

Identification of residual lignin markers in eucalypt kraft pulps by Py–GC/MS

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Abstract

Pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) has been used to characterize the residual lignin in eucalypt (*Eucalypt globulus*) kraft pulp during the pulping and bleaching processes. The composition and structure of eucalypt wood lignin and kraft lignin have also been studied by Py–GC/MS and ¹³C-nuclear magnetic resonance (NMR). Pulp samples were collected at different stages of the pulping process (after cooking, oxygen delignification, and bleaching with chlorine dioxide or hydrogen peroxide). By comparison with lignin pyrolysis products obtained from Py–GC/MS of eucalypt wood and kraft lignin, characteristic features of lignin in the different pulps have been established. The main lignin-derived markers detected in pulps were guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, syringol, 4-methylsyringol, 4-ethylsyringol, 4-vinylsyringol and *trans*-4-propenylsyringol, all of them in very low amounts. Analytical pyrolysis was also used to characterize the changes in the residual lignin after kraft pulping of eucalypt wood pretreated with two lignin-degrading fungi (*Bjerkandera adusta* and *Poria subvermispora*) in wood ‘biopulping’ experiments. In general, Py–GC/MS has shown to be valuable in the characterization of residual lignin markers in kraft pulps due to the sensitivity of the technique when individual-ion chromatographic profiles for selected lignin markers are used. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Residual lignin in kraft pulp is a three-dimensional polymer linked by condensed (i.e. C–C) bonds and some ether linkages between dihydrophenyl propionic, diphenylmethane and stilbene units, most of which are not readily hydrolyzable [1–3]. The structure of residual lignin in kraft pulps is significantly different from that of the lignin in wood, and even from lignin dissolved in black liquors from kraft cooking [2,4]. During kraft pulping (characterized by high-temperature alkaline cooking), aryl ethers are ‘depleted’, ‘condensed’ bonds are enriched, and new links to polysaccharides are formed [5].

Methods for measuring the effects of different delignification reactions on the structure of lignin in both pulp fibers and spent liquors are important in the development of new pulping and bleaching sequences. Kraft pulps have much lower lignin content than wood, and consequently, a method is needed for the ‘in situ’ characterization of residual lignin in pulp avoiding the risk of artifacts generated during lignin isolation. Analytical pyrolysis coupled with gas chromatography/mass spectrometry (Py–GC/MS) has already been used for the analysis of chemical and mechanical pulps [6]. Py–GC/MS is a powerful tool for the characterization of complex natural polymers, such as lignin and polysaccharides in wood that requires very small amount of sample and provides detailed information on molecular changes. Lignin is pyrolyzed to produce a mixture of relatively simple phenols, which result from cleavage of ether and certain C–C linkages [7,8]. Most of these phenols retain the ring-substitution patterns from the lignin polymer, and it is, thus, possible to identify products from the *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) lignin units [7].

In this work, we analyzed by Py–GC/MS (using lignin marker compounds), the residual lignin in eucalypt kraft pulp during the cooking and bleaching processes. We also studied the effect of pretreating wood with lignin-degrading fungi on the structure of residual lignin in pulp. By comparison with lignin breakdown products obtained from eucalypt wood and kraft lignin, characteristic features of lignin in the different pulps have been established. Syringyl/guaiacyl (S/G) ratios have also been calculated by monitoring characteristic ions in the Py–GC/MS profile. This study will give a better understanding of the chemical composition of residual lignin in kraft pulps and the effect of the different bleaching stages on its structure.

2. Material and methods

2.1. Collection of industrial kraft pulps

Eucalypt (*Eucalypt globulus*) pulp samples were collected from the ENCE mills (Pontevedra and Huelva, Spain) at the following stages of totally chlorine-free (TCF) and elementary chlorine-free (ECF) bleaching sequences; after kraft cooking and several washing stages (sample W with kappa number 16); after oxygen delignification stage (sample O with kappa number 10); and after bleaching with

chlorine dioxide (sample D with kappa number 0.5) or hydrogen peroxide (sample P with kappa number 4). Samples of *E. globulus* wood (15.7% Klason lignin content) and kraft lignin, obtained by acid precipitation of black liquor, were also provided by ENCE.

