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Analysis of pitch deposits produced in Kraft pulp mills using a totally chlorine free bleaching sequence

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Abstract

Two organic deposits accumulated in a Kraft pulp mill during pulping of *Eucalyptus globulus* wood and throughout a TCF (totally chlorine free) bleaching sequence were characterized. One deposit was collected after cooking and an oxygen delignification stage while the other was collected after bleaching with hydrogen peroxide. The deposits were Soxhlet extracted with acetone, and the extracts redissolved in chloroform and subsequently analyzed by gas chromatography (GC) and GC–mass spectrometry (MS) using short and medium length high temperature capillary columns, respectively. On the other hand, the insoluble residues left after the acetone extraction were analyzed by Curie-point flash pyrolysis–GC–MS and by pyrolysis–methylation–GC–MS. The compounds identified in the deposits arise from the *E. globulus* wood lipophilic extractives that survive the pulping and bleaching processes. Triglycerides were completely hydrolyzed during the Kraft cooking and the fatty acids dissolved. Steroids (alcohols, hydrocarbons, ketones and esters) and waxes were the main components in the deposit collected after the oxygen delignification stage. After the bleaching with hydrogen peroxide, content of the waxes were reduced and fatty acids appeared. High amounts of fatty acids salts were also identified in the deposit collected after the oxygen stage, and in minor amounts in the deposit collected after hydrogen peroxide bleaching. In contrast, this deposit was mainly made up of high amounts of lignin-derived phenolic moieties.

Keywords: *Eucalyptus globulus*; Wood; Pyrolysis; Kraft pulp; Pitch; Derivatization, pyrolysis; Sterols; Sterol esters; Tetramethylammonium hydroxide

1. Introduction

Chlorine chemicals are the best established and most widely used bleaching agents in the pulp and paper industry. However, the use of these reagents results in the formation of chlorinated organic compounds, some of them considered priority pollutants [1,2]. In order to produce paper pulp with environmental sound bleaching methods, oxygen, ozone or hydrogen peroxide (*totally chlorine free*, TCF bleaching) are replacing the chlorinated bleaching chemicals. However, new problems concerning pulp quality and effluent toxicity have arisen with the introduction of TCF process. Some of them are related to the compounds constituting the lipophilic fraction from wood extractives, which cause production and environmental problems in the pulp and paper industry. These compounds are difficult to

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remove in the washing stages and may lead to sticky deposits on process equipments resulting in blockages and causing shutdown of operations. These blockages have long been a serious problem in the pulp and paper industry and are responsible for reduced levels of production, higher equipment maintenance costs, higher operation costs, and an increased incidence of quality defects [3,4]. This problem is likely to aggravate with the actual trend towards reuse of process waters and closure of circuits in order to meet environmental requirements, which will result in higher pitch deposition.

In this work, we study the composition of two organic deposits accumulated in different parts of a pulp mill during the production of TCF Kraft pulp of *Eucalyptus globulus* wood. One of them was taken after the oxygen delignification stage (at the post-oxygen press) and the other after the bleaching with hydrogen peroxide. The acetone extracts were analyzed by gas chromatography (GC) and GC–mass spectrometry (MS) using short and medium length high temperature capillary columns [5–8]. The organic part of the insoluble residue, on the other hand, was studied by analytical pyrolysis coupled to GC–MS (Py–GC–MS), a powerful technique to analyze organic polymeric plant materials [9–11]. Pyrolysis in the presence of a methylating agent, tetramethylammonium hydroxide (TMAH), was also performed in order to obtain information of more polar moieties as well as fatty acid salts present in the residue [12–17].

2. Materials and methods

2.1. Description and extraction of the deposits

The organic deposits selected for this study were collected at the ENCE pulp mill at Pontevedra, Spain (Kraft, TCF process). Table 1 shows the origin and location of the different pitch deposits, the immediate analyses and the composition of the inorganic components.

The *E. globulus* wood chips were ground to wood sawdust. The different pitch deposits and the wood sawdust (200 mg) were Soxhlet-extracted with acetone (Panreac, Barcelona, Spain) for 24 h. The acetone extracts were evaporated to dryness and redissolved in chloroform (Merck, Darmstadt, Germany) before analysis by GC and GC–MS. The acetone extracts of the pitch deposits were completely soluble in chloroform. The residues left after the extraction of the pitch deposits were analyzed by Curie-point flash pyrolysis–GC–MS and pyrolysis–methylation–GC–MS.

