RECENT ADVANCES IN EUCALYPTUS WOOD CHEMISTRY: STRUCTURAL FEATURES THROUGH THE PRISM OF TECHNOLOGICAL RESPONSE

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ABSTRACT

The results on structural studies of macromolecular compounds from *Eucalyptus globulus* wood and some other eucalypt species (*E. grandis* and *E. urograndis*), carried out at the Department of Chemistry of the University of Aveiro (Portugal) during last decade, are summarized. The main structural features and abundance of lignin (including LCC), hemicelluloses (glucuronoxylan, glucans, glucomannan) and cellulose are discussed in context of their effect on pulping, bleaching and papermaking processes.

Keywords: *Eucalyptus globulus*, lignin, cellulose, xylan, glucan, glucomannan, kraft pulping, ECF bleaching

INTRODUCTION

Eucalypt wood is the increasingly dominating source of short fibers for the pulp and paper industry worldwide. Particularly, plantation eucalypt species are the dominant raw materials for bleached hardwood kraft pulp production in the Iberian Peninsula and South America [1]. These are also exported from South America to North Europe for the pulp and paper needs. In addition to the high wood growth rate determining the economical feasibility of eucalypt plantation, this wood requires rather mild pulping and bleaching conditions, when compared to other hardwoods, and possess high papermaking performance [2-4].

Among plantation eucalypt species (*E. globulus*, *E. grandis*, *E. urograndis*, etc.), *E. globulus* is the most cultivated in South Europe and calling growing attention in Brazil, and South Africa. *E. globulus* is the basic raw material for Portuguese pulp and paper industry [2].

In spite of the economic importance of plantation *Eucalyptus* species, there was clearly a lack of knowledge on its chemistry, which is crucial to understand the pulping, bleaching and papermaking response. Additionally, the information on the amount and the structure of wood components is essential for the optimization of technological processes and pulp and paper quality control. The chemistry of plantation eucalypt woods, particularly *E. globulus*, and the behaviour of its components during kraft pulping and ECF bleaching were the subjects of investigation in our research group at the Department of Chemistry of the University of Aveiro during the last decade. Significant advances were made on the composition and the structure of polysaccharides and lignin. This structural information allowed the better understanding of conventional pulping, bleaching and papermaking processes.

The main goal of this presentation is to review the most relevant results on the structure of macromolecular components of *E. globulus* wood and to emphasise the structure-property relationships regarding the wood pulping and the pulp bleaching performance.

RESULTS AND DISCUSSION

Chemical composition of eucalypt wood

The typical chemical composition of *E. globulus* wood in relation to some other hardwood species is presented in Table 1. Among the presented eucalypt species, *E. globulus* contains clearly the lowest amounts of lignin, extractives and ashes. At the same time the amounts of cellulose and hemicelluloses, expressed as pentosans, are higher in *E. globulus* than in *E. grandis* and *E. urograndis* woods. For the pentosanes content *E. globulus* wood is inferior only to *Betula pendula*.

Table 1. Chemical composition of *E. globulus* and some other hardwoods (%, w/w) [5].

	E. globulus	*E. urograndis*	*E. grandis*	*B. pendula*	*A. mangium*
Lignin[a]	20.5	26.7	25.7	20.4	27.1
Cellulose[b]	50.0	48.6	46.6	41.3	46.5
Pentosans	14.1	11.3	13.5	22.1	13.3
Extractives[c]	1.72	1.91	2.10	2.24	4.46
Ashes	0.17	0.53	0.25	0.49	0.22

[a] Klason lignin, uncorrected for polyphenolics content
[b] Cellulose Kürschner-Hoffer
[c] EtOH/toluene (2:1, v/v)

Cellulose

The amount of cellulose in *E. globulus* wood is around 50% (Table 1). The supramolecular structure of cellulose at different organization levels was studied employing wide-angle X-ray diffraction analysis (WAXRD), CP/MAS ^{13}C NMR spectroscopy, Atomic Force Microscopy (AFM) and wet chemistry methods [6-8]. The degree of crystallinity (X) of *E. globulus* cellulose was found to be about 68%, which is slightly higher than X determined for other eucalypt species, but similar to that found for birch and acacia woods (Table 2). The unitary cell dimensions of crystalline domains, according to Meyer-Mark-Misch model for the Cellulose I polymorph (Figure 1), in eucalypt cellulose are practically identical to that of cellulose

from other studied wood species (Table 2). The average crystallite width in the 002 plane (d_{002}) of cellulose fibrils (elementary fibrils) from all eucalypt woods was also similar and indifferent from d_{002} of fibrils from birch and acacia woods. Some difference was found, based on levelling off DP results, for the average crystallite length (La) in cellulose fibrils of *E. globulus* and *E. grandis* being 620 and 550 Å, respectively.

The fibrils assembly in *E. globulus* cell wall of holocellulose/kraft pulp was studied by solid state ^{13}C NMR and AFM [7, 8]. Coherent results were obtained by both techniques indicating that in average of 2-4 fibrils are assembled in a twisted mode (average diameter varied of 10-14 nm) thus forming the microfibrils. This is visualised in the AFM image of S_2 sublayer from cell wall fragment of *E. globulus* delignified fiber (Figure 2). Microfibrils forms also

Table 2. Degree of cellulose crystallinity (X), unitary cell and crystallite average width (d_{002}) dimensions (see Figure 1 for assignments).

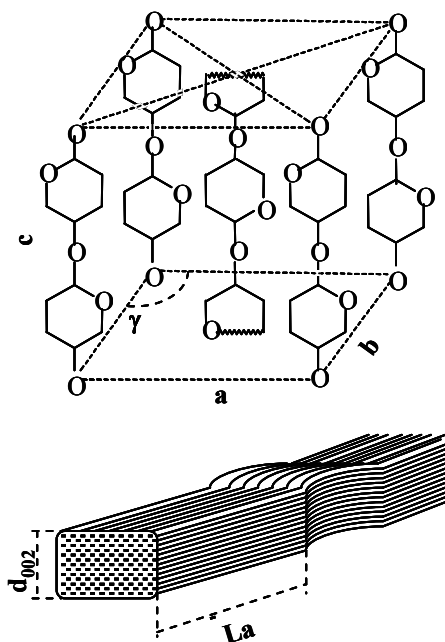| Wood	X %	d_{002} Å	a Å	b Å	c Å	γ deg.
E. globulus	67.7	46.2	8.1	7.9	10.3	97
E. grandis	63.4	47.3	8.0	7.9	10.3	96
E. urograndis	65.9	46.0	8.0	7.9	10.3	96
B. pendula	67.6	44.3	8.0	7.9	10.3	96
A. mangium	67.6	47.4	8.1	8.0	10.3	98

Figure 1. Schematic representation of Cellulose I cell unit (top image) according to Meyer-Mark-Misch model and the elementary fibril (bottom image) according to fringed-micellar concept.
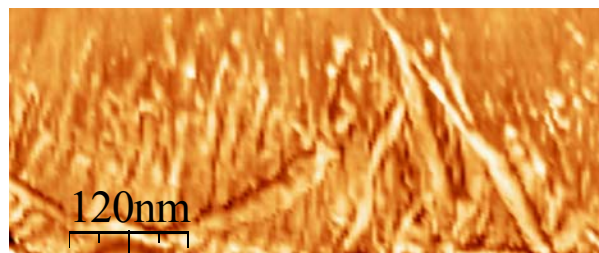

Figure 2. AFM image of S_2 sublayer from cell wall fragment of *E. globulus* delignified fiber.

aggregates of higher dimensions (about 15-30 nm of diameter) that may be defined as macrofibrils. These fibril aggregates are well visible in the AFM image (Figure 2). It was very difficult to estimate the fibril length, but this was certainly higher than 0.3 μm.

Hemicelluloses

Hemicelluloses are the second in abundance macromolecular component of *E. globulus* wood after cellulose. The amount of hemicelluloses varies of 24-27%, the most abundant being xylan (16-20%) and glucans (4-6%). The glucomannan and pectic compounds contribute of about 1-2% each.

