raman spectrometer @ 325nm (He-Cd UV laser, Kimmon IK Series) under backscattering configuration using a 40X NUV objective. Before the analyses, 100 mg of each pulp sample was pressed into 11 mm diameter pellets.

To avoid sample photodegradation, a neutral density filter (ND 0.6) was used for the spectral acquisition of the xylan samples. For the pulp samples 30 s of acquisition time was enough to avoid photodegradation. The spectral range was 750-1800 cm^{-1} in order to cover chromophores and carbohydrate related bands and for each 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 normalized to the 1375 cm^{-1} band. For the quantitative analysis, curve fitting was made using Lorentzian peak functions without smoothing the normalized spectra. An example of spectral data processing is given in Figure 14 for the case of a photodegraded cellulose sample

exhibiting an increased intensity in the 1600 cm^{-1} band related to photodegradation.

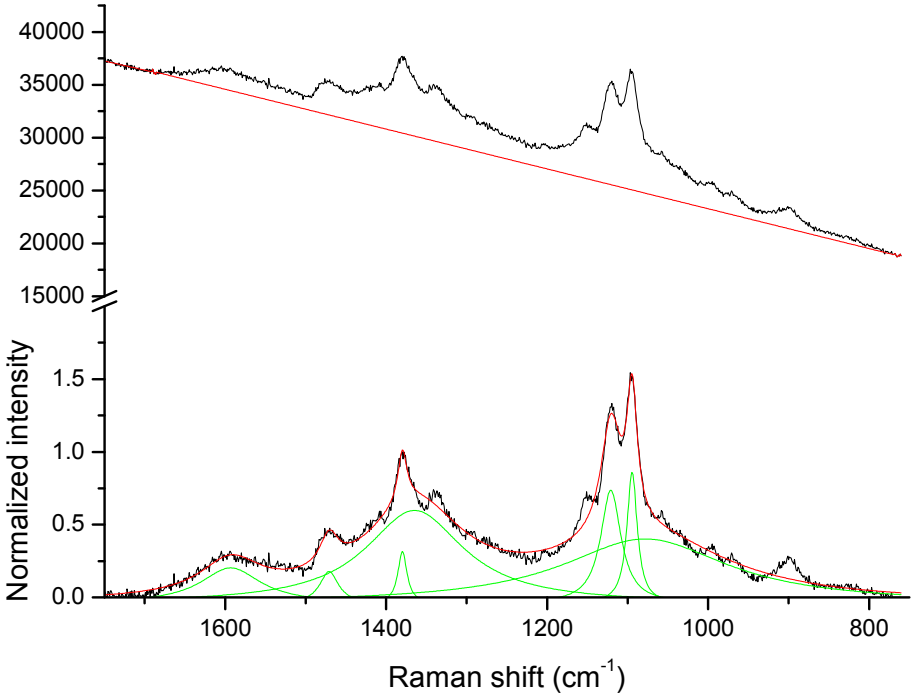

Figure 14. Example of spectral data processing (micro-Raman spectrum of a photodegraded Avicell® PH-101cellulose sample)[14].

IV. RESULTS & DISCUSSION

IV.1. Effect of xylan partial extraction on pulp chromophores

In Figure 15 it is observed that the partial removal of xylan after treatment of the bleached pulps with Me_2SO produced a removal of chromophores absorbing below *ca.* 300 nm for DED and DEDD pulps. In the case of the DEDP bleached pulp, the removal of chromophores, observed as change in k/s values, is less significant. Therefore, this means that during the alkaline hydrogen peroxide bleaching, xylan chromophores were removed from the fibre surface more extensively. Either residual HexA moieties in xylan or degraded residual lignin associated to xylan may explain these spectral features.