2.2. Gas chromatography and gas chromatography–mass spectrometry

The GC analyses of the extracts were performed in a Hewlett-Packard HP-5890 (Hewlett-Packard, Hoofddorp, The Netherlands) using a short fused-silica capillary column (DB-5HT; 5 m×0.25 mm I.D., 0.1 μm film thickness) from J&W Scientific (Folsom, CA, USA). The temperature program started at 100°C with a 1 min hold, and then raised to the final temperature of 350°C at 15°C/min and holding for 3 min. The injector (split–splitless) and flame ionization detector temperatures were set at 300°C and 350°C, respectively. The carrier gas was helium and the injection was performed in splitless mode.

The GC–MS analysis of the extracts was performed on a Varian Saturn 2000 (Varian, Walnut Creek, CA, USA) with an ion trap detector, equipped with a fused-silica capillary column (DB-5HT, J&W;

Table 1
Description and composition (%) of the pitch deposits studied in this work[a]

Sample	Location	Moisture content	Ash	Acetone extracts	Insoluble organic residue	Composition (ppm)					
						Fe	Mn	Ca	Mg	K	Na
1	After Kraft cooking and oxygen prebleaching	30	38	17 (52)	16 (48)	3140	8280	50 100	107 000	770	6660
2	After hydrogen peroxide bleaching	3	3	69 (73)	25 (27)	3950	34	1800	214	230	653

[a] The values in parentheses refer to the percentage of organic content.

15 m×0.25 mm I.D., 0.1 μm film thickness). The oven was heated from 120°C (1 min) to 380°C at 10°C/min and held for 5 min. The transfer line was kept at 300°C. The injector was temperature programmed from 120°C (0.1 min) to 380°C at a rate of 200°C/min and held until the end of the analysis. Helium was used as carrier gas. The compounds were identified by comparing the mass spectra thus obtained with those of the Wiley and NIST computer libraries, by mass fragmentography and when possible, by comparing with authentic standards.

A mixture of standard compounds (palmitic acid, stigmasta-3,5-diene, sitosterol, cholesterol oleate and triheptadecanoin) supplied by Sigma (St. Louis, MO, USA) with a concentration range between 0.1 and 1.0 mg/ml, was used to elaborate a calibration curve for the quantitation of wood extractives. The correlation coefficient was higher than 0.99 in all the cases. All peaks were quantified by peak area. Squalene was quantified by using the calibration curve for stigmasta-3,5-diene, while steroid ketones were quantified by using the sitosterol curve and the waxes by using the sterol esters curve.

2.3. Curie-point flash pyrolysis–gas chromatography–mass spectrometry

The analysis of the residue left after the acetone extraction was performed with a Varian Saturn 2000 GC–MS system, using a 30 m×0.25 mm DB-5 column (film thickness 0.25 μm) from J&W Scientific, coupled to a Curie-point pyrolyser (Horizon instruments). Approximately 100 μg of finely divided sample was deposited on a ferromagnetic wire, then inserted into the glass liner and immediately placed in the pyrolyser. The pyrolysis was carried out at 610°C. The chromatograph was programmed from 40°C (1 min) to 300°C at a rate of 6°C/min. 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, while the GC–MS interface was kept at 300°C.

2.4. Pyrolysis–methylation–gas chromatography–mass spectrometry

Approximately 100 μg of sample of residues in finely divided form, was deposited on a ferromagnetic wire and mixed with approximately 0.5 μl TMAH (25%, w/w, aqueous solution) supplied by Sigma. The wire was then inserted into the glass liner, which was subsequently placed in the pyrolyser. The pyrolysis was carried out as described above.

3. Results and discussion

As shown in Table 1, great differences were found among the composition of the selected deposits. The deposit collected at the post-oxygen press showed a higher content of ash and moisture and a lower content in organic fractions than the deposit collected after peroxide bleaching, which was more organic in nature. According to acetone solubility, two organic fractions could be distinguished, an acetone-soluble fraction and an acetone-insoluble residue. The deposit collected at the post-oxygen press showed almost equal amounts of acetone soluble fraction and acetone-insoluble organic residue, while the deposit collected after peroxide bleaching was mainly composed of acetone soluble fraction (73%) with lesser amounts of acetone-insoluble organic residues (27%). The analysis of the acetone soluble fractions was performed by GC and GC–MS while the composition of the acetone insoluble residue was characterized by pyrolysis–GC–MS, as shown below.