2.2. Laboratory kraft pulping of *Eucalypt* wood treated with fungi

Two white-rot fungal strains, known for their ability to degrade lignin, were selected for bio-kraft experiments; *Bjerkandera adusta* CBS 230.93 and *Poria* (synonym, *Ceriporiopsis*) *subvermispora* CBS 347.63. Eucalypt chips (2–4 × 20–40 mm) were treated with the fungi under solid-state fermentation conditions using a rotary fermentor including six 2-l bottles, each of them containing 350 g of chips. After 21 days, the treated chips were used in laboratory cooking and bleaching experiments. Kraft cooking was performed in a Lorentzen & Wettre digester at 165°C (50 min), with liquor–wood ratio 3.5, sulfidity 25%, and active alkali 15% (to obtain kappa 16). After cooking, the brown pulps were washed and dried in an aerated oven at 60°C. The conditions for fungal inocula preparation, eucalypt wood treatment, and laboratory cooking were described elsewhere [9].

2.3. Solid-state nuclear magnetic resonance

Solid-state ^{13}C -nuclear magnetic resonance (^{13}C -NMR) analyses under quantitative acquisition conditions were carried out in a Bruker MSL 300 spectrometer at 75.4 MHz with the cross polarization/magic angle spinning (CP/MAS) technique [10]. The pulse repetition rate was set to 5 s and the cross polarization contact to 1 ms. One thousand cycles were accumulated for each spectrum. The sweep width was 37.5 kHz and the acquisition time was 0.016 s. Magic angle spinning was performed at 4 kHz.

2.4. Curie-point flash pyrolysis–gas chromatography/mass spectrometry

The pyrolysis was performed with a Varian Saturn 2000 GC–MS, using a 30 m × 0.25 mm DB-5 column (film thickness, 0.25 μm), coupled to a Curie-point pyrolyzer (Horizon Instruments Ltd.). Approximately 100 μg of finely divided sample was deposited on a ferromagnetic wire, then inserted into the glass liner and placed immediately in the pyrolyzer. The pyrolysis was carried out at 610°C for 3.5 s. The chromatograph was programmed from 40°C (1 min) to 300°C at a rate of 6°C min^{−1}. The final temperature was held for 20 min. The injector, equipped with a liquid carbon dioxide cryogenic unit, was programmed from −30°C (1 min) to 300°C at 200°C min^{−1}, while the GC–MS interface was kept at 300°C. The compounds were identified by comparison with those reported in the literature [11] and in the Wiley and Nist computer libraries.

3. Results and discussion

3.1. Characterization of *Eucalypt* wood and kraft lignin

In order to gain information about the degradation of eucalypt (*E. globulus*) lignin under kraft pulping conditions, wood and kraft lignin were analyzed by solid-state ^{13}C -NMR and Py-GC/MS. The solid-state ^{13}C -NMR spectra of both samples are shown in Fig. 1.

The main ^{13}C -NMR signals can be assigned as shown in Table 1 [12]. The eucalypt wood spectrum is dominated by carbohydrate signals at 63, 74 and 105 ppm from the cellulose and hemicellulose moieties. Lignin signals observed in eucalypt wood corresponded to etherified syringyl and guaiacyl units (153, 136, 74 and 84 ppm). In contrast, the kraft lignin spectrum is dominated by lignin signals from phenolic units (148 ppm) and only a small shoulder at 153 ppm (corresponding to non-phenolic S units) was observed. Another important peaks in the kraft lignin spectrum are at 56 ppm, from methoxyl groups, and a small broad signal at 175 ppm that can be attributed to the presence of carbonyl groups due to an

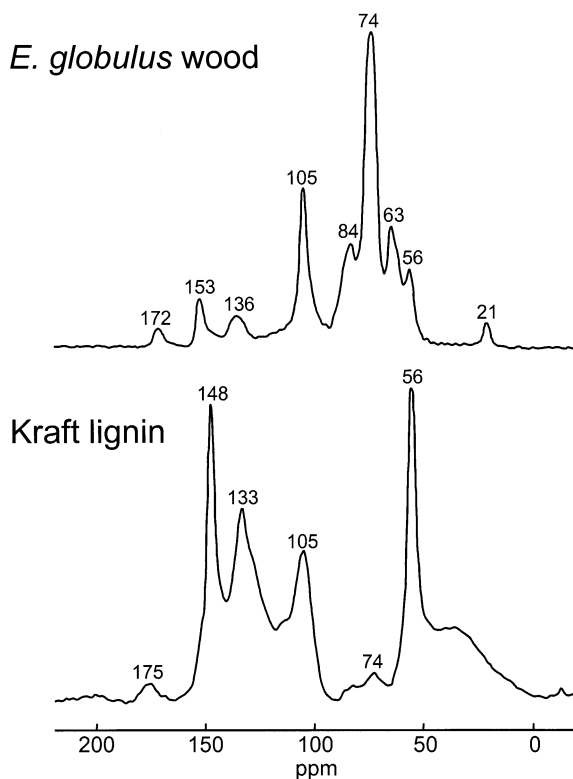


Fig. 1. Solid-state ^{13}C -NMR spectra of *E. globulus* wood and kraft lignin from *E. globulus* wood. Signal assignment is shown in Table 1.