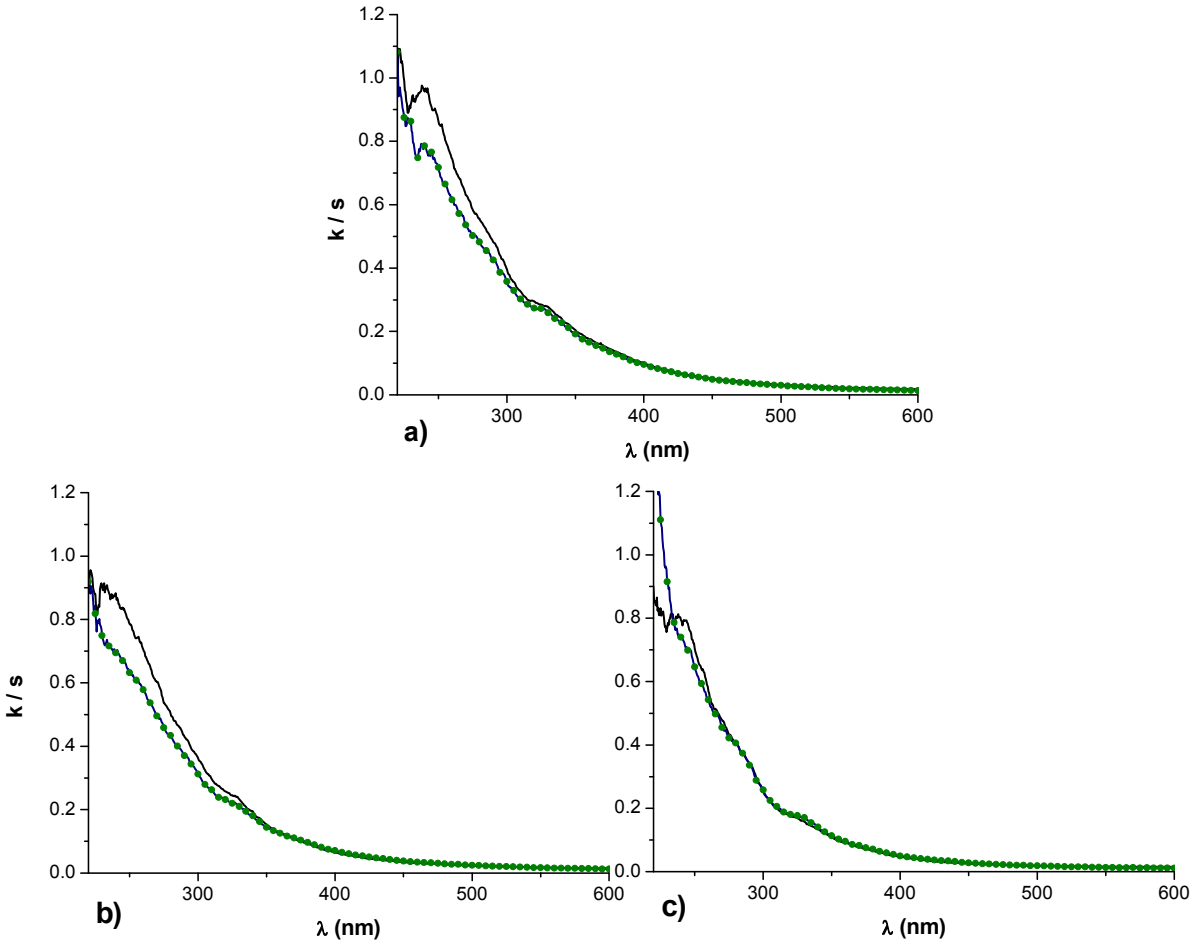

Figure 15. UV-vis Diffuse Reflectance spectra of **a)** $D_0(EOP)D_1$, **b)** $D_0(EOP)D_1D_2$ and **c)** $D_0(EOP)D_1P$ bleached pulps before (black line) and after partial extraction (green line) of xylan .

The analysis by UV-Resonance Raman spectroscopy (Fig. 16) reveals that the partial removal of xylan from the bleached pulps is reflected in a decrease of the band intensity at *ca.* 1600 cm^{-1}. The UV-RR signal at *ca.* 1595 cm^{-1} includes polyconjugated carbonyl structures (O=C–(C=C)n−), including aromatic structures, though polyunsaturated moieties also contribute at *ca.* 1630 cm^{-1}[15]. On the one hand, this selective assessment reveals that the xylan is an important source of polyconjugated carbonyl moieties in bleached pulps. On the other hand, confirms that the alkaline hydrogen peroxide treatment can reach a higher removal extent of xylan-related chromophores compared to the acidic chlorine dioxide treatment, which exhibits the highest decrease in the band height at *ca.* 1600 cm^{-1} after partial xylan removal. Thus xylan-related chromophores are retained to a higher degree after the final D stage which is consistent with the most pronounced decrease in the k/s values of the UV-Vis DR spectrum (Fig. 15).