Xylan. A xylan from plantation *E. globulus* wood shows several particular structural features [9, 10]. This hemicellulose is *O*-acetyl-(4-*O*-methylglucurono)xylan, which main backbone is constituted of (1→4)-linked β-D-xylopyranosyl units ramified with short side chains of terminal (1→2)-linked 4-*O*-methyl-α-D-glucuronosyl residues (MeGlcA) with molar ratio 1:10. Unlike xylans from other hardwoods, the eucalypt heteroxylan contained galactosyl and glucosyl structural units attached at *O*-2 of terminal MeGlcA originating from rhamnoarabinogalactan and glucan backbones respectively (Figure 3). About 30% of MeGlcA units are branched at *O*-2. Thus the *O*-2 of MeGlcA residues was suggested to be a linking point between xylan and other carbohydrates of the cell wall such as pectin and glucans. The same structural peculiarities were detected in xylans of other eucalypt
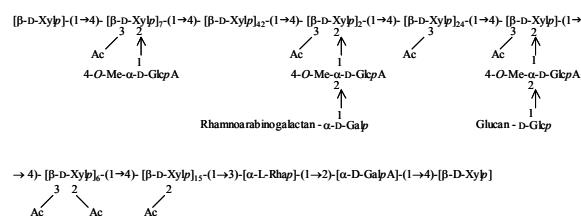

Figure 3. The empirical structure of the *E. globulus O*-acetyl-(4-*O*-methylglucurono)xylan ramified at *O*-2 of terminal MeGlcA with rhamnoarabinogalactan and glucan side-chains.

species, such as *E. grandis* and *E. urograndis* [11] and were not detected in xylans from such hardwoods, as *Populus tremula*, *B. pendula*, *Fagus silvatica* and *A. mangium*. The analysis of methylation products of *E. globulus* heteroxylan confirmed the presence of the specific reducing terminal structural fragment [→3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*A-(1→4)-D-Xyl*p*], which was previously suggested for several hardwoods xylans (Figure 3). The *O*-acetyl-(4-*O*-methylglucurono)xylan (GX) from *E. globulus* is partially acetylated showing an acetylation degree of 0.61. β-D-xylopyranosyl units of the heteroxylan backbone are acetylated at *O*-3 (34 mol %), *O*-2 (15 mol %) and *O*-2,3 (6 mol %). Practically all β-D-xylopyranosyl units linked at *O*-2 with MeGlcA residues are 3-*O* acetylated (10 mol %). Heteroxylan is the main source of acetyl groups in eucalypt wood second being the pectic compounds [10].

The distribution of acetyl groups in the heteroxylan backbone was assessed by analysis of xylo-oligosaccharide (XOS) fractions, obtained by partial acid hydrolysis of heteroxylan and fractionated by semi-preparative Ligand-Exchange/Size Exclusion Chromatography (LEX/SEC), employing Tandem Electrospray Ionisation Mass Spectrometry (ESI-MS/MS) for XOS structural analysis [12]. This allowed some propositions on the primary structure of the eucalypt heteroxylan (distribution patterns of different backbone substitutes such as MeGlcA, *O*Ac, etc.). It was suggested that the acetylation of xylan backbone is not random and possesses a mosaic distribution. The frequency of the acetylation is increased in the xylose residues directly linked to the MeGlcA residues or in neighbouring units. At the same time rather large molecular fragments are not acetylated and not ramified with MeGlcA residues.

The distribution patterns of acetyl groups and MeGlcA residues in GX backbone were assigned to its molecular packing mode in the cell wall and to thermodynamics of interaction with other biopolymers (lignin, cellulose). The proposed molecular packing
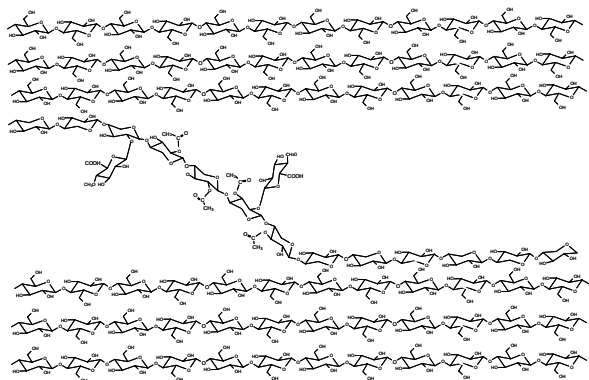

Figure 4. Schematic representation of xylan packing between CMF in the secondary cell wall. Xylan biosynthesis routes of cell wall polysaccharides [13], fragments enriched in MeGlcA residues and *O*Ac are located predominantly in the interfibrillar space.

patterns of heteroxylan in the secondary cell wall are presented in Figure 4. According to the known cellulose microfibrils (CMF) are deposited in the secondary cell wall practically simultaneously with xylan chains, which determines their close association. The ramification of xylan backnone with MeGlcA residues and *O*Ac occurs on the later phase of cell wall formation. It could be proposed that xylan backbone zones in the interfibrillar space are easier to derivatize via enzymatic catalysis than the backbone zones strongly associated by hydrogen bonds with CMF surface (Figure 4). This regioselectivity factor in xylan biosynthesis may explain our experimental results on mosaic distribution of xylan backbone substitutes (MeGlcA and *O*Ac).

The molecular weight of *E. globulus* heteroxylan, assessed by SEC, is about 36 kDa. According to results of methylation analysis, DP of the xylan backbone varies of 130-150 [10]. Similar results on molecular weights were obtained for xylan from *E. urograndis* but remarkably lower for xylans from *E. grandis*, *B. pendula* and *A. mangium* (Table 3) [11].

Table 3. Average molecular weights of xylans isolated from different wood species.

Wood specie	Mw, kDa
E. globulus	36
E. urograndis	34
E. grandis	28
B. pendula	26
A. mangium	30

Glucans. Glucans are the second in abundance hemicellulose of *E. globulus* wood after glucuronoxylan. The main proportion of glucans is represented by α-glucans (4-5% on wood weight) [14, 15]. About 80% of α-glucans are ramified at *O*-6 of α–(1→4) glucan thus containing →4,6)-Glc*p*-(1→ structural units (amilopectin) and about 20% are linear α–(1→4) α-glucans (amilose). The molecular weight of α-glucans is rather low ranging of 8-14 kDa. The molar ratio of →4)-Glc*p*-(1→ to →4,6)-Glc*p*-(1→ structural units is about 40. α-glucans are hard to extract from wood sawdust with hot water even at 120ºC, but easily soluble in 0.5M NaOH solutions at 90-100ºC.

As revealed by methylation and 1D/2D NMR analyses of *E. globulus* glucans, these also contain a small proportion of β-glucan (< 0.2% on wood weight). This β-glucan is constituted of →3)-Glc*p*-(1→ structural blocks, which are linked, more likely, by β-(1→4) linkages [15].

Glucomannan. Glucomannan is a minor hemicelulose of *E. globulus* wood, which amount not exceeds of 1-3%. According to results of recently performed studies the backbone of eucalypt glucomannan comprises of

β-D-Glc*p* and β-D-Man*p* structural units of molar ratio 1:1.3 linked by β-(1→4) linkages [16]. The enzymatic hydrolysis of glucomannan followed by LEX/SEC separation of formed mannooligosaccharide fractions and their analysis by ESI-MS/MS revealed the random distribution of β-D-Man*p* and β-D-Glc*p* units in the backbone, which were not acetylated. The molecular weight of glucomannan, estimated by SEC and methylation analysis, was suggested to be about 8 kDa (DP 50). Glucomannan is poorly extracted from wood material by hot water, but readily extracted with strong alkaline solutions (14-17% NaOH).

Pectic compounds. Rather scarce information on the pectic compounds of *E. globulus* wood is available. The small abundance of pectin (about 1-2%) and its strong association with other macromolecular wood constituents explains the main difficulties in its isolation and structural studies. Pectin in eucalypt wood is located in the middle lamella of the cell wall as calcium doped gel and in the form of pectic strands in the parenchyma [17]. According to indirect evidences obtained in the study of eucalypt heteroxylan, pectic compounds should contain neutral rhamnoarabinogalactans and partially acetylated acidic rhamnogalactonuran [10].