Table 1

Assignments of the main ^{13}C -NMR signals in *E. globulus* wood and kraft lignin [12]

^{13}C shift (ppm)	Assignment
<i>Cellulose and hemicellulose</i>	
172	Carbonyl C of acetyl groups in hemicellulose
105	C-1 in cellulose
103 Shoulder	C-1 in hemicellulose
89	C-4 in cellulose (crystalline)
84	C-4 in cellulose (amorphous)
74	C-2, C-3, C-5 in cellulose and hemicellulose
63	C-6 in cellulose (crystalline)
50–27	Alkyl C not attached to oxygen
21	Methyl C of acetyl groups in hemicellulose
<i>Lignin (S, syringyl, G, guaiacyl)</i>	
153	S C-3 and C-5 (4-O-R)
148	S C-3 and C-5 (4-O-H), G C-3 and C-4
136	S C-1 and C-4 (4-O-R), G C-1 (4-O-R)
133	S C-1 and C-4 (4-O-H), G C-1 (4-OH)
120	G C-6
115	G C-5
112	G C-2
105	S C-2 and C-6
84	C- β in β -O-4
74	C- α -OH in β -O-4
60	C- γ -OH
56	Methoxyl C
52–15	Aliphatic C not bound to oxygen

enrichment process during pulping [4]. In a previous paper, Camarero et al. [13] quantified the phenolic content *E. globulus* kraft lignin as high as 64% (using Py-GC/MS after sample permethylation) in agreement with the NMR spectrum shown in Fig. 1. The high phenolic content in kraft lignin is due to the degradation of aryl-ether linkages under the kraft cooking conditions. In kraft pulping (as in sulfite pulping), depolymerization of lignin depends on the cleavage of ether linkages, whereas the carbon-carbon linkages are essentially stable. This results in increased hydrophilicity and solubilization of lignin because of the liberation of phenolic hydroxyl groups.

The pyrograms of eucalypt wood and kraft lignin are shown in Fig. 2. The identities of the lignin-derived phenolic compounds released, as well as their relative abundances are shown in Table 2. Significant differences were observed among the distribution patterns of the lignin-derived compounds released from both samples. Major peaks were identified as 4-methylguaiacol (3), 4-ethylguaiacol (5), 4-vinylguaiacol (6), syringol (9), 4-methylsyringol (14), 4-ethylsyringol (17), 4-vinylsyringol (19), syringaldehyde (26) and *trans*-4-propenylsyringol (27). The differences between the lignin in eucalypt wood and the kraft lignin are especially evident in the relatively high abundances of guaiacol (1), 4-methylguaiacol (3), 4-ethylguaiacol (5),

syringol (9), 4-methylsyringol (14) and 4-ethylsyringol (17) in the latter. Small amounts of 3-methoxycatechol (4), 5-methyl,3-methoxycatechol (10), as well as a compound with a molecular weight at m/z 194 and tentatively assigned as an isomer of propenylsyringol (23) were also identified in the kraft lignin but were absent in the native eucalypt lignin. Some minor amounts of sulfur (S_8) were also detected in eucalypt kraft lignin.

Syringyl/guaiacyl ratios were calculated by quantifying the areas of the corresponding peaks in the Py–GC/MS profile. It is apparent that the syringyl/guaiacyl ratio in kraft lignin (4.3) is lower than in the corresponding sound lignin (6.4), suggesting a preferential degradation of S lignin upon kraft pulping (compared with