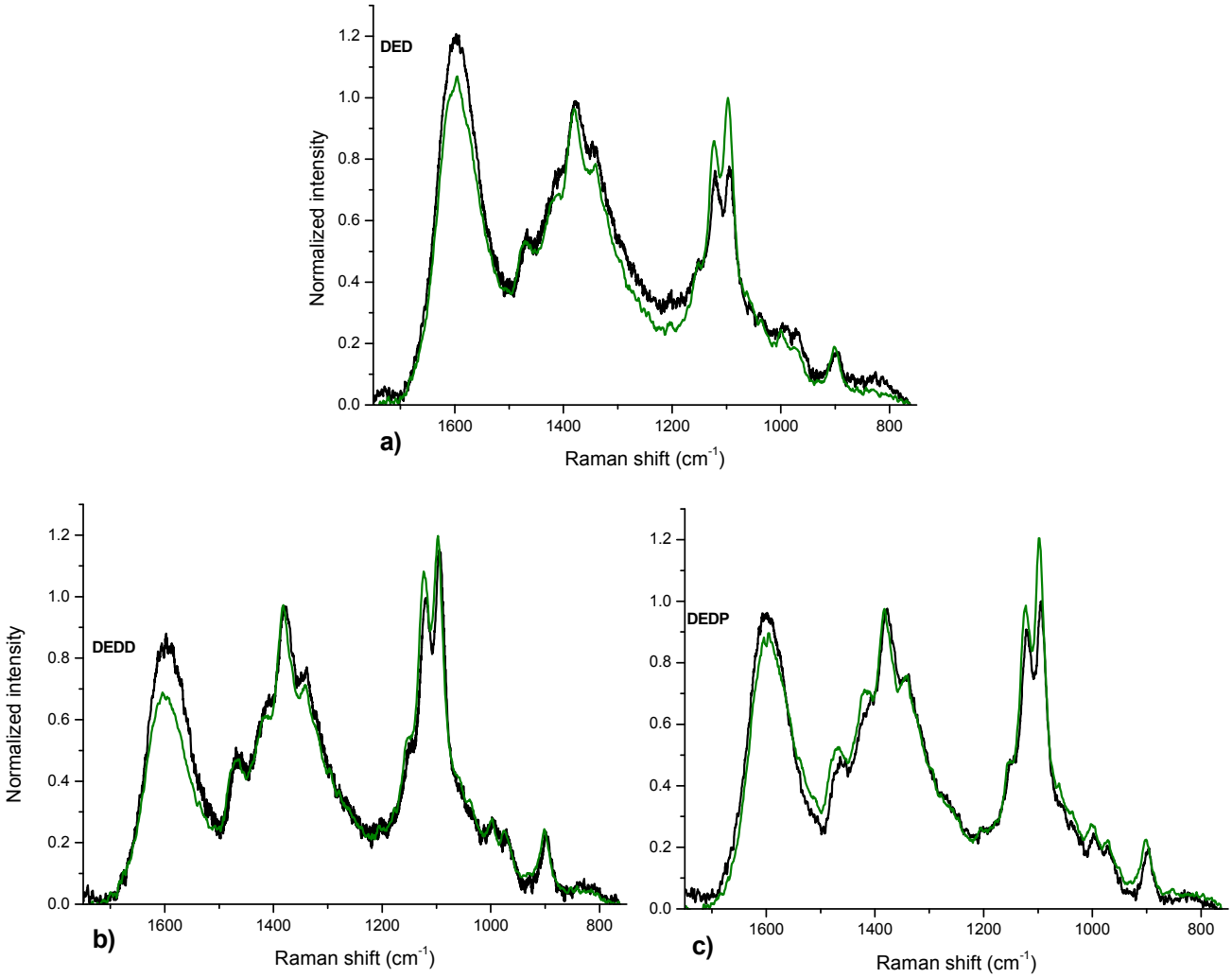

Figure 16. UV-vis Diffuse Reflectance spectra of **a)** $D_0(EOP)D_1$, **b)** $D_0(EOP)D_1D_2$ and **c)** $D_0(EOP)D_1P$ bleached pulps before (black line) and after partial extraction (green line) of xylan.

As for the increased intensity at 1093-1120 cm^{-1}, assigned to stretching vibration modes of COC/OCO groups, including carbonyl groups in hydrated and hemiacetal/hemiketal configuration, it can be explained by a greater cellulose exposition after the xylan removal. Hence, the highest increase is observed for the less exposed DED cellulose.

IV.2. Characterization of extracted and bleached xylans

IV.2.1. Wet-chemistry characterization

In Figure 17, The ^{1}H NMR spectra of the xylans isolated from DED, DEDD and DEDP bleached pulps did not show significant signals at 6.0-8.0 ppm assigned to aromatic protons in bound residual lignin. At the same time the notable absorption at 280 nm in UV spectra of all xylans dissolved in cadoxen is registered (Fig. 18). The absorption at this region is abnormal and indicates the presence of aromatic structures or other compounds with highly conjugated double bonds in xylans isolated from bleached pulps.

