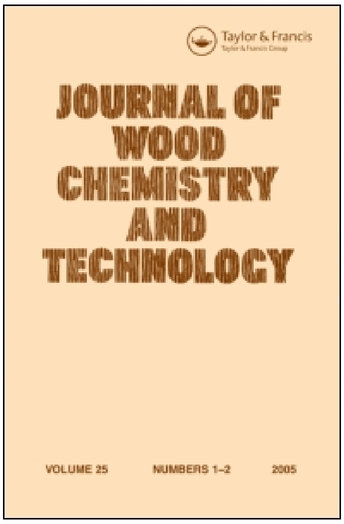
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

BEHAVIOR OF *EUCALYPTUS GLOBULUS* LIGNIN DURING KRAFT PULPING. I. ANALYSIS BY CHEMICAL DEGRADATION METHODS

Paula C. Pinto[a]; Dmitry V. Evtuguin[a]; Carlos Pascoal Neto[a]; Armando J. D. Silvestre[a]
[a] Department of Chemistry, University of Aveiro, Aveiro, Portugal

Online publication date: 08 August 2002

To cite this Article Pinto, Paula C. , Evtuguin, Dmitry V. , Neto, Carlos Pascoal and Silvestre, Armando J. D.(2002) 'BEHAVIOR OF *EUCALYPTUS GLOBULUS* LIGNIN DURING KRAFT PULPING. I. ANALYSIS BY CHEMICAL DEGRADATION METHODS', Journal of Wood Chemistry and Technology, 22: 2, 93 — 108

To link to this Article: DOI: 10.1081/WCT-120013355

URL: http://dx.doi.org/10.1081/WCT-120013355

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
Vol. 22, Nos. 2 & 3, pp. 93–108, 2002

BEHAVIOR OF *EUCALYPTUS GLOBULUS* LIGNIN DURING KRAFT PULPING. I. ANALYSIS BY CHEMICAL DEGRADATION METHODS

Paula C. Pinto, Dmitry V. Evtuguin,
Carlos Pascoal Neto,* and Armando J. D. Silvestre

Department of Chemistry, University of Aveiro,
3810-193 Aveiro, Portugal

Downloaded At: 12:15 25 January 2011

ABSTRACT

Eucalyptus globulus wood was subjected to kraft pulping, reaching different extents of delignification. The residual and dissolved lignins were isolated by soft acidolysis and acidic precipitation, respectively, and submitted to analysis of residual sugars and methoxyl groups, as well as to analysis by nitrobenzene and permanganate oxidation and thioacidolysis. Results from both residual and dissolved lignins analyses indicated that in the initial phase of pulping there is a preferential removal of lignin enriched in guaiacylpropane (G) and *p*-hydroxyphenylpropane (H) units, which is highly condensed and bonded with polysaccharides, predominantly with xylan. During the bulk and residual phases of pulping, lignin enriched in syringylpropane (S) units is progressively removed, leading

---

*Corresponding author.

DOI: 10.1081/WCT-120013355
0277-3813 (Print); 1532-2319 (Online)
www.dekker.com

Copyright © 2002 by Marcel Dekker, Inc.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

to the increase of S/G ratio of black liquor lignin. After a purification step of dissolved lignins, two fractions with distinct levels of carbohydrates and with different structural features were obtained. The overall results were interpreted in terms of the topochemistry of the kraft pulping process.

INTRODUCTION

In the last decades, *Eucalyptus globulus* wood has assumed an increasing importance as a raw material for the production of high quality pulp and paper. The knowledge of the chemical transformations undergone by wood components during industrial pulping and bleaching is crucial for the optimization of processes and product quality.

The nature of the dissolved and residual lignins produced during kraft pulping procedures has been the subject of many studies.[1–7] These studies have established the general chemical structure of dissolved and residual lignins and elucidated some of the chemical pathways of lignin degradation during the kraft pulping. As far as *E. globulus* is concerned, it was believed that its composition and the behavior of its components during kraft pulping should be similar to those described for other hardwoods. However, recent studies have shown that the components of plantation *E. globulus* wood (particularly hemicelluloses and lignin) bear specific structural features.[8,9] Such differences prompted us to investigate in detail the chemical behavior of *E. globulus* components during kraft pulping.