Lignin

The *E. globulus* lignin structure was comprehensively studied by a set of wet chemistry, spectroscopic and mass spectrometry techniques and showed several particular features. Below are presented the main details on the frequency of occurrence of different lignin substructures and the primary lignin structure.

Lignin structural units. The proportion of the main structural units, *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) types, was elucidated based on nitrobenzene oxidation, Py-GC-MS and NMR analyses [18, 19]. The average H:G:S ratio was found to be of about 2:14:84. Hence, eucalypt lignin is of S/G type with unusually high for hardwoods proportion of syringyl structural units.

Interunit linkages. The main interunit linkages in isolated *E. globulus* dioxane lignin and MWL were elucidated based on the GC-MS analysis of permanganate oxidation and thioacydolysis products as well as employing 1D/2D/3D NMR techniques [18-20]. The structures representing about 90% of lignin interunit linkages are shown in Figure 5. β-*O*-4′structures are prevalent in eucalypt lignin, second in abundance being the pino- and seringaresinol types. At least 4 mol-% of β-*O*-4′structures contain Cα=O groups and the same proportion of β-*O*-4′structures possess non-cyclic α-*O*-4 linkages. Among condensed structures 4-*O*-5′ are the most abundant, whereas the total amount of biphenyl and β-5′ structures is about half of those, which is explained by a low abundance 3 mol-%) types are the main terminal non-phenolic
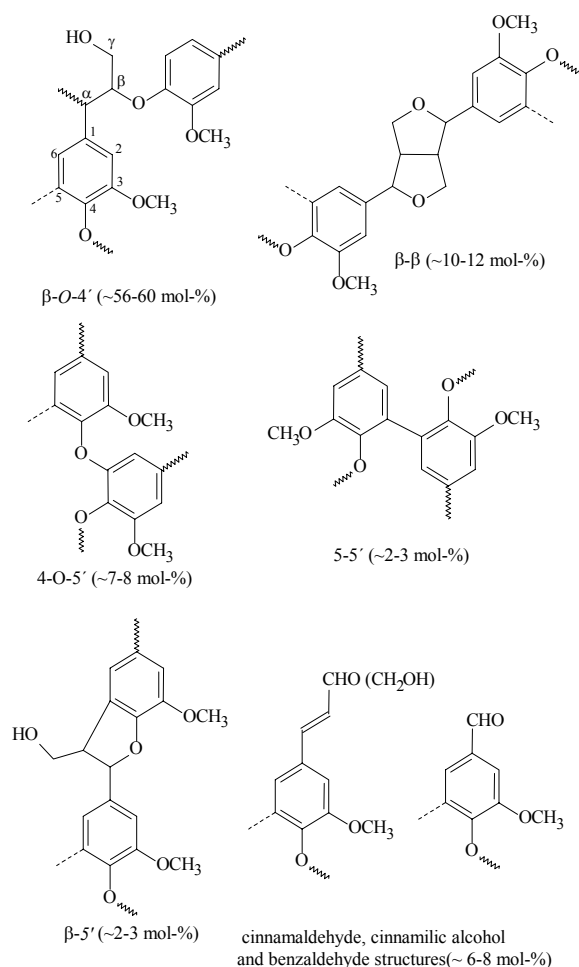

Figure 5. The most abundant structures of *E. globulus* lignin.

of G units in *E. globulus* lignin. Thus, this is a lignin with a low proportion of condensed structural units.

The structures of cinnamaldehyde (2-3 mol-%), cinnamalcohol (about 2 mol.-%) and benzaldehyde (2-structures (Figure 5) though a small proportion of cinnamic acid type structures (about 2 mol-%) have been also detected in dioxane lignin [18].

The structures with abundance lower than of 2 mol-% were impossible to detect and characterize by routine NMR techniques in lignin samples with natural ^{13}C abundance due to the low signal-to-noise ratio. Therefore, these structures were assessed in selectively [13]C-[α], [β] labelled lignins isolated from eucalypt soft xylem fed with corresponding labelled precursors [20]. This allowed the reliable assignment of lignin structures of minor abundance showed in Figure 6. These structures contribute to about 10 mol-% of lignin substructures. Rather small amounts of β-1′ and dibenzodioxocine structures, when compared to that found in softwood and even in hardwood lignins, are one of the peculiarities of eucalypt lignin.
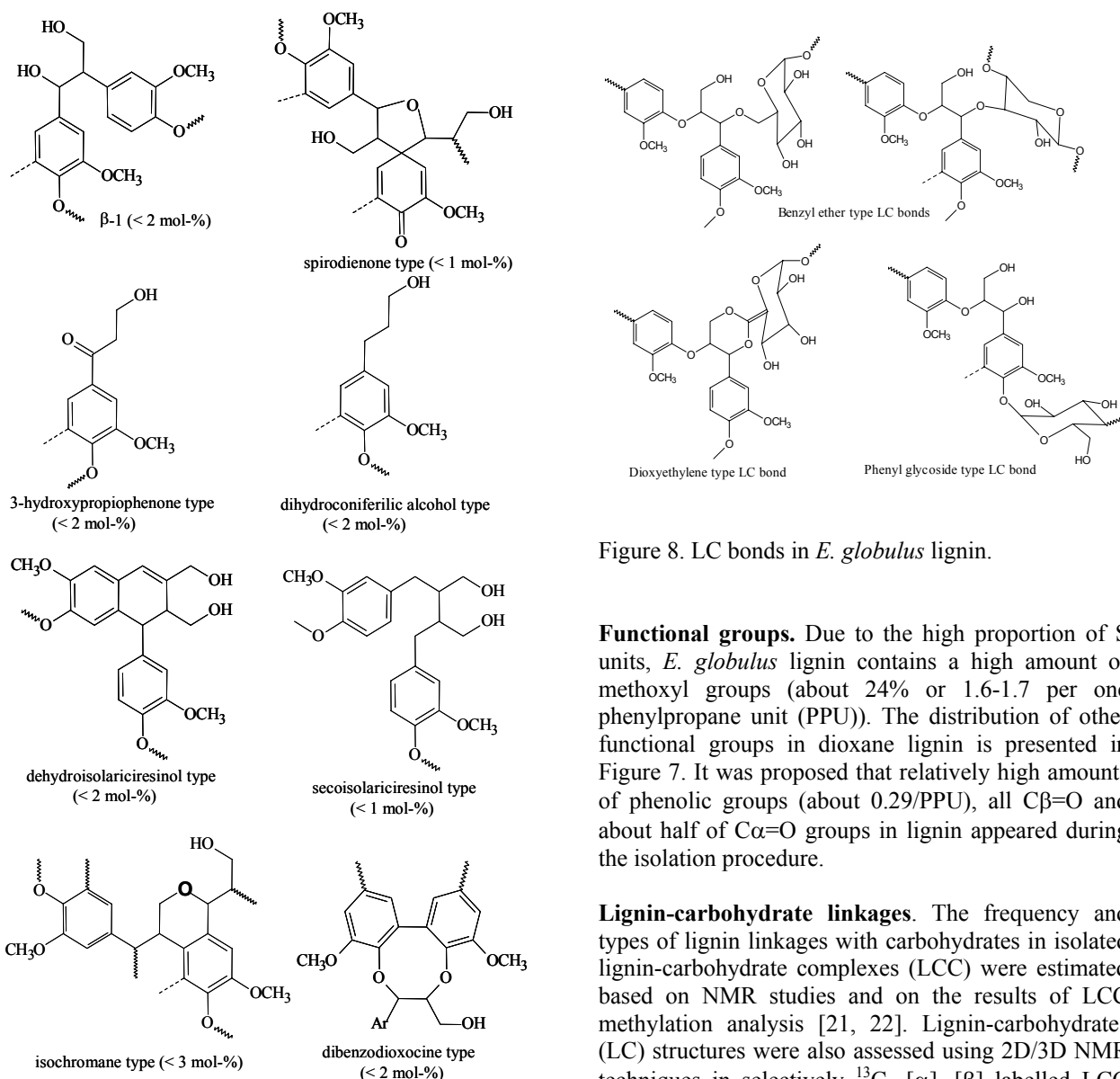
β-1 (< 2 mol-%)

spirodienone type (< 1 mol-%)

3-hydroxypropiophenone type
(< 2 mol-%)

dihydroconiferilic alcohol type
(< 2 mol-%)

dehydroisolariciresinol type
(< 2 mol-%)

secoisolariciresinol type
(< 1 mol-%)

isochromane type (< 3 mol-%)

dibenzodioxocine type
(< 2 mol-%)

Figure 6. The structures of minor abundance of *E. globulus* lignin.