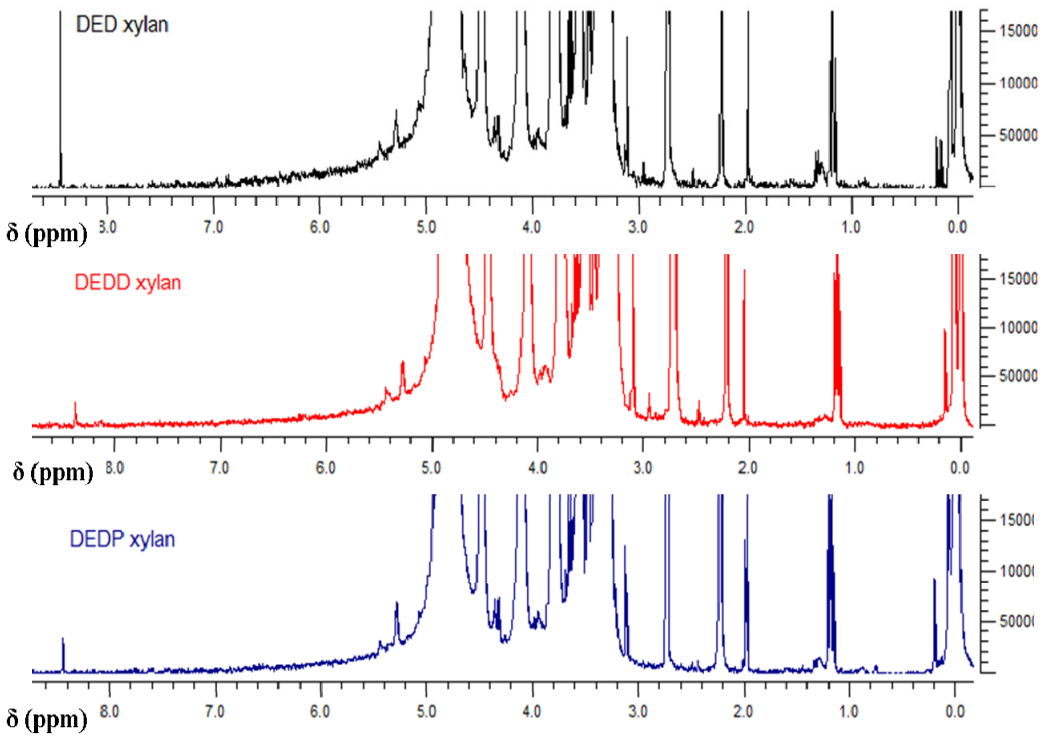

Figure 17. ^{1}H NMR spectra of the xylans isolated from $D_0(EOP)D_1$, $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps.

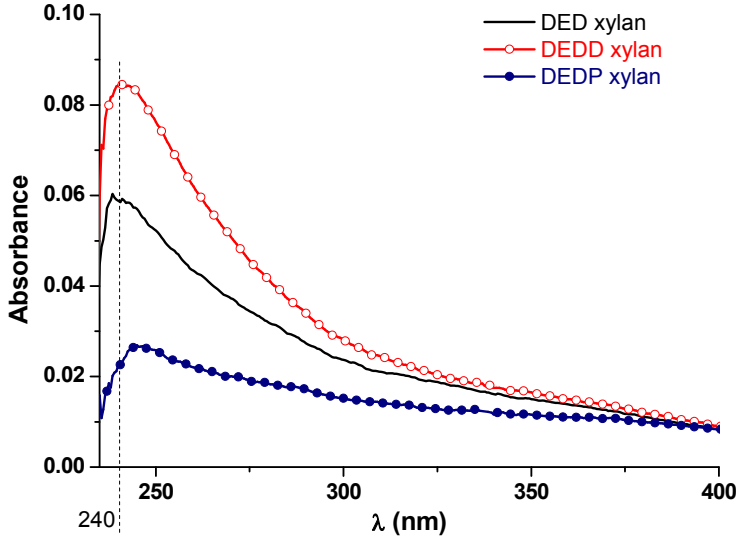

Figure 18. UV-vis spectra of the xylans isolated from $D_0(EOP)D_1$, $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps dissolved in cadoxen solution.

In addition, it is observed in Figure 18 that a new type of conjugated oxidized group, different than HexA, appeared at ca. 240-260 nm in the UV-vis spectra of xylans dissolved in cadoxen. In fact, the ^{1}H-NMR spectra from Figure 17 show that DED and DEDP xylans exhibit notable signals at 8.37 and 8.44 ppm, respectively, assigned to unknown unsaturated structures. Similar features were observed with HexA enriched Birch xylan treated with ozone and chlorine dioxide[95].

The SEC profiles of the xylans isolated from the DED, DEDD and DEDP bleached pulps are presented in Figure 19 and for the DED model-xylan either bleached with chlorine dioxide (DED-D) or hydrogen peroxide (DED-P) are shown in Figure 20. The average molecular weights of xylans and their polydespersities are presented in Table IV.

The harsh final bleaching treatment induced more xylan degradation with hydrogen peroxide (non stabilized conditions) than with chlorine dioxide, considering the molecular weight values of xylans extracted from the pulps and of the DED model-xylan treated with D and P stages. In general, the tendencies in degradation of xylan in DED pulp and xylan isolated from DED pulp as a model sample were similar after the treatments with D and P stages. Some more degradation of model xylan was observed than that obtained with the retained xylan in DED pulp after the P stage (bleached DED-P *vs.* DEDP xylans; Fig. 19 and 20) which may be explained by better accessibility of the former. Additionally, the oxidized xylan in pulp may suffer some structural association with cellulose, analogously as oxidized cellulose suffering

crosslinking and becoming difficult to dissolve in typical cellulose solvents[96].