3.1. Composition of the acetone soluble fractions

The chromatograms of the acetone extracts from the selected deposits are shown in Fig. 1 and their compositions are listed in Table 2. The chromatogram and the composition of the *E. globulus* wood extractives are also shown for comparison. The composition of the acetone extracts of both deposits are similar to that of *E. globulus* wood extractives confirming that the major lipophilic components of the eucalypt wood survive the cooking and TCF bleaching processes producing pitch depositions. Steroid compounds (hydrocarbons, alcohols, ketones and fatty acyl esters) were the major lipophilic components in all the samples (wood and pitch deposits). Fig. 2 shows the chemical structures of the steroid compounds identified in these samples. Only small differences were found in the composition of

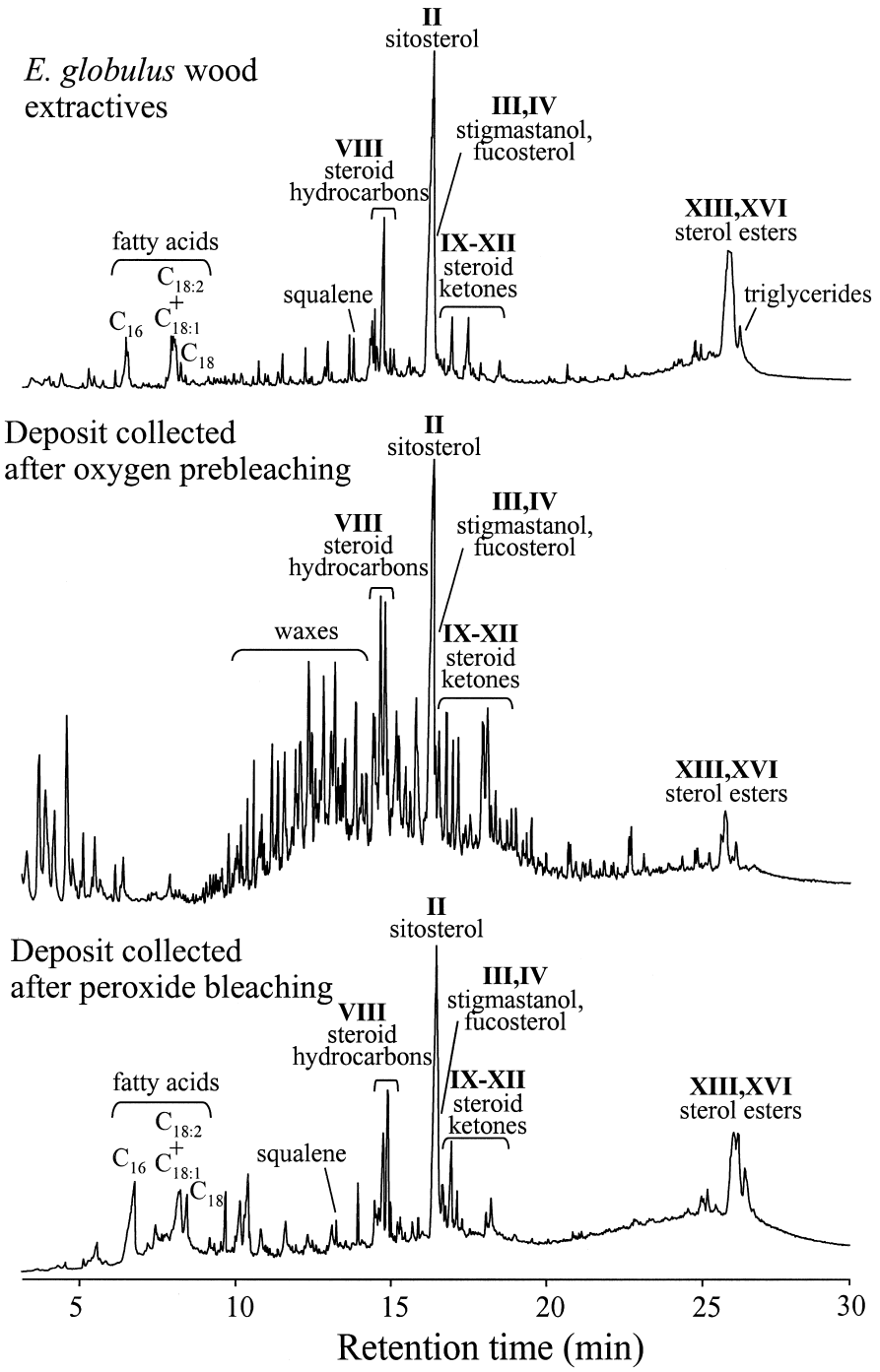

Fig. 1. Gas chromatograms of the acetone extracts isolated from *E. globulus* wood and the deposits collected at the post-oxygen press and after peroxide bleaching. The identities of the major peaks are shown. See Fig. 2 for the chemical structures of steroid compounds (in Roman numbers).

Table 2
Relative composition of main compounds from *E. globulus* wood extractives and the selected deposits[a]

Compound	*E. globulus* wood	After oxygen prebleaching	After peroxide bleaching
Fatty acids	*14.0*	*1.1*	*26.0*
Tridecanoic acid	0	n.i.	0.1
Tetradecanoic acid	0.4	0.1	0.6
Pentadecanoic acid	0.3	0.2	1.5