OH_γ – 0.72
$C\gamma HO$ – 0.04
$C\gamma OOH$ – 0.02

OH_β – 0.02
$C\beta HO$ – 0.02
$C\beta=O$ – 0.02

OH_α – 0.28
$C\alpha HO$ – 0.03
$C\alpha=O$ – 0.08
$C\alpha OOH$ – 0.02

OCH_3 – 1.65

OH_{Ph} – 0.29
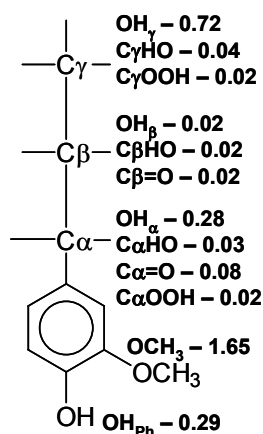
Figure 7. Distribution of functional groups per one PPU in *E. globulus* dioxane lignin [18].

Benzyl ether type LC bonds

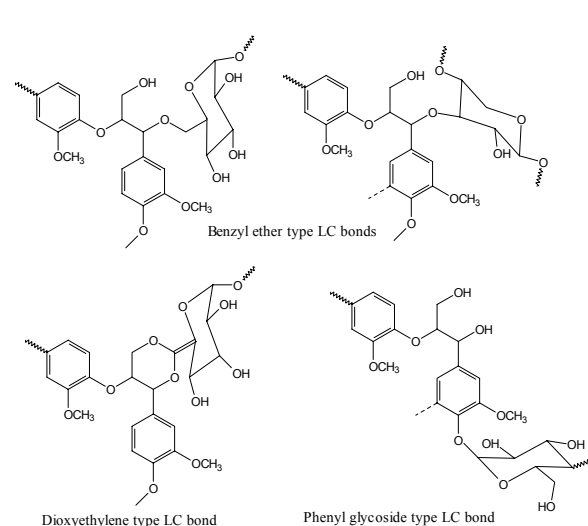Dioxyethylene type LC bond

Phenyl glycoside type LC bond

Figure 8. LC bonds in *E. globulus* lignin.

Functional groups. Due to the high proportion of S units, *E. globulus* lignin contains a high amount of methoxyl groups (about 24% or 1.6-1.7 per one phenylpropane unit (PPU)). The distribution of other functional groups in dioxane lignin is presented in Figure 7. It was proposed that relatively high amounts of phenolic groups (about 0.29/PPU), all Cβ=O and about half of Cα=O groups in lignin appeared during the isolation procedure.

Lignin-carbohydrate linkages. The frequency and types of lignin linkages with carbohydrates in isolated lignin-carbohydrate complexes (LCC) were estimated based on NMR studies and on the results of LCC methylation analysis [21, 22]. Lignin-carbohydrates (LC) structures were also assessed using 2D/3D NMR techniques in selectively [13]C- [α], [β] labelled LCC from eucalypt soft xylem fed with labelled lignin precursors [23]. The most abundant LC bonds were suggested to be the benzyl ether linkages between benzylic carbon of lignin unit and C-6 of hexoses, mainly glucose and galactose (Figure 7). The occurrence of benzylether linkages with xylan at *O*-3 of D-xylopyranosil units was suggested. In fact, xylan and glucans were the most closely structurally associated with lignin. It was also proposed the existence of phenylglucoside linkages essentially between the syryngyl units and hexoses [23]. The absence of detectable amounts of benzyl ester linkages with pectin or glucuronoxylan was tentatively explained by the formation of dioxyethylene type structures suggested to be presented in eucalypt *in situ* lignin as the intermediate of glucuronosil moiety migration between Cα and Cγ of the side chain in β-*O*-4 substructures [23]. The total amount of LC linkages apparently does not exceed of 4 mol-% [21].

Molecular weight. The molecular weight of *E. globulus* lignin was assessed by SEC, Vapour Pressure

Osmometry (VPO) and ESI-MS [18, 24]. Rather coherent results were obtained employing all these techniques. The average molecular weight (Mw) was about 2400 Da, which is a very similar value obtained for dioxane lignins isolated from eucalypt species and some other hardwoods (Table 4). Therefore the major part of lignin molecules are roughly decamers tough according to ESI-MS analysis the molecules with molecular weight of > 7000 Da are also present in lignin [24].

Table 4. Average molecular weights of dioxane lignins isolated from different wood species.

Wood specie	Mw, Da
E. globulus	2360
E. urograndis	2290
E. grandis	2160
B. pendula	2230
A. mangium	2230
P. tremula	2330

Primary structure. The tandem ESI-MS technique with Collision Induced Dissociation (CID) was used for the first time to elucidate the primary structure of *E. globulus* lignin [25, 26]. The knowledge on fragmentation patterns of lignin dilignols was gained using a series of dimeric model compounds and allowed inferring the structures of more complex oligomers (trimers, tetramers, pentamers, etc.) studied after fractionation by SEC. The information obtained on oligolignol structures from ESI-MS/MS experiments was projected to assign the main signals in the ESI-MS spectrum of the integral lignin sample (Figure 9). The experimental results evidenced the prevalence of linear fragments in *E. globulus* lignin constituted predominantly by β-*O*-4′ linked S and G units with a moderate proportion of β-β′ structures. These linear molecules are ramified with other lignin chains linked to the main backbone by α-*O*-4′ and 4-*O*-5′ bonds thus forming macromolecules in the interfibrillar space of the secondary cell wall (Figure 9). The lignin fragments of relatively low abundance constituted predominantly by G units linked mostly by biphenyl and β-5′ bonds belong, more likely, to the lignin of the middle lamella.

Effect of macromolecular components structure on pulping, bleaching and papermaking performance

Eucalypt wood is recognized as a raw material possessing high pulping and bleaching performance. Among plantation eucalypt species *E. globulus* usually shows outstanding results, which are not clearly explained [27]. Based on structural information on *E. globulus* wood components several relationships between the kraft pulping and pulp bleaching performance and the particular structural features of
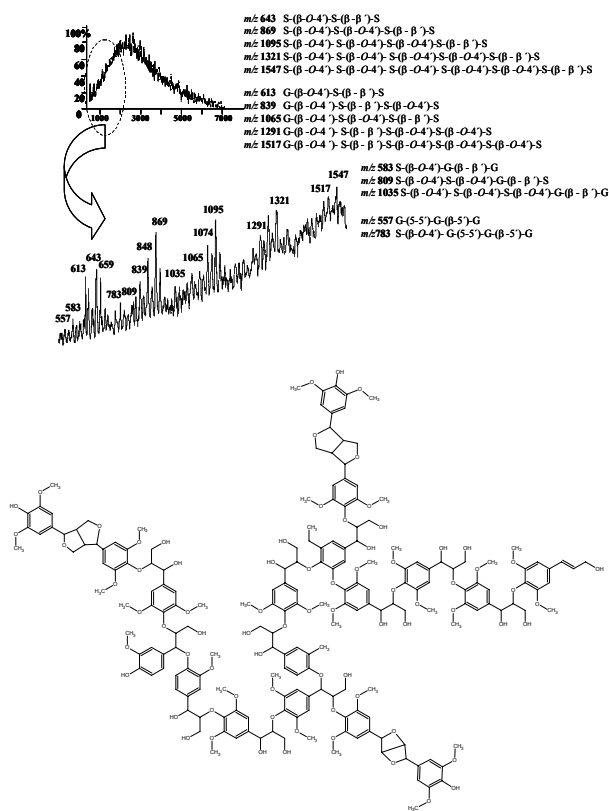

Figure 9. Negative mode ESI-MS spectrum of *E. globulus* dioxane lignin and its expanded region at *m/z* 500-1550 (top image). The structures of major oligolignols are presented at the right of the spectra. The inferred model for the lignin in the secondary cell wall of wood is depicted in the bottom.

lignin, cellulose and hemicelluloses may be established as discussed below. For comparative reasons several hardwoods were kraft pulped (160ºC, liquor-to-wood ratio 4, sulfidity -28%) to similar degree of delignification (kappa number 16-19), adjusting the charge of alkaline chemicals. Kraft pulps were bleached by DEDED to 90% brightness, adjusting the chlorine dioxide charge. Some results of the pulping and bleaching experiments are summarized in Table 5 [28].