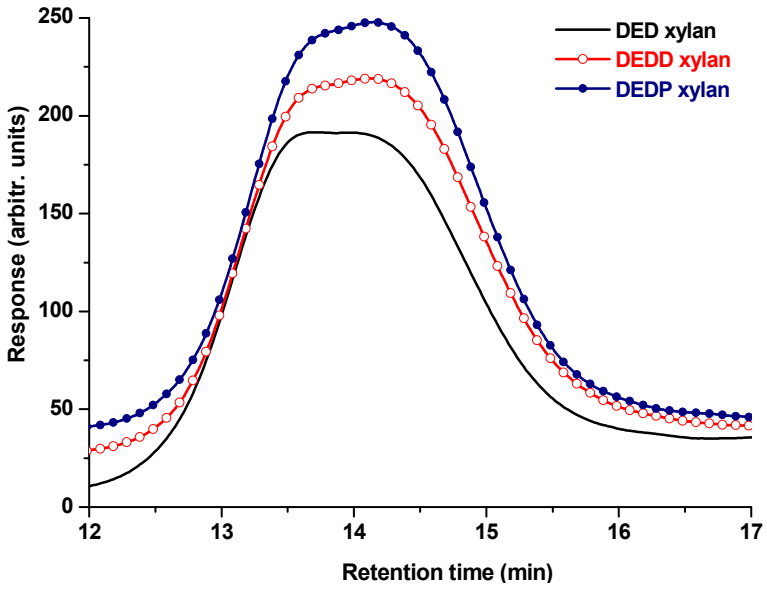

Figure 19. SEC curves (offset) of the xylans isolated from $D_0(EOP)D_1$, $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps.

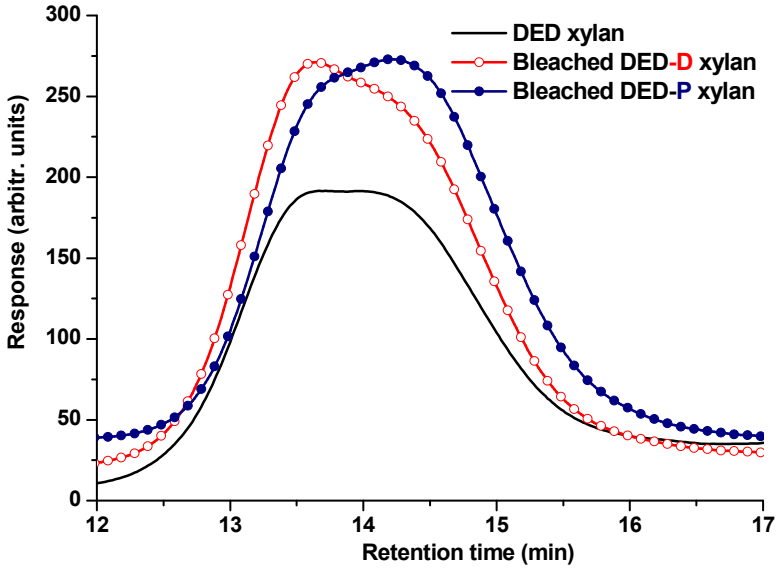

Figure 20. SEC curves (offset) of the $D_0(EOP)D_1$ xylan before and after bleaching with chlorine dioxide ($D_0(EOP)D_1$-D) and hydrogen peroxide ($D_0(EOP)D_1$-P).

Table IV. Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) values of the isolated and bleached xylans.

Xylan ID	M_w (KDa)	M_n (KDa)	PD *
isolated DED	14.8	9.2	1.62
isolated DEDD	13.2	8.6	1.54
isolated DEDP	12.9	7.9	1.64
bleached DED-D	14.4	8.7	1.65
bleached DED-P	12.0	6.9	1.73

* Polydispersity index: Mw/Mn

IV.2.2. Solid-state characterization

In previous studies using UV-RR spectroscopy coupled to UV-vis DR spectroscopy, xylan was highlighted as an important source of chromophores in bleached eucalypt pulps[14,15]. Particular selectivity in the detection and identification of chromophores in pulps is achieved using 325 nm laser beam excitation[14,15] rather than under deep-UV excitation for the detection of aromatic lignin[92,97,98] and HexA moieties[93]. This band (325 nm) at the diffuse reflectance (DR) spectra corresponds to the absorption of polyunsaturated chromophore structures[15].

The UV-RR spectra of the xylan isolated from the DED bleached pulp and post-treated with chlorine dioxide and hydrogen peroxide are presented in Figure 21. It is observed that alkaline hydrogen peroxide treatment has reduced the amount of polyconjugated chromophore structures detected at *ca.* 1600 cm^{-1} in the UV-RR spectra. As for the acidic chlorine dioxide treatment, the amount of chromophores did not change. This is in agreement with the previous results of UV-Vis DR and UV-RR spectroscopy from pulps before and after partial extraction of xylan (Fig. 15 and 16). Once again it is confirmed the role of xylan as an important source of chromophores by the high intensity at *ca.* 1600 cm^{-1} in the UV-RR spectra. In addition, it can be concluded that the nature of chromophores in xylan is different in relation to the particular final bleaching stage, as observed in Table V.