In this work, we report an integrated study on the chemical transformations of *Eucalyptus globulus* lignin during kraft pulping using different degradation and non-degradation techniques (NMR, Electrospray Ionization Mass Spectrometry (ESI-MS) and Gel Permeation Chromatography (GPC)). The first part of the paper deals with the results obtained by different chemical degradation techniques.

EXPERIMENTAL

Materials

Standard wood chips of 12 years old *E. globulus* trees were used for pulping experiments. The chemical composition (%, o.d. wood) was as follows: Klason lignin—20.0%; extractives (ethanol/toluene)—2.2%; holocellulose (chlorite method)—78.0%. All solvents and chemicals used were pro-analysis grade products supplied by Aldrich and Sigma, Chem. Co. (Madrid).

Downloaded At: 12:15 25 January 2011

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

Pulping Experiments

Laboratory-made *E. globulus* kraft pulps were obtained using standard conditions: liquor-to-wood ratio—4 : 1; active alkali (Na_2O)—15% o.d.w; sulfidity—28%; initial temperature—40°C; final temperature—160°C; time to final temperature—120 min. The pulping was performed in a M/K System batch digester (model 409 MII). All pulps (or partially delignified wood) were defiberized in a disc refiner, thoroughly washed with distilled water and air-dried. In order to remove extractives, pulps were extracted with dichloromethane for 8 h in a Soxhlet extractor. Kappa number, Klason and acid soluble lignins were determined by standard TAPPI methods. After pulping, the black liquors were immediately saturated with nitrogen and placed in a freezer at 4°C.

Ten pulping experiments were carried out with cooking times varying from 30 to 180 min. The delignification curve obtained, together with the temperature profile, is shown in Fig. 1.

Isolation and Purification of Lignins

Residual lignins from initial wood and from kraft pulps were isolated following the published method of mild acidolysis, which basically involves refluxing the pulp in a 1.5% HCl 9 : 1 (v/v) dioxane : water solution in nitrogen atmosphere using three short extraction steps.[8] The yield of lignin was

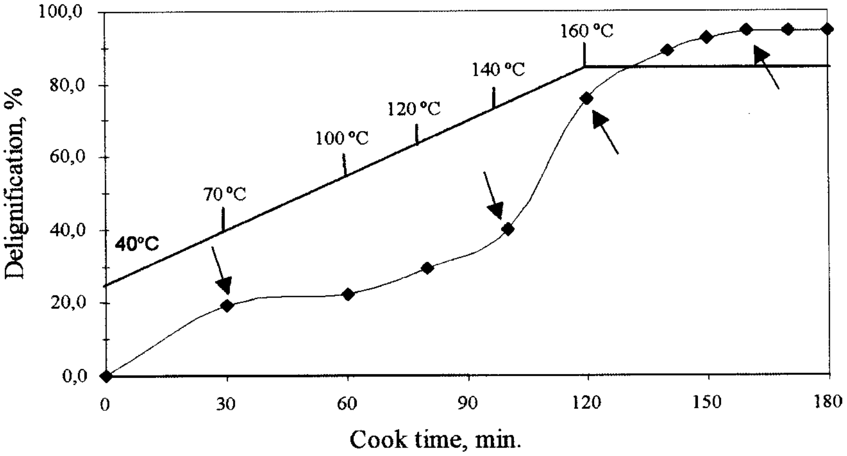


Figure 1. Delignification degree of *E. globulus* wood vs. pulping time.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

around 70% (based on Klason lignin content) for wood and poorly delignified pulps, decreasing to about 40% as the degree of delignification of pulps increases. The ash content in isolated lignin samples was about 1% (w/w). The sugar composition of lignin samples was determined by acid hydrolysis[10] followed by GC analysis of sugars as TMS derivatives.[11] In isolated residual lignins the sugar content was quite low (1.3–1.8% w/w).

Lignins from black liquors were isolated by acidic precipitation to pH 3 with aqueous H_2SO_4 (1 : 1). The precipitated material was washed with distilled water and centrifuged several times until the pH of the washing solution reached 6. Lignins were extracted with ethyl ether at room temperature, filtered, washed with water and freeze-dried. The isolated lignins were submitted to ash and carbohydrate analyses. The ash contents were in the range of 1.0–9.2%. The total carbohydrate contents were quite high and highly dependent on the degree of delignification (Table 2). Xylose was always the most abundant sugar, representing more than 76% of the weight of total sugars.