Table 5. Results on kraft pulping (kappa number 16-19) of hardwoods and kraft pulps bleaching by DEDED sequence to 90% ISO brightness [28].

Species	Active alkali, % Na$_2$O	H factor	Pulp yield, %	ClO$_2$ %/pulp
E. globulus	16	530	55.6	4.4
E. urograndis	20	760	49.6	5.3
E. grandis	19	580	50.6	5.4
B. pendula	18	880	49.8	7.2
A. mangium	24	640	51.1	7.4

Table 6. Chemical composition (%, wood basis) of unbleached kraft pulps (kappa number 16-19) [5].

	E. globulus	*E. urograndis*	*E. grandis*	*B. pendula*	*A. mangium*
Lignin*	1.3	1.0	1.2	1.3	2.4
Neutral sugars					
Glc	45.0	40.2	40.5	38.8	42.2
Xyl	10.6	6.8	6.6	12.4	6.7
Rha	0.1	0.2	0.2	0.1	0.2
Ara	0.1	0.1	0.0	0.1	0.0
Man	0.1	0.1	0.1	0.3	0.2
Gal	0.4	0.1	0.1	0.1	0.0
Uronic acids	4.5	4.5	4.0	2.6	4.0

* Klason lignin.

It is notable that *E. globulus* wood was easier to delignify and the corresponding kraft pulps were easier to bleach when compared to other hardwoods studied. The significantly higher yield of *E. globulus* kraft pulp than that of pulps from other hardwoods certainly cannot be explained only by the relatively low lignin content in *E. globulus* wood (Table 1). In fact, different yields are obtained from hardwoods with the same lignin content. The chemical analysis of unbleached pulps (Table 6) clearly shows that their yields are determined by the proportion of remained cellulose and xylan, which in turn depends on the abundances of these polysaccharides in wood and the easiness of the lignin removal during pulping.

Effect of cellulose content. The cellulose content in wood is one of the determinant factors affecting the pulp yields [4]. Such a conclusion follows also from the comparison of results presented in Tables 1, 5 and 6. This is one of the reasons of highest yield of *E. globulus* kraft pulp, when compared to other hardwoods (Table 5).

Effect of hemicelluloses structure. At least 2% of the *E. globulus* kraft pulp yield was attributed to the retained glucans. This hemicellulose is almost completely dissolved at the initial period of the pulping [11, 15]. However, due to the high affinity of low ramified glucans to cellulose microfibrils on the fibre surface, a remarkable proportion of these polysaccharides are adsorbed on kraft pulp surface on the final stage of the pulping [15]. Hence, α-glucans also contribute to the high eucalypt kraft pulp yield.

Xylan is a second after cellulose contributor of polysaccharides to pulp yield. It is interesting to note that the amount of dissolved xylan during the pulping is rather low for *E. globulus* wood (Figure 10). For example, the amounts of xylan dissolved during kraft pulping of *B. pendula* wood were almost three times higher than the amount of xylan from *E. globulus* wood. As a consequence, the xylan percentage in eucalypt and birch kraft pulps is similar, whereas the
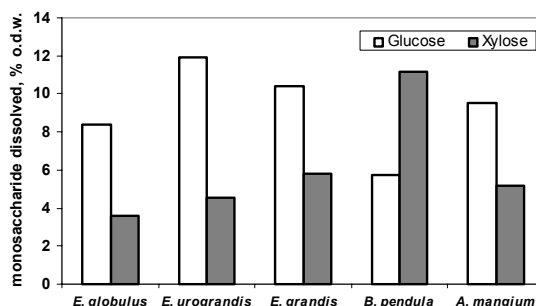

Figure 10. Percentage of glucose and xylose (as anhydrous monosaccharides based on xylose analysis) dissolved during the kraft pulping.

difference of xylan contents in corresponding woods was rather significant (Table 1).

This fact affects significantly the pulps yield (Table 5) contributing to the highest yield of *E. globulus* and to the rather low yield for *B. pendula* pulps. Unusually high retention of *E. globulus* xylan may be explained, at least partially, by its structural features such as relatively high molecular weight (Table 3) and structural association with other polysaccharides in the cell wall (Figure 3). The ramification of 4-*O*-methyl-α-D-glucuronic acid residues in eucalypt xylans at *O*-2 (sMeGlcA) with backbones of glucan and rhamnoarabinogalactan favours their higher retention in pulp during the kraft pulping than, for example, the xylan of birch wood [11]. The proportion of terminal 4-*O*-methyl-α-D-glucuronic acid residues without ramification at *O*-2 (tMeGlcA) in *E. globulus* xylan isolated from unbleached pulp is much lower than in xylan from wood (Figure 11).
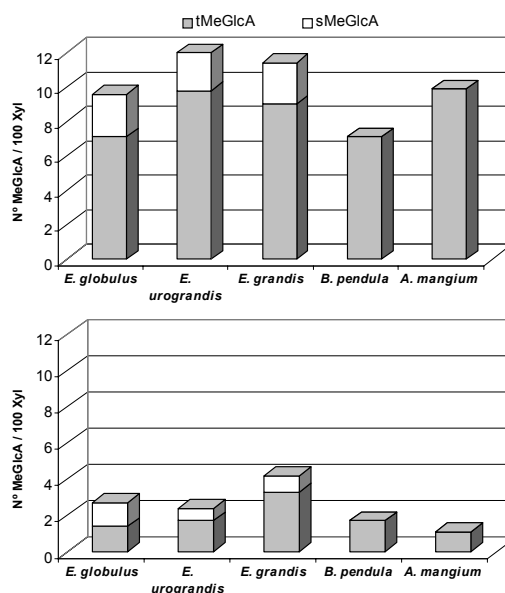

Figure 11. Relative abundance of terminal (tMeGlcA) and *O*-2 substituted (sMeGlcA) 4-*O*-methyl-α-D-glucuronic acid residues in xylans extracted from woods (top) and from unbleached pulps (bottom).

Thus xylan with higher sMeGlcA proportion (more associated with other polysaccharides) is better retained in pulp than xylan containing the less amounts of sMeGlcA. Data of Figure 11 shows also the relatively high proportion of intact MeGlcA residues in eucalypt kraft pulps that were not transformed to hexeneuronic acid (HexA) residues and were not cleaved from the xylan backbone during the kraft pulping. This structural feature (intact MeGlcA residues) provide a positive effect on bleachability and brightness stability of eucalypt pulps since HexA residues contribute to the consumption of bleaching reagents (ozone, chlorine dioxide and peroxoacids) and to the formation of chromophores [29]. It was recently highlighted that a low rate of HexA formation during the kraft pulping of *E. globulus* wood explains its relatively low content in pulp (about 40-45 mmol/kg pulp) and contribute positively to pulp bleachability with chlorine dioxide [30, 31].

Referred structural features of eucalypt xylans, favouring their high retention in pulp, naturally affect the papermaking properties of kraft pulps. Thus, the ability of bleached *E. globulus* kraft pulp to the hornification during drying is significantly diminished while the xylan content in pulp is increased [7]. This promotes the papermaking properties of pulp. Xylan also provides better beating performance of *E. globulus* bleached kraft pulp and improve its mechanical strength, especially the tear resistance. The high tear resistance is a particular reason for the high "runnability factor" of *E. globulus* bleached kraft pulp defined as [breaking length x tear resistance]$^{0.5}$ [4].