The characteristic signals of chromophores belonging to the DED xylan bleached with alkaline hydrogen peroxide are down-shifted in wavenumbers compared to the original xylan. Conversely, the signals from chromophores of DED xylan bleached with chlorine dioxide are high-shifted in wavenumbers. The signal at *ca.* 1627 cm^{-1} (Table V) can be assigned to a more extended chromophore system such as conjugated units bearing aromatic, ethylenic and carboxylic acid groups (e.g., 3,5-dimethoxy-4-hydroxycinnamic acid)[15] which is present in DED-D xylan. This is in close agreement with a previous study[14] about extracted xylans from fully bleached pulps where the final chlorine dioxide treatment increased the structural conjugation of xylan. However, in that same study this fact was more noticeable from the increased intensity of the Raman signal at ca. 1600 cm^{-1} (increased amount of polyconjugated structures) in the xylan isolated from the DEDD bleached pulp[14]. This difference in chromophores between xylan oxidized in bulk and in solution can be explained, at least partially, by poor dissolution of oxidized xylan fragments extracted from bulk in solution during bleaching. On the other hand, previous studies indicated that the influence of charge transfer complexes on the intensity of the signal at ca. 1600 cm^{-1} can be minimized by appropriate pH control, which was the case of these xylan samples precipitated to the same pH[14].

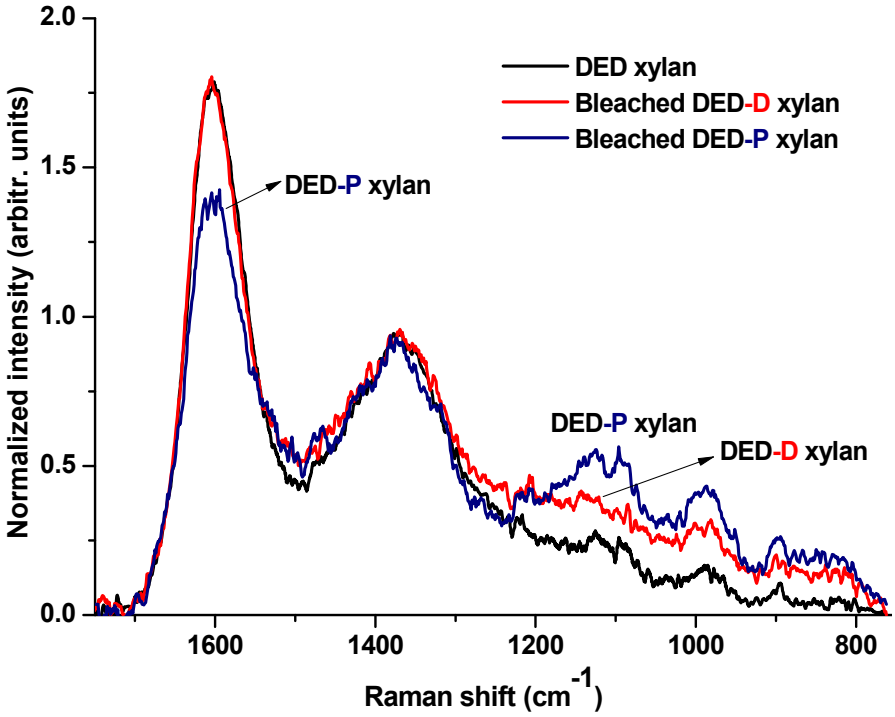

Figure 21. UV-RR spectra of the $D_0(EOP)D_1$ xylan before and after bleaching with chlorine dioxide ($D_0(EOP)D_1$ – D) and hydrogen peroxide ($D_0(EOP)D_1$ – P).

Table V. Characteristic Raman signals of xylan-related chromophores: model xylan (DED) before and after bleaching with chlorine dioxide (DED-D) and hydrogen peroxide (DED-P).

Xylan ID	Chromophores signals (cm^{-1})			
	Maximum intensity	Band deconvolution		
DED	1601	1623	1600	1573
DED-D	1604	1627	1605	1578
DED-P	1594	1621	1591	1540

In contrast to the treatment with chlorine dioxide, the removal of chromophores from xylan bleached with hydrogen peroxide is easier. However, this xylan showed an increased oxidation degree as revealed by increased bands at 1120 and 1093 cm^{-1} in the UV-RR spectra (Fig. 21) co-responsible to O-C-O vibrations in hydrated carbonyls[14]. This fact is reflected by more extended xylan degradation (lower molecular weights) in final P than in D stage (Table IV).

In terms of furan-type chromogen structures detectable at *ca.* 1480 cm^{-1} in the UV-RR spectra[15] (Fig. 21) this signal was observed in the Raman spectra of the three xylan samples. After final D bleaching stage the intensity of this signal is most noticeable. This fact may explain why xylan chromophores are more difficult to remove upon chlorine dioxide bleaching and why DEDD bleached pulp possesses high brightness reversion, due to conversion of chromogens into chromophore structures.