The black liquor lignin samples were submitted to further purification by dissolution in dioxane. The dioxane-non-soluble fractions, enriched in carbohydrates, were washed thoroughly with dioxane, filtered off, and freeze-dried. The dioxane-soluble fractions, enriched in lignin, were recovered by precipitation in water and freeze-dried. Sugar analysis of both fractions was performed as described above.

The designations used for lignin samples were as follows: RL—residual lignins; BL—black liquor lignin without purification; BLp—purified black liquor lignin (soluble in dioxane) and BLs—black liquor lignin fraction remaining after purification (non-soluble in dioxane, rich in sugars).

Chemical Analysis

Nitrobenzene oxidation (NO) was performed with 30 mg of BL lignin samples, or with a corresponding amount of sugar contaminated lignin, BLs, (calculated as lignin).[12] TMS derivatives (derivatization performed according to a published method[11]) of oxidation products were analyzed by GC (130–270°C). The quantification of nitrobenzene oxidation products was performed using dimethylphtalate as an internal standard.

Potassium permanganate oxidation (PO) was performed with 50 mg of lignin or with a corresponding amount of sugar contaminated lignin.[12,13] Oxidation products were methylated with diazomethane and analyzed by GC (150–270°C). The quantification of permanganate oxidation products was performed using pyromellitic acid tetramethyl ester as an internal standard.[13]

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Table 1. Empirical Formula of Wood Lignin, RL and BLp

% Delignification	RL	BLp
0*	$C_9H_{7.9}O_{2.9}\ (OCH_3)_{1.49}$	–
19.0	$C_9H_{8.3}O_{3.3}S_{0.1}(OCH_3)_{1.77}$	$C_9H_{7.4}O_{3.1}S_{1.0}(OCH_3)_{1.43}$
40.0	$C_9H_{8.8}O_{3.9}S_{0.05}(OCH_3)_{1.62}$	$C_9H_{7.6}O_{3.0}S_{0.4}(OCH_3)_{1.46}$
76.0	$C_9H_{8.1}O_{3.3}S_{0.1}(OCH_3)_{1.60}$	$C_9H_{7.3}O_{3.2}S_{0.2}(OCH_3)_{1.67}$
94.4	$C_9H_{8.1}O_{2.5}S_{0.2}(OCH_3)_{1.49}$	$C_9H_{8.0}O_{3.4}S_{0.2}(OCH_3)_{1.64}$

*Initial wood.

Thioacidolysis (TA) was carried out using an established methodology.[14] Thioacidolysis products were quantified as TMS derivatives by GC (160–290°C), using *n*-icosane as internal standard.

Analyses were performed on a Varian Star 3400CX chromatograph equipped with a fused silica capillary column SPB-5 (30 m × 0.25 mm i.d.; 0.25 μm film thickness; Supelco) with hydrogen as carrier gas (55 cm/s). Temperature programs consisted of an initial temperature of 130–160°C and a programmed rate of 5°C/min to a final temperature of 270–290°C. The FID temperature was the same as the program final temperature and injector temperature was 230°C.

The NO, PO and TA products were identified based on their retention times and mass spectra using a GC-MS HP 5890 equipped with a selective mass detector MSD series II using Helium as carrier gas (35 cm/s).

Methoxyl group contents in lignins were determined by a modified Zeisel method[15] while the elemental composition was determined using a LECO instrument, CHNS-932. Table 1 shows the empirical formula of lignins based on their elemental analysis and methoxyl groups determination. The results are corrected for ash and sugar contents.

Downloaded At: 12:15 25 January 2011

RESULTS AND DISCUSSION

Four pulping experiments were selected as representative of the different delignification phases: initial (30 min, 19.0% delignification), initial-to-bulk transition (100 min, 40.0% delignification), bulk (120 min, 76.0% delignification, kappa number 59.8) and residual phases (160 min, 94.4% delignification, kappa number 16.6). The selected pulping experiments are assigned in Figure 1.

Aiming to identify the structural and chemical changes taking place during the process of *E. globulus* kraft pulping, we isolated and

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

characterized the residual lignins from these pulps (RL) and dissolved lignins from the correspondent black liquors (BL).

Black liquor lignins isolated by acidification contained high amounts of carbohydrates, primarily composed by xylose. Such contamination is particularly high (33.7%) in the initial stage of delignification (30 min), decreasing then as the delignification proceeds. After the purification process (see Experimental), a lignin fraction containing low carbohydrate content (BLp) was obtained (60–75% reduction of carbohydrates content) together with a higher carbohydrates content lignin fraction (BLs) (Table 2). Both lignin fractions (BLp and BLs) were analyzed in order to investigate the eventual differences in their structure.