Effect of lignin structure. Particular structural features of lignin explain reasonably the easiest *E. globulus* delignification and the bleachability of correspondent kraft pulp when compared to some other industrially important hardwoods [27]. Figure 12 shows the highest proportion of S units in *E. globulus* lignin from wood and unbleached kraft pulp. As it is known S units, due to the presence of the two methoxyl groups in positions 3 and 5 of the aromatic nuclei, are more reactive than the guaiacyl counterparts in both pulping and bleaching reactions. Additionally, the extent of lignin condensation occurring in the alkaline or acidic reaction media at position 5 of aromatic ring is hindered due to the presence methoxyl group in S units. The clear correlation was observed plotting the S:G ratio of wood and kraft pulp lignins against the chemical charges used in the pulping and bleaching, respectively (Figure 13), thus confirming the importance of S units proportion in lignins. Overall, *Eucalyptus* species and, particularly *E. globulus*, having the higher S:G ratio, showed the best pulping and bleaching performance (Table 4).

Besides high S:G ratio, *E. globulus* lignin possess a high proportion of β-*O*-4´structures and a low proportion of the main condensed structures (Figures 5, 6), which significantly affect the pulping and bleaching processes [28, 32]. The cleavage of β-*O*-4´
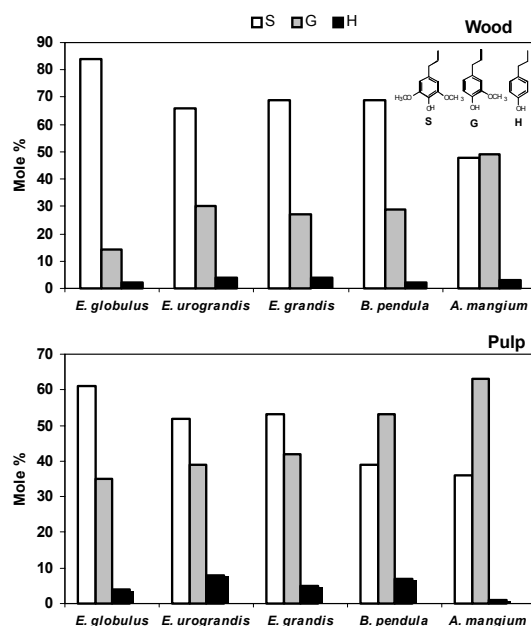

Figure 12. Relative abundance of S, G and H units in the wood and in unbleached pulp lignins as determined by ^{13}C NMR.
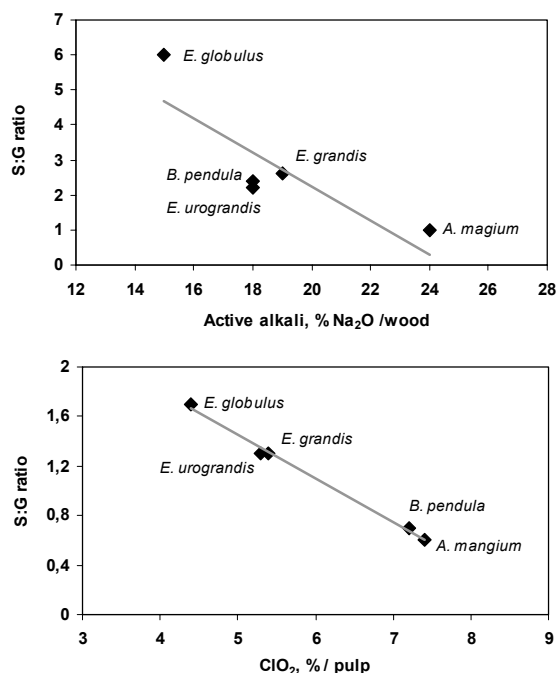

Figure 13. Relationship between syringyl:guaiacyl ratio (S:G) of lignins from wood and unbleached pulps and the kraft pulping performance (top figure) and ECF bleachability to 90% ISO (bottom figure).

bonds is crucial for the depolymerization and removal of lignin from the fibre cell walls. The ^{13}C NMR analysis of isolated series of hardwood lignins showed that these contained about 51-56 β-*O*-4´ structures per 100 aromatic units excepting *A. mangium* lignin (43/100 C$_6$) (Figure 14). Although the lower β-*O*-4´
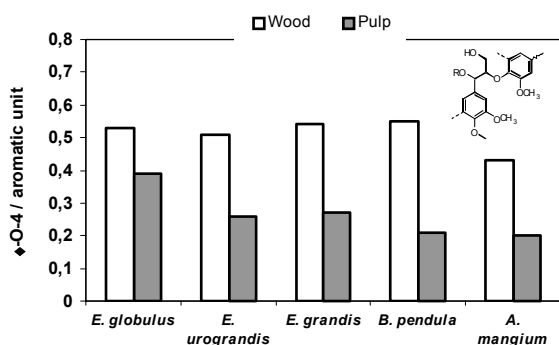
Figure 14. Relative abundance of β-*O*-4′ structures in lignins from wood and unbleached kraft pulps as determined by ^{13}C NMR.

Figure 15. Ratio of "non condensed:condensed" units (nC:C) in lignins from woods and unbleached pulps as revealed by analysis of permanganate oxidation products.

content of *A. mangium* is coherent with the higher alkaline charge required for the wood pulping (Table 4), this lignin structural feature does not explain the different pulping performance, for example, of *Eucalyptus* and *B. pendula* woods. Hence other structural features of lignin are also contributing significantly to the pulping ability. One of these features is the proportion of "non-condensed units / condensed units" (nC:C), which vary significantly in lignin of hardwood species. The results of analyses on nC:C ratio, determined based on permanganate oxidation products, are presented in Figure 15. The *Eucalyptus* lignins and, particularly, *E. globulus*, have the degree of condensation lower than lignins from other hardwoods investigated [32]. The most abundant condensed structures in *Eucalyptus* lignins are those of 4-*O*-5' type, whereas in *B. pendula* and *A. magium* the biphenyl type 5-5' units predominate [28]. During the kraft pulping the nC:C ratio decreases, denoting the preferential removal of non-condensed units and the consequent enrichment of condensed units in residual lignins (Figure 15). The nC:C ratio decreases particularly significantly during pulping of *A. mangium* wood. The proportion of β-*O*-4′ structures in residual lignins of hardwood kraft pulps is inversed to the proportion of condensed structures (compare Figures 14 and 15). Taking into consideration that condensed structures are difficult to oxidise with chlorine dioxide and to remove from unbleached pulp, the relationship between the kraft pulps bleachability, expressed as the ClO₂ consumption in DEDED bleaching to reach 90% ISO brightness, and the degree of condensation of residual lignin is rather expectable. The key role played by the extent of lignin condensation on the pulping and bleaching ability is demonstrated in Figure 16. Hence a clear tendency was observed between the proportion on non-condensed units in lignin and the ease of wood pulping and pulp bleaching. Since the proportion of diaryl ether structures in residual lignins of all hardwood kraft pulps were rather similar (13-16 mol-%), the relative abundance of biphenyl and phenylcoumaran structures was suggested to be mainly responsible for
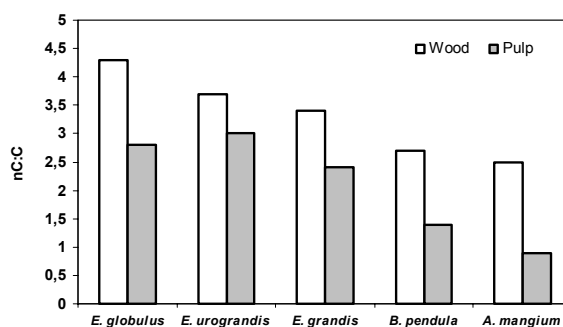
the deterioration of pulp bleachability. For example, the abundance of biphenyl structures in residual lignin of *A. mangium* kraft pulp was 5 times higher than in the residual lignin of *E. globulus* pulp.