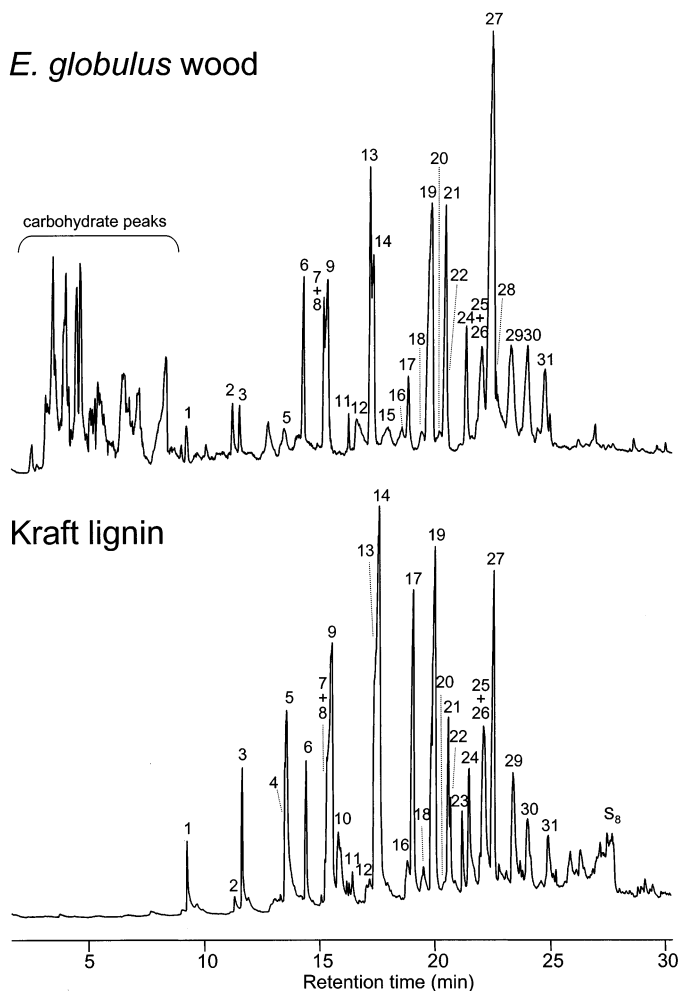


Fig. 2. Py–GC/MS of *E. globulus* wood (15.7% lignin) and kraft lignin from *E. globulus* wood. Peak identities for the lignin-derived compounds are shown in Table 2.

Table 2

Lignin-derived compounds (%) released upon Py-GC/MS of *E. globulus* wood and kraft lignin

Number	Compound	<i>E. globulus</i> wood	Kraft lignin
1	Guaiacol	1.1	1.4
2	3,4-Dihydroxybenzaldehyde	1.4	0.3
3	4-Methylguaiacol	0.5	2.7
4	3-Methoxycatechol	0.0	3.1
5	4-Ethylguaiacol	0.5	4.2
6	4-Vinylguaiacol	2.7	2.5
7	Eugenol	0.4	0.3
8	4-Propylguaiacol	0.1	0.8
9	Syringol	6.5	10.8
10	5-Methyl,3-methoxycatechol	0.0	1.9
11	<i>cis</i> -Isoeugenol	0.4	0.2
12	Vanillin	0.7	0.6
13	<i>trans</i> -Isoeugenol	4.2	2.4
14	4-Methylsyringol	3.7	17.5
15	Homovanillin	0.7	0.0
16	Acetoguaiacone	0.4	0.6
17	4-Ethylsyringol	1.1	7.2
18	Guaiacyl acetone	1.1	0.8
19	4-Vinylsyringol	15.2	12.8
20	Propiovanillone	0.7	1.2
21	4-Allylsyringol	5.7	2.0
22	4-Propylsyringol	0.4	1.0
23	Isomer of propenylsyringol	0.0	1.2
24	<i>cis</i> -4-Propenylsyringol	2.7	3.2
25	Propynylsyringol	3.6	2.1
26	Syringaldehyde	4.4	4.1
27	<i>trans</i> -4-Propenylsyringol	25.8	7.4
28	Homosyringaldehyde	2.8	0.0
29	Acetosyringone	5.8	3.6
30	Syringylacetone	4.2	2.4
31	Propiosyringone	3.4	1.4
	Syringyl/guaiacyl ratio	6.4	4.3
	Ph-C ₁₋₂ /Ph-C ₃ ratio ^a	1.1	3.3

^a Ratio of phenylmethane + phenylethane to phenylpropane-type compounds.

G lignin). Fergus and Goring [14] showed that S-rich fibers were delignified easily as compared with G-rich vessels under kraft and sulfite pulping conditions, and concluded that the ratio of delignification did not depend on the accessibility of lignin but rather on its chemical structure. Further, the rate of delignification was found to be directly proportional to the syringyl/guaiacyl ratio [15,16].

During delignification of wood in the kraft process, the lignin component is solubilized via degradation and ionization to free the fiber for the manufacture of paper pulp. The lignin alteration is characterized by degradation of the side-chain, including a partial loss of C γ atoms, β -O-4 bond cleavage, limited demethylation and formation of stilbene structures from phenylcoumarans [17,18]. These changes

are corroborated by the ^{13}C -NMR spectra and Py-GC/MS analyses shown in Figs. 1 and 2, respectively. In this sense, the ratio of phenylmethane (ph-C₁) and phenylethane (ph-C₂) compounds with respect to phenylpropane (ph-C₃) units increases in the eucalypt kraft lignin (3.3) compared with the native lignin in *E. globulus* wood (1.1) confirming the degradation of the lignin side chains during kraft pulping.