Analysis of Methoxyl Groups

Table 3 summarizes data from the methoxyl group analysis of all the isolated lignins. The results on methoxyl group contents were corrected for the lignin ash and sugars contents.

The content of methoxyl groups in the initial phase RL (after 30 min of pulping) is even higher than that in wood. Then, a decrease of the methoxyl content in residual lignin occurs. On the other hand, the methoxyl content of BL in the early stages of pulping is rather low when compared with the methoxyl content of wood. Although there is a tendency for increasing, the BL methoxyl content is always low until the end of cook, when compared to RL. The comparison between data from BL, BLp and BLs analyses shows that the lignin present in the carbohydrates rich fraction (BLs) has a low methoxyl groups content (7–8%), while the purified black liquor lignin (BLp) has methoxyl groups content not very different, on average, from RL. These data indicate that the lignin dissolved in the initial stage of the

Table 2. Total Sugar Contents in Black Liquors Lignin Without Purification (BL) and in Lignin Fractions After Purification (BLp and BLs)

Pulping Time (min)	% of Delignification	BL % (w/w)	BLp % (w/w)	BLs % (w/w)
30	19.0	33.7	14.2	41.8
100	40.0	17.6	7.0	32.4
120	76.0	10.7	4.5	33.9
160	94.4	6.0	1.5	18.9

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

Table 3. Methoxyl Group Content of Residual Lignins (RL) and Black Liquor Lignins (BL, BLp, BLs)

% Delignification	RL % (w/w)	BL % (w/w)	BLp % (w/w)	BLs % (w/w)
0*	22.2	–	–	–
19.0	24.3	9.3	18.3	7.1
40.0	21.7	12.4	20.4	8.1
76.0	22.4	18.2	23.0	7.6
94.4	22.2	16.9	22.6	6.6

*Initial wood.

kraft pulping is enriched in *p*-hydroxyphenylpropane (H) and guaiacylpropane (G) type units. Furthermore, it also suggests that there is a preferential association between hemicelluloses and lignin fractions enriched in H and G units.

Nitrobenzene Oxidation (NO)

The method of NO is a technique that covers the analysis of uncondensed structures of lignin.[16,17] Thus, G type units yield vanillin while S type units yield syringaldehyde as major products in NO.[17] The frequency of occurrence of each product issued from NO of BLp and BLs, as well as the oxidation yields, are shown in Tables 4 and 5. For comparison, the frequency of occurrence of NO products from eucalypt dioxane lignin is also presented in Table 4.

The NO yield of BLp decreases as the delignification proceeds. This observation can be assigned to an increase in the abundance of condensed structures in black liquor lignins.

In the initial phase, the dissolved lignin shows a higher content of G type units than that of wood lignin. In the following delignification stages, particularly during the bulk phase, the V : S (Vanillin : Syringaldehyde) ratio is close to that found in wood. These observations are in agreement with results on the methoxyl group analysis.

The low yield of oxidation products obtained for BLs (Table 5) may be assigned to a high abundance of structures resistant to degradative oxidation (condensed structures) in this fraction. The V : S ratio of BLs fractions is not as small as it could be expected from the methoxyl results. This discrepancy can be due to a high level of condensed structures involving

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

Table 4. Frequency of Occurrence of NO Products from Purified Black Liquor Lignin (BLp)

% Delignification	Products Frequency (Analyzed as TMS Derivatives), mol %		Yield %, w/w
	Vanillin	Syringaldehyde	
0	13	87	36.5
19.0	26	74	37.8
40.0	23	77	28.8
76.0	16	84	27.6
94.4	17	83	19.8

Table 5. Frequency of Occurrence of NO Products from Sugar-Rich Black Liquor Lignin Fraction (BLs)

	Product Frequency (Analyzed as TMS Derivatives), mol %		
% Delignification	Vanillin	Syringaldehyde	Yield %, w/w
19.0	25	75	4.8
40.0	22	78	9.1
76.0	20	80	3.8
94.4	20	77	2.3

H and G units, which is in accordance with the low yield of NO products observed.

Permanganate Oxidation (PO)

Although only the phenolic phenylpropane units are accessible to this analysis (25–35% of total units), they should represent the main structural tendencies of lignin as a whole.[18] The nine most prominent degradation acids obtained after the PO of lignins are presented in Fig. 2.