In contrast to condensed structures, β-*O*-4′ structures are readily cleaved both during pulping and bleaching. The fact of easiest *E. globulus* wood delignification explains also unusually high proportion of β-*O*-4′ structures in residual lignin of corresponding kraft pulp (Figure 14). At the similar level of β-*O*-4′ structures in *E. globulus* and birch wood lignin, their abundance in residual birch lignin was only half to that of eucalypt. The plot of the amount of β-*O*-4′ structures in residual lignin against the consumption of chlorine dioxide during the bleaching (Figure 17)
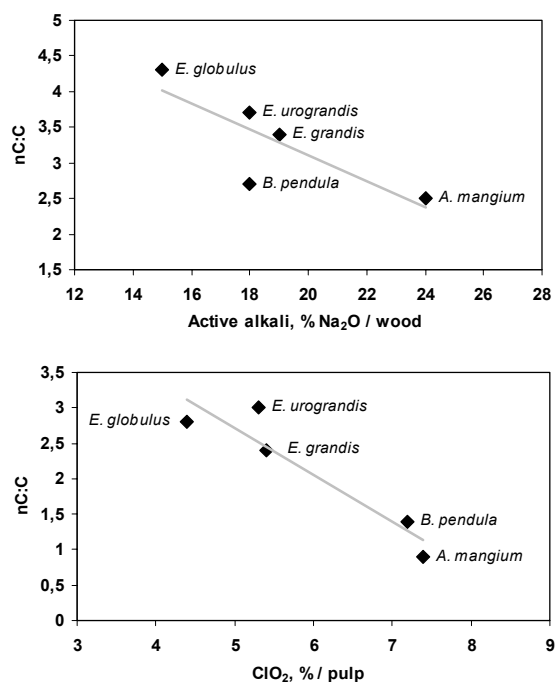

Figure 16. Relationship between "non condensed: condensed" units ratio (nC:C) in wood and unbleached pulp lignins and kraft pulping performance (top image) and ECF bleachability (bottom image), respectively.
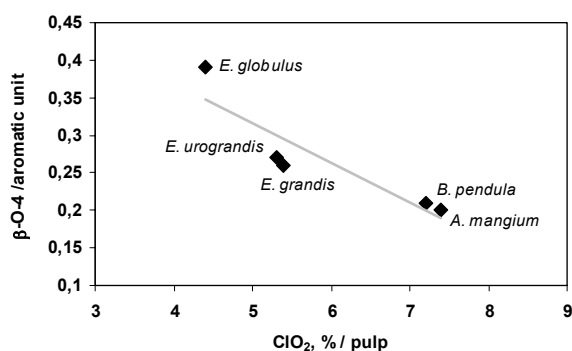
Figure 17. Relationship between the abundance of β-O-4′ structures in residual lignin of unbleached pulps and their ECF bleachability (90% ISO).
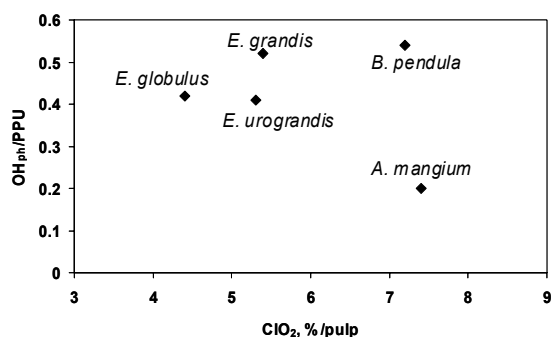

Figure 18. Relationship between the abundance of terminal phenolic structures in residual lignin of unbleached pulps and their ECF bleachability (90% ISO).

clearly shows that the ease of bleaching increases with the content of alkyl aryl ether linkages. Again, the kraft pulps from *Eucalyptus* species, having the higher content of β-O-4′ structures, showed the best bleachabilities. The proportion of β-O-4′ and condensed structures in residual lignin correlated better with pulp bleachabilities (Figures 16, 17) when compared to the amount of phenolic groups as determined by ^{1}H NMR analysis of acetylated samples (Figure 18). Therefore, the reactivity of the lignin structures towards oxidation with chloride dioxide is more important factor than simply the abundance of terminal phenolic structures.

CONCLUSIONS

The chemical composition of *E. globulus* wood and the structure of its macromolecular constituents were reviewed. These features were interrelated with kraft pulping, ECF bleaching and the papermaking performance of this wood and compared to the corresponding responses of some other hardwoods (*E. grandis*, *E. urograndis*, *B. pendula,* and *A. mangium*). Among studied hardwoods, *E. globulus* wood showed the lowest lipophilic extractives and ash contents, which indicate on the potentially smaller risks of the pitch deposition and accumulation of non-process elements in the pulp and paper production.

In general terms, *Eucalyptus* woods are easier to delignify and the respective kraft pulps are easier to bleach when compared to *B. pendula,* and *A. mangium* wood and pulps, respectively. Particularly, *E. globulus* shows the best pulping and bleaching performance. It was suggested that the rather distinct kraft pulping and bleaching performance of *E. globulus* wood is strictly related both to the proportion of macromolecular constituents and to their particular structure. Thus, the impressive yield of *E. globulus* kraft pulp is determined of high cellulose content and the relatively low lignin amounts in this wood. At the same time, the particular structure of hemicelluloses (glucuronoxylan and glucans) contributed significantly to the pulp yield. At least one percent of pulp yield is determined by glucans adsorption on pulp at the last stage of kraft pulping. This fact may be explained by high affinity of this hemicellulose to cellulose microfibrils on the pulp surface. The dissimilar retention of xylan in fibre during hardwoods kraft pulping was associated, at least partially, with differences in the abundance and structure of uronsil moieties and xylan molecular weight. The higher retention of xylans in *Eucalyptus* species, when compared, for example, to *B. pendula*, was explained by the higher molecular weight of the formers and due to the presence of terminal MeGlcA residues ramified at O-2 with rhamnoarabinogalactan and glucan backbones. The easiness of delignification of *E. globulus* wood and, consequently, the lower alkalinity used to achieve the same delignification degree of the other species, also contributes to the higher retention of xylan during the pulping of this *Eucalyptus* specie. A relatively low rate of HexA formation during the kraft pulping of *E. globulus* wood may be explained by the rather low liquor alkalinity and the particular structure of xylan (the conversion of O-2 substituted MeGlcA to HexA is slower than that of non-substituted MeGlcA residues) and contribute positively to pulp bleachability with chlorine dioxide. The relatively high proportion of xylan in *E. globulus* kraft pulp contributes significantly to its papermaking properties (hornification ability, beating behaviour, tear strength, etc.).

The easiness of wood pulping and pulp ECF bleaching was shown to be determined by the structural features of lignins rather than by their relative content in woods and pulps. Thus, the consumption of pulping and bleaching reagents positively correlated with the ratio of syringyl and guaiacyl (S:G) units and with the proportion of non-condensed and condensed (nC:C) units. *E. globulus* wood and pulp lignins possessed highest S:G and nC:C ratios. Unlike the abundance of condensed structures, the proportion of β-O-4′ structures was not a limiting factor for the pulping

performance tough the content of β-*O*-4´ correlated positively to the bleaching ability of kraft pulps with chlorine dioxide. The last feature was explained, at least partially, by the inverse proportion of β-*O*-4´ and condensed lignin structures. Condensed structures were suggested to play a key role in pulps bleachability with chlorine dioxide. Furthermore, diaryl ether type structures in residual lignin possess less detrimental effect on the pulp bleachability than biphenyl and phenylcoumaran type structures.

No clear relationship was observed between the bleaching performance and the amount of terminal lignin phenolic groups in residual lignin of hardwood kraft pulps.