3.2. Composition of residual lignin in Eucalypt kraft pulps: analysis of marker compounds

In order to avoid excessive carbohydrate degradation, kraft pulping protocols are determined typically at a lignin content of 4–5% for softwoods and 2–3% for hardwoods. Structural studies of the residual lignin remaining with the fibre at this stage have shown that significant amounts of arylglycerol- β -aryl ether structures are still present [19,20].

Fig. 3 shows the pyrograms of the eucalypt kraft pulps collected at different stages of pulping and bleaching. In all cases, the main peaks corresponded to carbohydrate-derived compounds, and their identities are shown in Table 3. The lignin-derived peaks are very minor, as corresponds to kraft pulps, and only syringol (9), 4-methylsyringol (14), 4-vinylsyringol (19) and *trans*-4-propenylsyringol (27) could be easily detected in the pyrograms of all samples except in the chlorine dioxide bleached kraft pulp (sample D). However, by selecting specific *m/z* ions, more lignin-derived compounds could be detected in the pyrograms of the pulp samples. Fig. 4 shows the reconstructed chromatogram (by selecting the molecular ions for the main lignin markers shown in Table 4) of the unbleached eucalypt kraft pulp (sample W, with 2.4% lignin content calculated from kappa number). The reconstructed chromatogram of the eucalypt wood sample is also shown for comparison. It is interesting to note the close resemblance of the lignin fingerprints in both the total ion chromatogram (Fig. 2) and reconstructed ion chromatogram (Fig. 4) of eucalypt wood.

The main lignin-derived markers detected in the reconstructed chromatograms of the unbleached pulp (sample W) were guaiacol (1), methylguaiacol (3), 4-ethylguaiacol (5), 4-vinylguaiacol (6), syringol (9), 4-methylsyringol (14), 4-ethylsyringol (17), 4-vinylsyringol (19) and *trans*-4-propenylsyringol (27), all of them in low amounts. A comparison between the pyrolysis data of native lignin and residual lignin in kraft pulps suggests that significant changes to the lignin occurred during pulping. From the relative peak intensities, it can be seen that, in comparison to eucalypt wood, the residual lignin in the unbleached pulp gives rise to higher amounts of 4-ethylguaiacol (5), 4-vinylguaiacol (6) as well as syringol (9), 4-ethylsyringol (17) and 4-vinylsyringol (19), whereas the amounts of *trans*-isoeugenol (13) and *trans*-4-propenylsyringol (27) are much smaller. Similar results have been reported by Py-GC/MS of kraft pulps by Kleen and Gellerstedt [6]. In the unbleached pulp, it was possible to calculate a syringyl/guaiacyl ratio of 5.5. However, it was not possible to determine this ratio with accuracy in the bleached pulps due to the extremely low content of residual lignin.

Eucalypt kraft pulp after oxygen delignification (sample O, with 1.5% lignin content) still gives rise to similar lignin-derived compounds as in the unbleached kraft pulp (sample W) upon Py–GC/MS (Fig. 3), with syringol (9), 4-methylsyringol (14), 4-vinylsyringol (19) and *trans*-4-propenylsyringol (27) as the most abundant lignin compounds. In general terms, oxygen delignification removes up to 50% of the lignin present in a kraft pulp without affecting seriously the pulp quality