9-Hexadecenoic acid	0.5	n.i.	n.i.
Hexadecanoic acid	4.4	0.4	8.2
Heptadecanoic acid	0.1	<0.1	1.1
9,12-Octadecadienoic acid	3.8	0.1	1.7
9-Octadecenoic acid	2.0	0.3	4.6
Octadecanoic acid	1.3	<0.1	2.5
Nonadecanoic acid	n.i.	<0.1	0.5
Eicosanoic acid	0.3	<0.1	1.0
Heneicosanoic acid	n.i.	n.i	0.7
Docosanoic acid	0.4	<0.1	1.5
Tricosanoic acid	n.i.	n.i.	0.8
Tetracosanoic acid	0.5	n.i.	1.2
Sterols	*32.0*	*26.4*	*29.0*
Campesterol (I)	0.6	<0.1	0.4
Sitosterol (II)	25.0	17.0	21.0
Stigmastanol (III)	3.0	6.0	5.4
Fucosterol (IV)	1.2	2.1	1.2
Cycloartenol (V)	0.9	0.7	0.5
24-Methylenecycloartanol (VI)	0.5	0.3	0.3
Citrostadienol (VII)	0.8	0.3	0.2
Hydrocarbons	*7.5*	*6.2*	*10.0*
Squalene	1.9	n.i.	0.4
Stigmasta-3-5-diene (VIII)	4.2	3.5	4.6
Other steroid hydrocarbons	1.4	2.7	5.0
Steroid ketones	*11.0*	*5.4*	*6.4*
Stigmasta-3,5-dien-7-one (IX)	4.6	2.2	3.7
Stigmast-4-en-3-one (X)	4.8	1.6	1.2
Stigmastan-3-one (XI)	0.6	0.6	1.0
Stigmasta-3,6-dione (XII)	1.0	1.0	0.5
Waxes	*2.8*	*48.0*	*1.6*
Sterol esters	*26.0*	*12.9*	*27.0*
Sitosterol esters (XIII)	17.3	6.5	11.0
Stigmastanol esters (XIV)	3.5	3.6	5.0
Other sterol esters	5.2	2.8	11.0
Triglycerides	*6.7*	*n.i.*	*n.i.*

[a] See Fig. 2 for chemical structure of steroid compounds.

both deposits. The deposit collected at the post-oxygen press showed high amounts of waxes and a remarkable absence of fatty acids, while the deposit collected after peroxide bleaching showed lower concentration of waxes and the fatty acids were present in high concentrations.