Table 6 presents the frequency of occurrence of PO products from residual lignin in each selected phase of kraft delignification. During the initial delignification phase, in which approximately 19% of the lignin is dissolved, the number of G units (product **2**) in residual lignin increases. This is in apparent conflict with methoxyl analysis and NO results.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

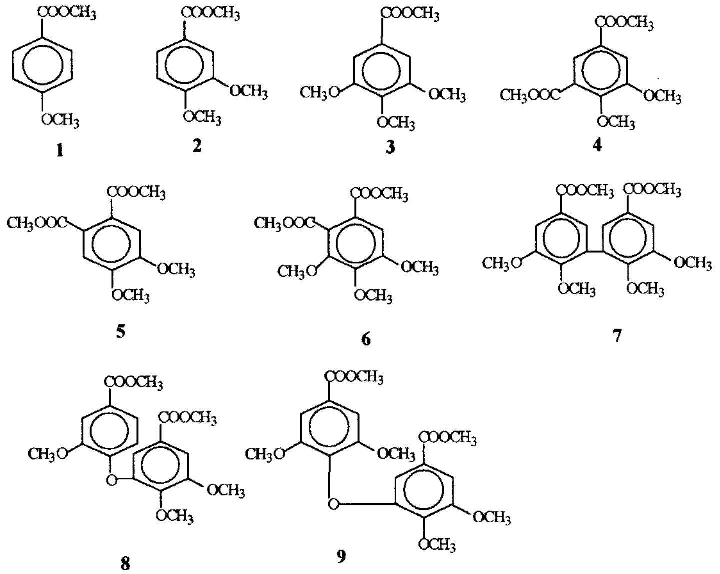


Figure 2. Carboxylic acid methyl esters obtained by PO of lignins.

Table 6. Frequency of Occurrence of PO Products of Residual Lignins (RL)

% Delignification	Frequency of Occurrence of Carboxylic Acids$^+$ (Analyzed as Methyl Esters), mol %									Yield of Esters, %, w/w
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	
0*	2	26	54	2	2	3	2	1	8	16.3
19.0	2	34	49	2	2	3	2	1	5	13.8
40.0	2	26	50	3	2	3	3	2	9	14.0
76.0	2	22	52	3	2	2	4	3	10	14.7
94.4	2	21	53	4	1	1	4	3	11	15.2

*Initial wood; $^+$Key to products designations in Fig. 2.

A tentative explanation is the formation of new guaiacyl end-groups (which become accessible to PO analysis) due to cleavage of α-or β-aryl ether structures early in the cook. This suggests a higher accessibility of morphological regions rich in G units in the early stages of the cook.

Downloaded At: 12:15 25 January 2011

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

As the delignification proceeds, there is a small increase in the frequency of occurrence of S units (product **3**). During the bulk delignification phase, the frequency of occurrence of biphenyl structure **7** and diaryl ether structures **8** and, particularly **9**, increases. Such structures resist the alkaline degradation and their content increases in pulp along the delignification. The residual lignin condensation during the pulping is reflected by appearance of increasing amounts of product **4** arising from α-5 structures.

Table 7 presents the frequency of occurrence of PO products of BLp in each selected phase of kraft delignification. The higher frequency of products **1** and **2** at the beginning of the kraft cook, comparatively to that observed in wood lignin, supports the previous suggestion that H and G enriched lignin is firstly dissolved. The delignification process is clearly accompanied by chemical changes in the structure of dissolved lignin. The transition point between initial and bulk delignification clearly shows an increase in the abundance of S type units in the black liquor lignins (Table 7). Simultaneously, the data obtained shows a decrease of G type condensed lignin structures of biphenyl type (product **7**) and, in some extent, a decrease of G type condensed structures in positions 5 and 6 of aromatic ring (products **4** and **5**, respectively). This indicates a predominant removal of condensed structures of this type in the initial stage of delignification. The complex variation of the relative abundance of lignin condensed structures represented by product **4** (Table 7) is explained by two simultaneously occurring processes: (i) removal of a lignin fraction containing phenylcoumaran structures; (ii) condensation of G type structural units in the pulping solution. Additionally, the removal of lignin enriched in S units in

Table 7. Frequency of Occurrence of PO Products of Purified Black Liquor Lignin (BLp)

% of Delignification	Frequency of Occurrence of Carboxylic Acids^{+} (Analyzed as Methyl Esters), mol %									Yield of Esters, %, w/w
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	
19.0	3	45	32	8	2	1	5	1	3	20.4
40.0	1	32	47	7	1	1	3	1	7	34.4
76.0	2	30	45	9	1	1	3	3	6	11.9
94.4	1	18	60	6	1	0	3	2	9	26.3

$^{+}$Key to products designations in Fig. 2.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

the bulk phase of the delignification, naturally leads to the decrease of the relative abundance of G type structures in black liquor.