IV.3. 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 bleached 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 ºC, 30% pulp humidity for 5 days (Table VI). 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 (Table III; 100 ºC,

100% R.H., 1 h)[14], 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).

Table VI. Effect of the final D and P bleaching stages applied to the industrial $D_0(EOP)D_1$ pulp on the ageing behaviour of the fully bleached pulps.

Pulp	ISO brightness (%)	HexA (mmol/kg)	Brightness reversion* 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

* measured at 457 nm of the corresponding k/s spectra before and after ageing.

As the brightness reversion did not correlate with the HexA content in pulps (Table VI), 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 amount of degradation structures have been carried out by the assessment of ageing products released from aged pulps extractable with ethanol-water (1:1, v/v).

IV.4. Analysis of ageing products by mass spectrometry

The ESI-MS spectra in Figure 22 revealed a mixture of dissolved oligomers with molecular mass until 1500 Da in the extracts from aged DED and DEDD pulps and till 700 Da in the corresponding DEDP extract. The lowest abundance and diversity of oligomeric products were observed in extract from aged DEDP pulp.

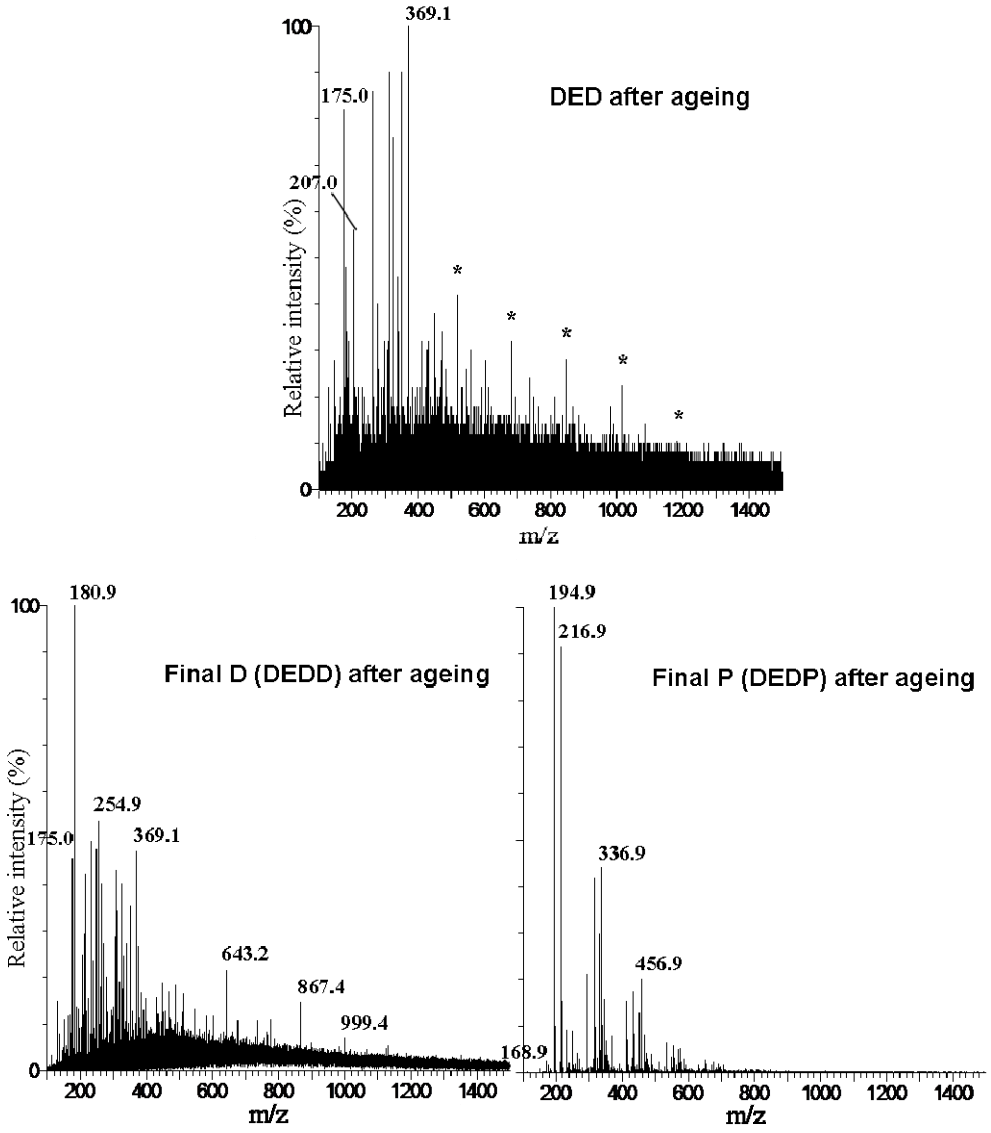

Figure 22. Negative mode ESI-MS spectra of the ethanol-water extracts from the aged $D_0(EOP)D_1$, $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps (* - denotes contaminants).