REFERENCES

1. Hillman, D.C., Rooks, A. Single-species pulping: the world's preferred market pulps. **Solutions 85**: 27 (2002).
2. Mata M.G. Sustainable fibre resources for papermaking. Eucalyptus resources in Europe and South America. **Review ATIP 52** (1): 21 (1998).
3. Lehtonen, J. Papermaking furnish: A story of disruptive innovations. **Pulp Paper Intern**. (3): 25 (2005).
4. Patt, R., Kordsachia, O., Fehr, J. European hardwoods versus *E. globulus* as a raw material for pulping. **Wood Sci. Technol. 40**: 39 (2006).
5. Pascoal Neto, C., Silvestre, A.J.D., Evtuguin, D. V., Freire, C.S.R., Pinto, P.C., Santiago, A.S., Fardim, P. and Holmbom, B. Bulk and surface composition of ECF bleached hardwood kraft fibers. **Nordic Pulp Paper Res. J. 19**(4): 512 (2004).
6. Pascoal Neto, C., Evtuguin D.V. Capítulo V. Biopolímeros e biomateriais. Em livro: **Química de Polímeros.** J. S. Seixas de Melo, M. J. Moreno, H. D. Burrows, M.E. Gil, Coord., Coimbra, Imprensa da Universidade, p. 545 (2004).
7. Rebuzzi, F. and Evtuguin, D.V. Effect of glucuronoxylan on the hornification of *Eucalyptus globulus* bleached pulps. **Macromol. Symp. 232**: 121 (2006).
8. Paiva, A.T., Sequeira, S.M., Evtuguin, D.V., Kholkin, A., Portugal, I. Investigação da estrutura microscópica das fibras de papel produzida da pasta branca de *Eucalyptus globulus* pelo microscópio de força atómica (AFM). **Actas do XIX Encontro Nacional TECNICELPA,** 20-23 de Abril, Tomar, Portugal, pp.129-135 (2005).
9. Shatalov, A.A., Evtuguin, D.V., Pascoal Neto, C. **Carbohyd. Res. 320**: 93 (1999).
10. Evtuguin, D.V., Tomás, J.L., Silva, A.M.S., Pascoal Neto. C. Characterization of acetylated heteroxylan from *Eucalyptus globulus* Labill. **Carbohyd. Res. 338**: 597 (2003).
11. Pinto, P.C., Evtuguin, D. V., Pascoal Neto, C. Structural changes and behaviour of *E. globulus* xylan during kraft pulping. **Carbohydr. Polym. 60**: 489 (2005).
12. Reis, A., Pinto, P.C., Evtuguin, D. V., Pascoal Neto, C., Domingues P., Ferrer-Correia A.J., Goodfellow, B. J., Domingues M. R. M. Electrospray Tandem Mass Spectrometry of underivatised acetylated xylo-oligosaccharides. **Rapid Commun. Mass Spectr. 19**: 3589 (2005).
13. **Chemistry of Hemicelluloses.** Hon, D. N.-S.; Shirashi, N., Eds. Wood and Cellulosic Chemistry; Marcel Dekker, Inc., 1991.
14. Lisboa, S.A., Evtuguin, D.V., Pascoal Neto C., Goodfellow, B.J. Isolation and structural characterization of polysaccharides dissolved in *Eucalyptus globulus* kraft black liquors. **Carbohydr. Polym. 60**: 77 (2005).
15. Lisboa, S.A., Evtuguin, D.V. and Pascoal Neto C. Structural characterization of glucans from *E. globulus* wood and their fate in kraft pulping. **Proceedings of 9th EWLP**, August 27-30, Vienna, Austria, p. 362 (2006).
16. Evtuguin, D.V., Gonçalves, V., Domingues, R. Characterization of glucomannan from *Eucalyptus globulus* Labill. **Carbohyd. Res.** (2007). Submitted article.
17. Carr, S.G.M.; Carr, D.J. Intercellular pectic strands in parenchyma: studies of plant cell walls by scanning electron microscopy. **Austr. J. Botany**, **23**: 95 (1975).
18. Evtuguin, D.V., Pascoal Neto, C., Silva, A.M.S., Domingues, P.M., Amado, F.M.L., Robert, D., Faix, O. Comprehensive study on the chemical structure of dioxane lignin from plantation *Eucalyptus globulus* Labill wood. **J. Agric. Food Chem. 49**: 4252 (2001).
19. Pinto, P., Evtuguin, D., Pascoal Neto, C., Silvestre, A. J. Behaviour of *Eucalyptus globulus* lignin during kraft pulping. Part 1. Analysis by chemical degradation methods. **J. Wood Chem. Technol. 22**: 93 (2002).
20. Evtuguin, D.V., Balakshin, M.Yu., Terashima, N., Pascoal Neto, C. and Silva, A.S.M. New Complementary Information on the *E. globulus* Lignin Structure Obtained by 13C Selective labelling and advanced NMR techniques. **Proceedings of 12th ISWPC**, June 9-12, Madison, USA, Vol.3, p.177 (2003).
21. Balakshin, M.Yu, Evtuguin, D.V., Pascoal Neto, C. Studies on lignin and lignin-carbohydrate complex by application of advanced spectroscopic techniques. **Proceedings of 11th Intern Symp. on Wood and Pulping Chem.**, June 11-14, Nice, France, p. 103- 106 (2001).
22. Balakshin, M.Yu, Evtuguin, D.V., Pascoal Neto, C., Silva A.M.S. Lignin-carbohydride complex in *Eucalyptus globulus* wood and kraft pulps. **Proceedings of 11th Brazilian Symp.on the Chem. and other Wood Comp**. Sept. 2-5, Belo Horizonte, Brazil, p. 53 (2001).
23. Evtuguin, D.V., Goodfellow, B.J., Pascoal Neto, C. and Terashima, N. Characterization of lignin-

carbohydrate linkages in *Eucalyptus globulus* by 2D/3D NMR spectroscopy using specific carbon-13 labelling technique. **Proceedings of 13th ISWFPC**, May 16-19, Auckland, New Zealand, Vol. 2, p. 439 (2005).

24. Evtuguin D. V., Domingues Pedro N., Amado Francisco L., Pascoal Neto C., Ferrer Courreia, A. Electrospray ionization mass spectrometry as a tool for lignins molecular weight and structural characterisation. **Holzforschung 53** (5): 525 (1999).

25. Evtuguin, D.V. and Amado F.M.L. Application of Electrospray Ionization Mass Spectrometry to the Elucidation of the Primary Structure of Lignin. **Macromol. Biosci. 3** (6): 339 (2003).

26. Evtuguin, D.V., Domingues, M.R., Amado, F.M.L., Domingues P. and Pascoal Neto C. Structural characterization of cell wall biopolymers employing electrospray ionization mass spectrometry. **Proceedings of 8th European Workshop on Lignocellulosic and Pulp**, Aug. 26 - 29, Riga, Latvia, p. 45 (2004).

27. Pascoal Neto, C., Evtuguin, D., Furtado, F.P. and Mendes Sousa, A.P. Effect of Pulping Conditions on the ECF Bleachability of *Eucalyptus globulus* Kraft Pulps. **Ind. Eng. Chem. Res. 41**(24): 6200 (2002).

28. Pinto, P.C., Evtuguin, D. V., and Pascoal Neto, C. Effect of Structural Features of Macromolecular Components of Hardwood Cell Walls on Wood Pulping and Bleaching Performance. **J. Ind. Eng. Chem Res. 44**: 9777 (2005).

29. Sevastyanova O, LI J.B., Gellerstedt G. Influence of various oxidizable structures on the brightness stability of fully bleached chemical pulps. **Nordic Pulp Paper Res. J. 21**: 49 (2006).

30. Daniel, A.I.D., Pascoal Neto, C., Evtuguin, D.V. and Silvestre A.J.D. Hexenuronic acid contents of *Eucalyptus globulus* kraft pulps: Variation with pulping conditions and effect on ECF bleachability. **Tappi J. 2**(5): 3 (2003).

31. Daniel, A.I.D., Evtuguin, D.V., Silvestre, A.J.D. and Pascoal Neto, C. Chemical features of unbleached kraft pulps and their ECF bleachability. **J. Pulp Paper Sci. 30** (4): 94 (2004).

32. Pinto, P., Evtuguin, D., Pascoal Neto, C. and Silvestre, A. J. Behaviour of *Eucalyptus globulus* lignin during kraft pulping. Part 2. Analysis by NMR, ESI/MS and GPC techniques. **J. Wood Chem. Technol. 22**: 109 (2002).