Table 8 presents the frequency of occurrence of PO products of BLs in the transition point between initial and bulk phase (40.0% delignification) and in bulk phase (76.0% delignification). The PO yields of BLs samples are very low. This suggests that lignin fractions enriched in carbohydrates carry a small content of free phenolic structures.

The results presented in Table 8 show a frequency of occurrence of products **1**, **2** and **3** (derived from uncondensed H, G and S units, respectively), which is clearly different from that of BLp. In early stages of the cook (40.0% delignification) G units predominate over S units while in the bulk phase (76.0% delignification) S units are predominant. This result confirms again that lignin is removed from wood in a non-homogeneous way: H and G enriched lignin is dissolved intensively in early stages of kraft delignification and this lignin is strongly bonded to carbohydrates. On the other hand, it is clear from these results that such lignin (BLs, 40.0% delignification) has a high frequency of products **4**, **5** and **6** coming from condensed structures involving C-5 or C-6 positions in aromatic rings.

Thioacidolysis (TA)

Thioacidolysis is a chemical degradation method for the analysis of uncondensed lignin fraction, which involves the cleavage of ether structures.[19] Table 9 presents the frequency of occurrence of TA products from RL in each selected phase of the delignification.

The high yield of TA products (such as **G**(**S**)-CH(SEt)-CH(SEt)-CH_2(SEt)) from a RL sample at the initial stage of the delignification

Table 8. Frequency of Occurrence of PO Products of Sugar-Rich Black Liquor Lignin Fraction (BLs)

	Frequency of Occurrence of Carboxylic Acids$^+$ (Analyzed as Methyl Esters), mol %									
% Delignification	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	Yield of Esters, %, w/w
40.0	8	40	28	9	5	3	3	1	3	2.3
76.0	4	26	47	7	2	1	4	2	7	3.5

$^+$Key to products designations in Fig. 2.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

Table 9. Frequency of Occurrence of TA Products of Residual Lignins (RL)

% Delignification	Frequency of Structure Types (Analyzed as Thioethyl Ether and TMS Derivatives), $\mu mol\,g^{-1}$					Yield, $\mu mol\,g^{-1}$
	Enol Ether (G)	Enol Ether (S)	β-*O*-4 (G)	β-*O*-4 (S)	β-*O*-4 (S′)	
0*	30	98	262	1191	0	1581
19.0	29	119	510	1782	0	2440
40.0	20	79	263	1147	0	1509
76.0	14	47	310	979	29	1350
94.4	11	29	238	783	45	1106

*Initial wood.
S′: 3,4-di-hydroxy-5-methoxyphenyl derivative.

indicates a high abundance of β-*O*-4 type structures. The data demonstrate that this lignin contains even a smaller amount of condensed structures than that wood does. The dissolution of a fraction of condensed lignin structures from wood at the beginning of the pulping is the most likely reason for this feature, as previously suggested by the PO results. The decrease in yield of TA products during the course of delignification shows that the residual lignin is progressively more condensed and poorer in β-*O*-4 structures.

Enol ether type structures are known intermediates of alkaline degradation of β-aryl-ether lignin structures.[20] Thus, their presence in residual lignin of kraft pulp is expectable. In the thioacidolysis procedure, enol ether structures give rise to characteristic products ($\mathbf{G}(\mathbf{S})\text{-}CH_2\text{-}CH(SEt)_2$) that were detected and quantified.[14] The relative proportion of these structures, in reference to the total yield of TA, did not show significant changes along the pulping.

The results of TA of BLp samples (Table 10) revealed the same tendencies as suggested by other analyses: the first dissolved lignin is enriched in G units (when compared to wood lignin) while the dissolution of S units increases with cooking time.

On the other hand, the results show a clear decrease of β-*O*-4 type structures in the lignin dissolved in the liquor and an increase of relative abundance of enol ether type structures as pulping pursues. Finally, the observed decrease of TA products yield can be attributed to the fewer ether linkages and an increase of condensation reactions.