In terms of general patterns, the ESI-MS spectra of DED and DEDD extracts were similar to that reported for the eucalypt lignin, whereas the ESI-MS spectrum of DEDP extract was closer to the oligomers of carbohydrate origin[99]. 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. 15) and likewise in the UV-RR spectra of xylans (Fig. 21). The extremely important contribution of xylan-lignin complex to the amount of chromogen/chromophore structures is thus confirmed[14]. This explains, to some extent, the significant diminishing of brightness reversion of eucalypt kraft pulp which was alkali-extracted (E-stage) before the final D stage (DEDED *vs.* DEDD)[15].

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[100]. 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[95,101]. Thus, the series of acidic XOS were identified: 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[43]. The signals at m/z 111.1 and at m/z 175.0 were assigned to 2-furoic and HexA acids, respectively[95]. 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[101]. These signals were assigned to the carbohydrate-derived adducts with iron $[M+Fe-H]^-$. 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 in aged pulps, different furan derivatives are produced under carbohydrate hydrothermal decay[57,70,81,102]. Furans form linear or cyclic furan-derived oligomers *via* aldol condensation reaction and are typical chromophores[65,71,103]. 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 keto-glycosides under acidic treatment[81] and has been also identified as an ageing product of bleached pulps[65,78]. Reductic acid was not clearly identified by GC-MS among degradation products in extract as TMS derivative (not shown) but its presence is suspected as an iron complex (m/z 168.9) and was detected in DEDP extract (Fig. 22). Reductic acid participates in condensation reactions with furan derivatives[65] 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[104].

Low molecular weight degradation products formed during pulp ageing may suffer condensation reactions leading to the formation of aromatic structures[26,70,81]. Dihydroxyacetophenone[81] and hydroxybenzoquinone-type structures[26] 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 by mass spectrometry.

IV.5. Assessment of acidic and alkaline treatments on the ageing behaviour of bleached pulp

In order to verify whether a mild acidic or alkaline pH treatment can affect the brightness reversion tendency, the same DEDD and DEDP bleached pulps were submitted to either alkaline or acidic conditions, respectively. At 0.5 % consistency and room temperature overnight (*ca.* 12h), the DEDD bleached pulp was submitted to pH 11 while the DEDP bleached pulp was submitted to pH 4. The results on brightness and wet-thermal ageing (TAPPI T 260 procedure at 100 ºC and 100 % R.H.) are presented in Table VII.

It is observed in Table VII that the pH to which the pulp was exposed before making the handsheets for the measurement of ISO brightness and ageing testing can have a significant role on the optical properties of the bleached pulp. This is mainly the case of the DEDD bleached pulp which exhibited more significant changes in terms of ISO brightness and reversion results than the DEDP bleached pulp. It is thus verified that even with a mild alkaline treatment some chromogen structures are extracted from the DEDD pulp which benefits the brightness stability under wet-thermal conditions. The reduction in brightness after treatment at pH 11 of the DEDD pulp can be explained by the so-called effect of alkali-darkening[105,106]. As for the DEDP bleached pulp, the treatment at pH 4.0 led to only slightly worst results. It can be concluded that the final pH of the last bleaching stage is itself an

important parameter controlling the extent of brightness reversion. In other words, the property of brightness reversion is dependent on the degree of retention in pulp of the aforementioned xylan-lignin degraded structures that are leachable under alkaline conditions.

Table VII. Effect of a polishing alkaline or acidic treatment at room temperature in brightness reversion, respectively applied to the $D_0(EOP)D_1D_2$ and $D_0(EOP)D_1P$ bleached pulps.

Pulp	ISO brightness (%)	Brightness reversion	
		Δ (%)	PC number
DEDD (pH 2.5)	90.9	3.8	0.51
DEDD* (pH 11)	90.4 (-0.5)	2.9 (-0.9)	0.38 (-0.13)
DEDP (pH 10.2)	91.8	2.2	0.24
DEDP* (pH 4.0)	91.6 (-0.2)	2.4 (+0.2)	0.27 (+0.03)

V. CONCLUSIONS

Final bleaching with chlorine dioxide produces unsaturated moieties in xylan, absorbing at 240-260 nm, different from HexA residues and from those present in the original xylan isolated from a DED bleached pulp. This was also noticeable by employing UV-Resonance Raman spectroscopy from the increased amounts of conjugated structures in model-xylan bleached with chlorine dioxide. Compared to chlorine dioxide, the final alkaline hydrogen peroxide stage is more efficient in terms of the removal of xylan-related chromophores, though it is more detrimental regarding the xylan integrity.

UV-visible Diffuse Reflectance and UV-Resonance Raman spectroscopy coupled to mass spectrometry analysis of ageing products revealed that 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.

The content of partially oxidized structures was significantly higher in the DEDD than in the DEDP bleached pulp thus pre-determining the worst brightness stability of the former. However, the amount of oxidized 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 stage 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 ageing products of carbohydrate origin arisen during pulp ageing 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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