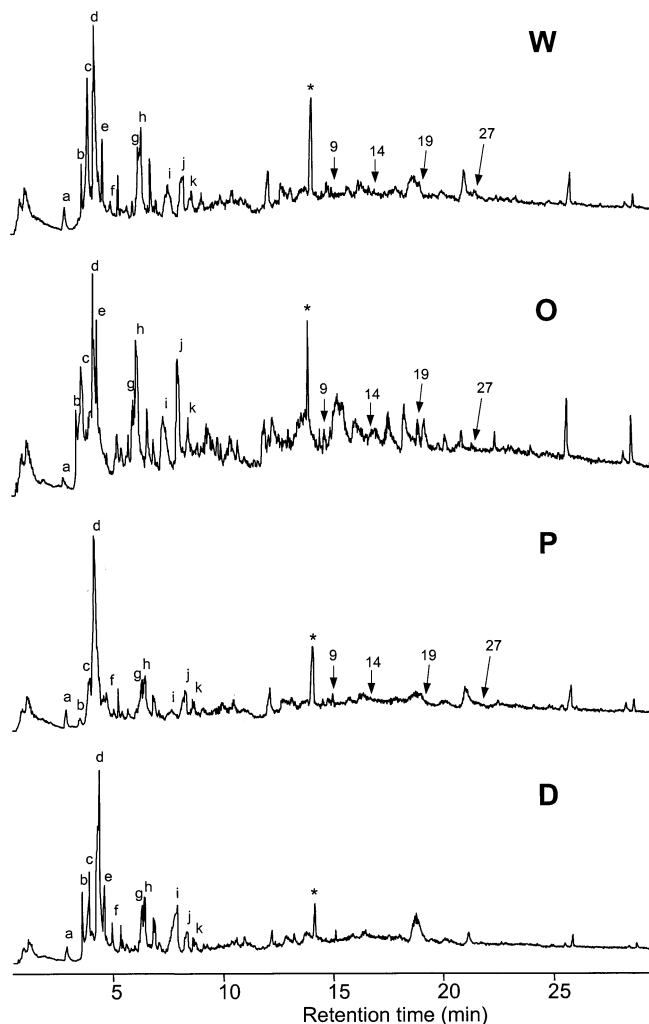


Fig. 3. Py–GC/MS of eucalypt kraft pulp from TCF and ECF bleaching sequences. W, after kraft cooking and washing stages (2.4% lignin content); O, after oxygen delignification (1.5% lignin); P, after hydrogen peroxide bleaching (0.6% lignin); D, after chlorine dioxide bleaching (0.07% lignin). The identities of the carbohydrate-derived peaks (in letters a–k) are shown in Table 3. The identities of the lignin-derived peaks (in arabic numerals) are shown in Table 2. (*) unknown, probably a carbohydrate-derived product.

Table 3

Main carbohydrate-derived compounds released upon Py–GC/MS of kraft pulp

Number	Molecular weight	Compound
a	86	2,3-Butanedione
b	82	1,4-Pentadiene-3-one
c	74	3-Hydroxypropanal
d	96	2-Furaldehyde
e	96	Cyclopenten-1-ene,3,4-dione
f	98	Hydroxymethylfuran
g	98	2,5-Dihydro-5-methylfuran-2-one
h	98	2,3-Dihydro-5-methylfuran-2-one
i	114	4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one
j	112	2-Hydroxy-3-methyl-2-cyclopenten-1-one
k	126	Levoglucosenone

and therefore, the amounts of lignin-derived markers are lower and only the most abundant compounds can be detected by analytical pyrolysis.

After the oxygen delignification stage, the pulp was bleached either with hydrogen peroxide or with chlorine dioxide (in TCF and ECF sequences, respectively). In the hydrogen peroxide bleached pulp (sample P, with 0.6% lignin content), some lignin-derived compounds such as syringol (9), 4-methylsyringol (14), 4-vinylsyringol (19) and *trans*-4-propenylsyringol (27) could still be detected upon Py–GC/MS (Fig. 3), although in very low amounts. The lignin-derived markers that could be detected were mainly of S structure because they are more abundant than the G ones. Hydrogen peroxide is thought to react mainly with the carbonyl structures present in lignin, therefore, its action on residual lignin may not be very significant since small amounts of such species are present [21,22]. However, in the chlorine dioxide bleached pulp (sample D, with 0.07% lignin content), no traces of lignin markers could be detected upon Py–GC/MS (Fig. 3). The overall efficiency of chlorine dioxide during the D stage is due to the combined effects of both chlorination and oxidation, especially at higher charges of chlorine dioxide. The concerted action of these two pathways on lignin results in an extremely effective combination of reactions.

3.3. Composition of residual lignin in *Eucalypt biopulps*

Analytical pyrolysis was also used to characterize the composition of residual lignin in kraft pulp made of eucalypt wood pretreated with two selected ligninolytic fungi (*B. adusta* and *P. subvermispora*). The most important problem in the production of paper pulp is the removing of lignin in order to recover cellulosic fibers. Because of the insoluble and cross-linking nature of lignins, delignification requires drastic pulping conditions, and lignin must be removed at a tremendous environmental and process cost. Biotechnological processes based on ligninolytic fungi can be used as a low-environmental impact pulping process instead of

chemical delignification. Analytical pyrolysis can provide information on the changes in the composition of residual lignin in pulp after biological pretreatment of wood.

Fig. 5 shows the Py–GC/MS analysis of the kraft pulps obtained after fungal pretreatment of eucalypt wood with the fungi *P. subvermispora* and *B. adusta*. The main peaks corresponded to carbohydrate-derived compounds and their identities are shown in Table 3. Some lignin markers are also present although in low amounts. However, by monitoring the characteristic ions outlined in Table 4, a series of lignin-derived compounds could also be detected in the reconstructed chromatograms for the unbleached biopulps (Fig. 6). The main lignin markers are