Kraft pulping is accompanied by demethylation of aromatic methoxyl groups.[20] This reaction gives compounds such as methyl mercaptan,

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

Table 10. Frequency of Occurrence of TA Products Purified Black Liquor Lignin (BLp)

	Frequency of Structures (Analyzed as Thioethyl Ether and TMS Derivatives), μmol g^{-1}					
% Delignification	Enol Ether (G)	Enol Ether (S)	β-*O*-4 (G)	β-*O*-4 (S)	β-*O*-4 (S′)	Yield, μmol g^{-1}
19.0	25	47	472	1004	0	1548
40.0	38	52	308	628	0	1026
76.0	29	76	180	644	40	929
94.4	47	101	99	249	36	532

S′: 3,4-di-hydroxy-5-methoxyphenyl derivative.

dimethyl sulfide and dimethyl disulfide, with the concomitant formation of cathecol-type structures.[20] These reactions occur essentially during the bulk and residual stages of kraft pulping as suggested by the appearance of a cathecol-type structure (aromatic structure with an OH group in position 3 of the aromatic ring, designated by S′) both in residual and black liquor lignins (Tables 9 and 10).

CONCLUSIONS

The results from the analyses of residual and black liquor lignins isolated on different stages of *E. globulus* kraft pulping revealed significant differences in their structure. Particularly, in an early stage of the delignification, lignin enriched in H and G type units with high proportion of condensed structures is removed. The dissolution of lignin enriched in S type units increase gradually as the pulping proceeds, reaching an S/G ratio similar to that in wood. The residual lignin undergoes condensation during the pulping (appearance of α-5 structures) and the contents of 5-5′ and 4-*O*-5′ structures increases. Simultaneously, the abundance of β-*O*-4 structures gradually decreases as pulping proceeds. The dissolved lignin contains significant amounts of enol ether structures. A considerable demethoxylation of both residual and dissolved lignins was observed in the residual phase of the delignification.

The heterogeneity in lignin removal during the pulping of *Eucalyptus globulus* can be explained in terms of the heterogeneous lignin structure in cell wall tissues and the topochemistry of the delignification. It is well

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

established that lignin of vessel cells and middle lamella of libriform cells is constituted by high proportions of G and H type condensed structures.[21,22] Our experimental results indicate that these morphological regions in wood tissues are the first to be attained by the pulping reagents. An intensive removal of S type lignin fractions, presumably from the S_2 layer of secondary cell wall, was observed after the delignification degree reached 20–40%. These delignification features are similar to those previously observed in kraft pulping of sweetgum (*Liquidambar styraciflua*) and, probably, are common to all angiosperm dicotyledonous plants.[23]

ACKNOWLEDGMENTS

The authors thank FCT-PRAXIS XXI for the financial support of the research project 3/3.2/PAPEL/2327/95 and for the awarding of a research grant (BIC/3700/96) to Paula Pinto. The authors also thank RAIZ—The Forest and Paper Research Institute for their collaboration and pulp preparation facilities.

REFERENCES

1. Gellerstedt, G.; Lindfors, E.-L. Structural Changes in Lignin During Kraft Pulping. Holzforschung **1984**, *38*(3), 151–158.
2. Robert, D.R.; Bardet, M.; Gellersted, G.; Lindfors, E.-L. Structural Changes in Lignin During Kraft Cooking. Part 3: On the Structure of Dissolved Lignins. J. Wood Chem. Technol. **1984**, *4*(3), 239–263.
3. Gellerstedt, G.; Gustafsson, K. Structural Changes in Lignin During Kraft Cooking. Part 5: Analysis of Dissolved Lignin by Oxidative Degradation. J. Wood Chem. Technol. **1987**, *7*(1), 65–80.
4. Hortling, B.; Tamminen, T.; Tenkanen, M.; Teleman, A.; Pekkala, O. Investigations of Residual Lignin and a Its Interaction with Polysaccharides in Chemical Pulps. In *Proceedings of the 8th International Symposium on Wood and Pulping Chemistry*, Helsinki, Finland, 1990; Vol. I, 231–238.
5. Gellerstedt, G.; Pranda, J.; Lindfors, E.-L., Structural and Molecular Properties of Residual Birch Kraft Lignins. J. Wood Chem. Technology **1994**, *14*(4), 467–482.
6. Froass, P.M.; Ragauskas, A.J. Chemical Structure of Residual Lignin from Kraft Pulp. J. Wood Chem. Technol. **1996**, *16*(4), 347–365.
7. Jiang, Z.-H.; Argyropoulos, D.S. Isolation and Characterization of Residual Lignins in Kraft Pulps. J. Pulp Paper Sci. **1999**, *25*(1), 25–29.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