Sitosterol (II) was found to be the dominant sterol in all the deposits and in *E. globulus* wood ex-

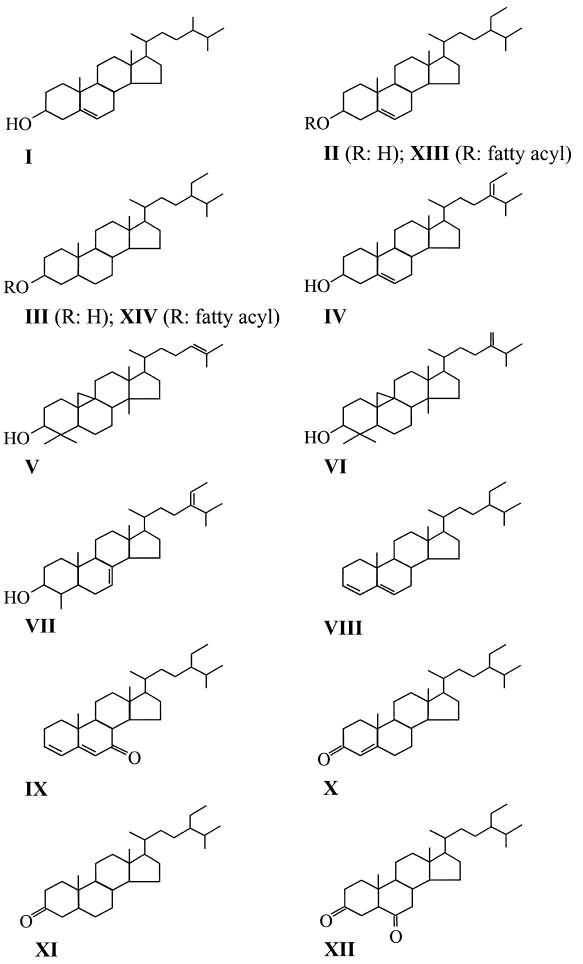

Fig. 2. Structures of the steroid compounds identified in the selected samples.

tractives. Furthermore, the samples contained campesterol (I), stigmastanol (III), fucosterol (IV), cycloartenol (V), 24-methylenecycloartanol (VI) and citrostadienol (VII) (Fig. 2). Several steroid ketones (compounds IX–XII) and steroid hydrocarbons (mainly stigmasta-3,5-diene, VIII), which have been reported as sterol oxidation products [18], were also identified in the pitch deposits and in the wood. However, the triglycerides originally present in *E. globulus* wood were completely hydrolyzed during the cooking and therefore they were not present in the acetone extracts of the pitch deposits.

No major structural changes were observed among the composition of sterols and sterol esters during Kraft cooking and TCF bleaching with hydrogen peroxide. The composition of sterols and sterol esters in the deposits collected before and after bleaching with hydrogen peroxide remained similar as the original sterols present in the *E. globulus* wood extractives, sitosterol (II) and sitosterol esters (XIII) being the main components, in contrast to what occurs after elementary chlorine free (ECF) bleaching [4]. After bleaching with chlorine dioxide (ECF), only the saturated sterols, stigmastanol (III) and stigmastanol esters (XIV), which are more resistant to oxidation, were present in the deposits, while no traces of sitosterol were found [4]. This result is in agreement with Jansson et al. [18] that found that the amount of sitosterol in a birch Kraft pulp decreased more than 99% after bleaching with chlorine dioxide to full brightness, whereas the amount of stigmastanol only decreased about 30%. In contrast, the decrease of sitosterol in the peroxide bleached pulp was around 25% which indicates that hydrogen peroxide bleaching may have a lower potential to oxidize unsaturated sterols than chlorine dioxide. Therefore, these results demonstrate that TCF bleaching removes lower amounts of unsaturated free and esterified sterols, the main lipophilic compounds in eucalypt wood responsible of pitch problems, than ECF bleaching [3]. A similar trend occurs with the fatty acids. Chlorine dioxide bleaching led to an almost complete reduction of the content of unsaturated fatty acids [4], while hydrogen peroxide bleaching has lower effects on the content of unsaturated fatty acids.

3.2. Composition of the insoluble organic residues

The organic residues left after acetone extraction were analyzed by pyrolysis–GC–MS, both in the absence and in the presence of a methylating agent, TMAH. Figs. 3 and 4 show the pyrograms (in absence and in the presence of TMAH, respectively) of the residues, and Tables 3 and 4 list the compounds identified. Pyrolysis of the organic residue of the deposit collected at the post-oxygen press released mainly series of *n*-alkanes/*n*-alkenes, ranging up to C_{28}, while the organic residue from the deposit collected after peroxide bleaching showed a completely different pattern, with the predominant release of lignin-derived phenolic compounds. Similar