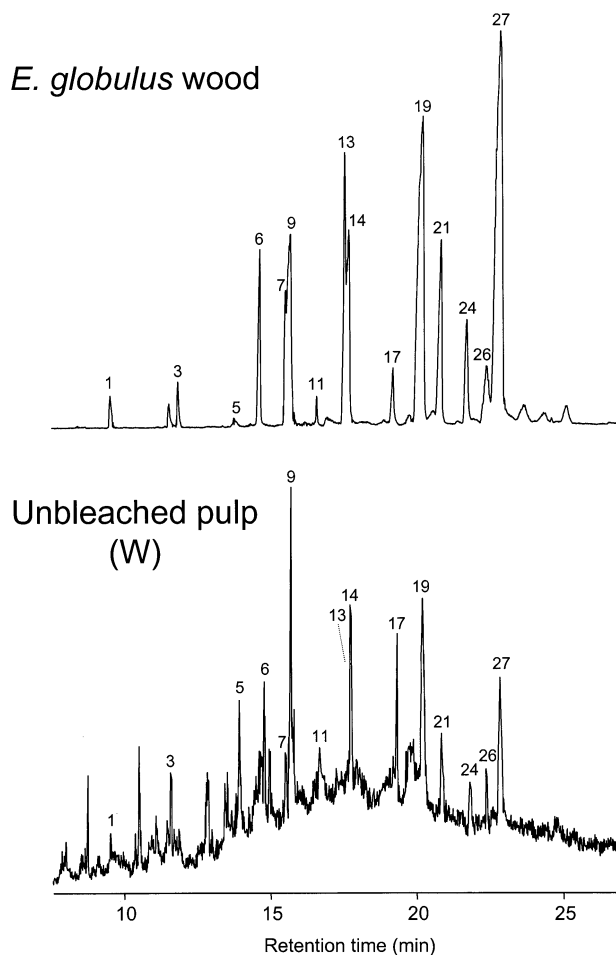


Fig. 4. Reconstructed ion-chromatogram showing the main lignin markers in eucalypt wood and in the unbleached eucalypt kraft pulp (W). Table 4 shows the ions selected for the different lignin markers. Peak identities for the lignin-derived compounds are shown in Table 2.

Table 4

List of m/z fragments used to build the reconstructed ion chromatograms for lignin-derived peaks in kraft pulps

m/z Fragments	Compounds
<i>Guaiacyl units</i>	
124	Guaiacol (1)
138	4-Methylguaiacol (3)
152	4-Ethylguaiacol (5)
150	4-Vinylguaiacol (6)
164	Eugenol (7)
	<i>cis</i> -Isoeugenol (11)
	<i>trans</i> -Isoeugenol (13)
<i>Syringyl units</i>	
154	Syringol (9)
168	4-Methylsyringol (14)
182	4-Ethylsyringol (17)
	Syringaldehyde (26)
180	4-Vinylsyringol (19)
194	4-Allylsyringol (21)
	<i>cis</i> -4-Propenylsyringol (24)
	<i>trans</i> -4-Propenylsyringol (27)

4-ethylguaiacol (5), 4-vinylguaiacol (6), syringol (9), 4-methylsyringol (14), 4-ethylsyringol (17), 4-vinylsyringol (19), 4-allylsyringol (21) and *trans*-4-propenylsyringol (27). Relative distributions of polysaccharide fractions, S and G lignin moieties in the ‘biopulps’ showed rather small differences in their relative abundances compared with the untreated control pulp. It is apparent that syringol (9) is being reduced after fungal pretreatment. A relatively small decrease of *trans*-4-propenylsyringol (27) was also produced by *P. subvermispota*. Syringyl/guaiacyl ratios were calculated for the residual lignin in these pulps and it was apparent that *P. subvermispota* decreased strongly this ratio (from 7.6 to 5.6) while *B. adusta* did not change it much (7.4). The same trend has been found upon Py–GC/MS of the pretreated woods that showed that *P. subvermispota* caused the most intense removal of lignin from eucalypt wood with a marked decrease of the syringyl/guaiacyl ratio while *B. adusta* slightly decreased this ratio [23].

4. Conclusions

In this work, we have studied the composition of residual lignin in eucalypt kraft pulp along the pulping and bleaching processes. Py–GC/MS has been shown to be a powerful tool for characterizing residual lignin in kraft pulps without the need of a previous isolation. By comparison with lignin breakdown products obtained from eucalypt wood and kraft lignin, characteristic features of lignin in the different pulps have been established. Furthermore, analytical pyrolysis also provided infor-

mation on the changes in the composition of residual lignin in biopulps prepared after fungal pretreatment of eucalypt wood with the ligninolytic fungi *P. subvermispora* and *B. adusta*.