Downloaded At: 12:15 25 January 2011

8. Evtuguin, D.V.; Pascoal Neto, C.; Silva, A.; Domingues, P.M.; Amado, F.M.L.; Robert, D.; Faix, O. Comprehensive Study on the Chemical Structure of Dioxane Lignin from Plantation *Eucalyptus globulus* wood. J. Agric. Food. Chem. **2001**, *49*, 4252–4261.
9. Shatalov, A.A.; Evtuguin, D.V.; Pascoal Neto, C. (2-*O*-α-D-Galactopyranosyl-4-*O*-Methyl-α-D-Glucurono)-*D*-Xylan from *Eucalyptus globulus* Labill. Carbohydr. Res. **1999**, *320*, 93–99.
10. Coimbra, M.A.; Waldron, K.W.; Selvendran, R.R. Isolation and Characterization of Cell Wall Polymers from Olive Pulp (*Olea europaea L.*). Carbohydr. Res. **1994**, *252*, 245–262.
11. Browning, B.L. *Methods in Wood Chemistry*; Interscience Publishers: New York, 1967; Vol. 2, 608–611.
12. Chen, C.-L. Characterization of Lignin by Oxidative Degradation: Use of Gas Chromatography–Mass Spectrometry Technique. In *Methods in Enzymology*; Wood, W.A., Kellogg, S.T., Eds.; Academic Press, Inc.: San Diego, California, 1988; Vol. 161, 110–136.
13. Gellerstedt, G. Chemical Degradation Methods: Permanganate Oxidation. In *Methods in Lignin Chemistry*, Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin, Germany, 1992; 322–332.
14. Rolando, C.; Monties, B.; Lapierre, C. Thioacidolisys. In *Methods in Lignin Chemistry*; Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin, Germany, 1992; 334–348.
15. Girardin, M.; Metche, M. Microdosage Rapide des Groupements Alkoxyles par Chromatographie en Phase Gazeuse. J. Chromatography **1983**, *264*, 155–158.
16. Schultz, T.; Templeton, M. Proposed Mechanism for the Nitrobenzene Oxidation of Lignin. Holzforschung **1986**, *40*(2), 93–97.
17. Kirk, T.K.; Obst, J.R. Lignin Determination. In *Methods in Enzymology*; Wood, W.A., Kellogg, S.T., Eds.; Academic Press, Inc.: San Diego, California, 1988; Vol. 161, 87–100.
18. Gellerstedt, G.; Gustafsson, K.; Lindfors, E.L. Structural Changes in Lignin During Oxygen Bleaching. Nordic Pulp Paper Res. J. **1986**, *3*, 13–18.
19. Lapierre, C. Application of New Methods for the Investigation of Lignin Structure. In *Forage Cell Wall Structure and Digestibility*; Jung, H.G., Buxton, D.R., Hatfield, R.D., Ralph, J., Eds.; American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc.: Madison, U.S.A., 1993; 133–163.
20. Gierer, J. Chemistry of Delignification. Part 1: General Concept and Reactions During Pulping. Wood Sci. and Technol. **1985**, *4*, 289–312.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

21. Saka, S.; Goring, D.A.I. The Distribution of Lignin in White Birch Wood as Determined by Bromination with TEM-EDXA. Holzforshung **1988**, *42*(3), 149–153.
22. Terashima, N.; Fukushima, K.; He, L.-F.; Takabe, K. Comprehensive Model of the Lignified Plant Cell Wall. In *Forage Cell Wall Structure and Digestibility*; Jung, H.G., Buxton, D.R., Hatfield, R.D., Ralph, J., Eds.; American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc.: Madison, U.S.A., 1993; 247–266.
23. Chiang, V.L.; Funaoka, M. The Dissolution and Condensation Reactions of Guaiacyl and Syringyl Units in Residual Lignin During Kraft Delignification of Sweetgum. Holzforshung **1990**, *44*(2), 147–155.

Downloaded At: 12:15 25 January 2011