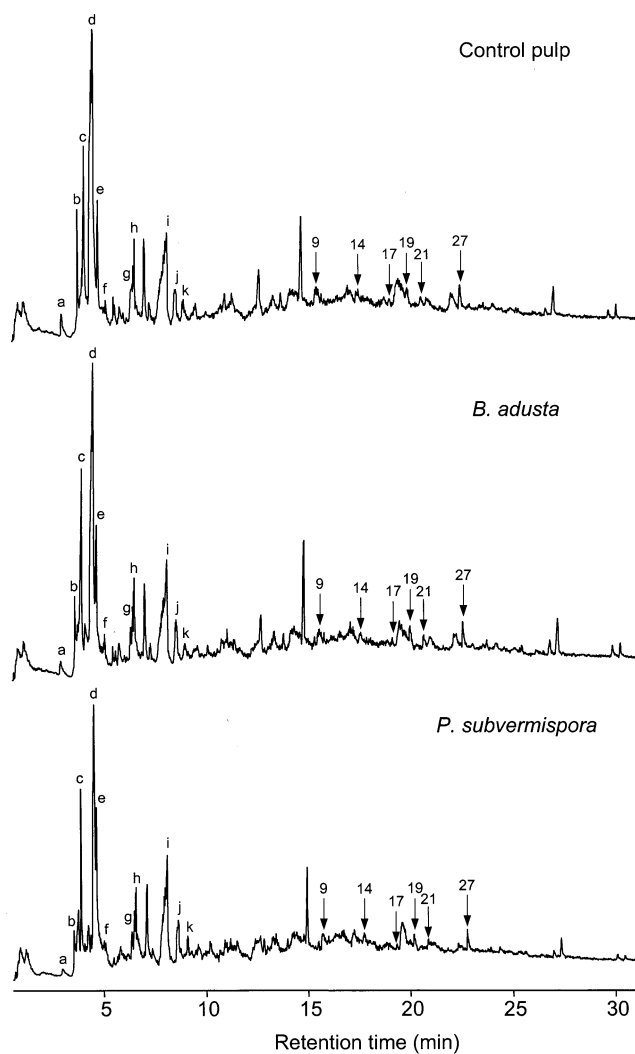


Fig. 5. Py-GC/MS of *E. globulus* kraft pulp after wood pretreatment with the fungi *B. adusta* and *P. subvermispora*. The identities of the carbohydrate-derived peaks (in letters a–k) are shown in Table 3. The identities of the lignin-derived peaks (in arabic numerals) are shown in Table 2.

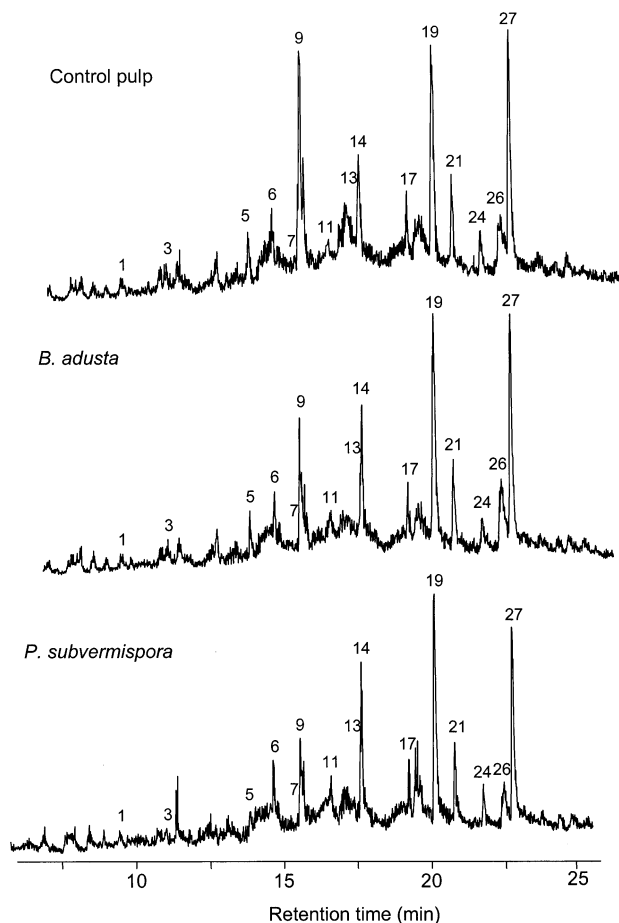


Fig. 6. Reconstructed ion-chromatograms showing the main lignin markers in laboratory eucalypt kraft pulp after wood pretreatment with *B. adusta* and *P. subvermispora*. A pulp from laboratory kraft cooking of untreated wood is shown as control. Table 4 shows the ions selected for the different lignin-derived markers. Peak identities for the lignin-derived compounds are shown in Table 2.

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