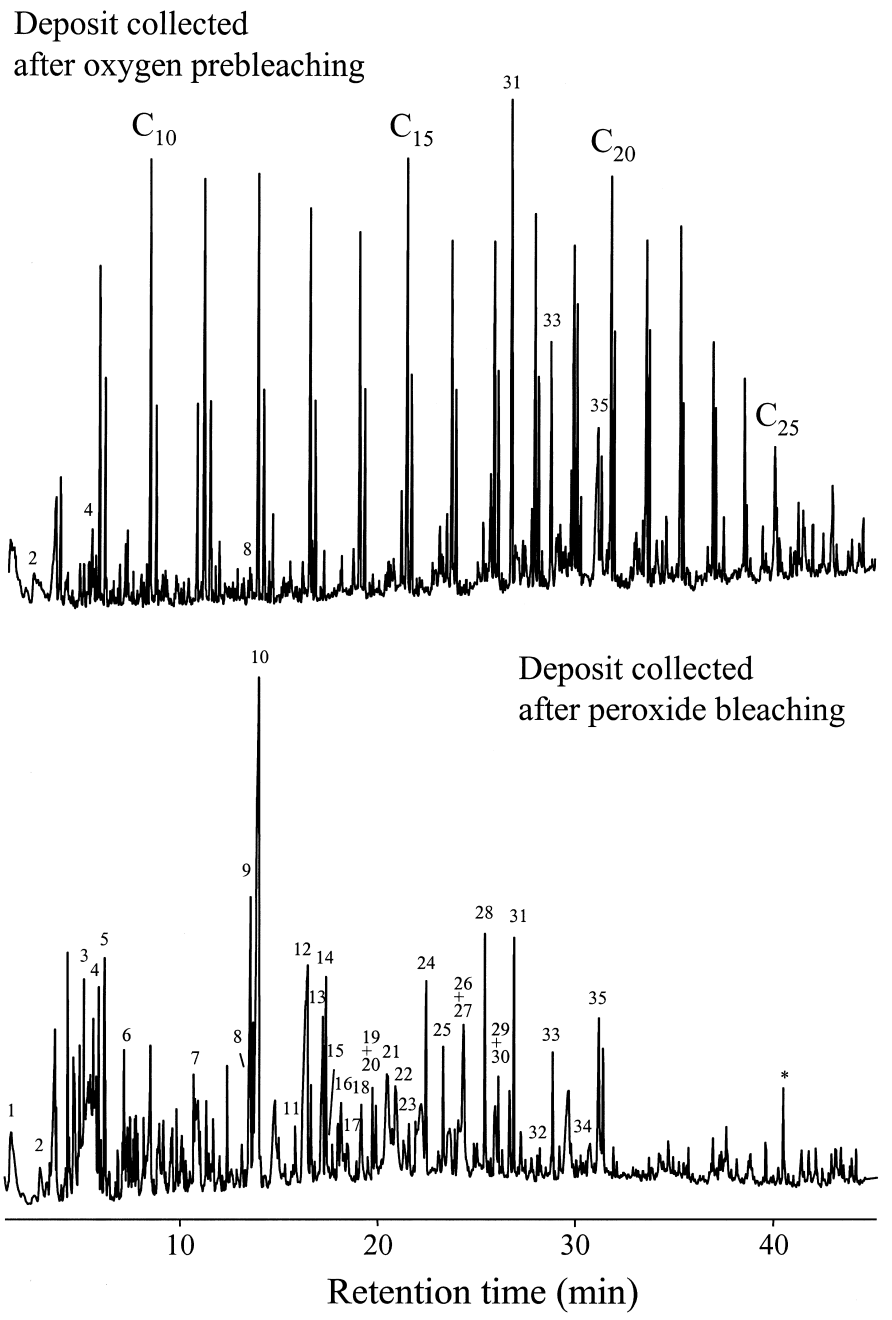

Fig. 3. Pyrolysis–GC–MS of the organic residues left after acetone extraction of the selected deposits. For peak identities refer to Table 3. C_n refers to the chain length of the *n*-alkane/*n*-alkene series.

compounds have been identified in the pyrolysis of lignin from different softwoods and hardwoods, including eucalypt wood [9–11]. It is interesting to note that lignin moieties are only present in the deposit collected after hydrogen peroxide bleaching and only minor amounts of lignin-derived aromatic

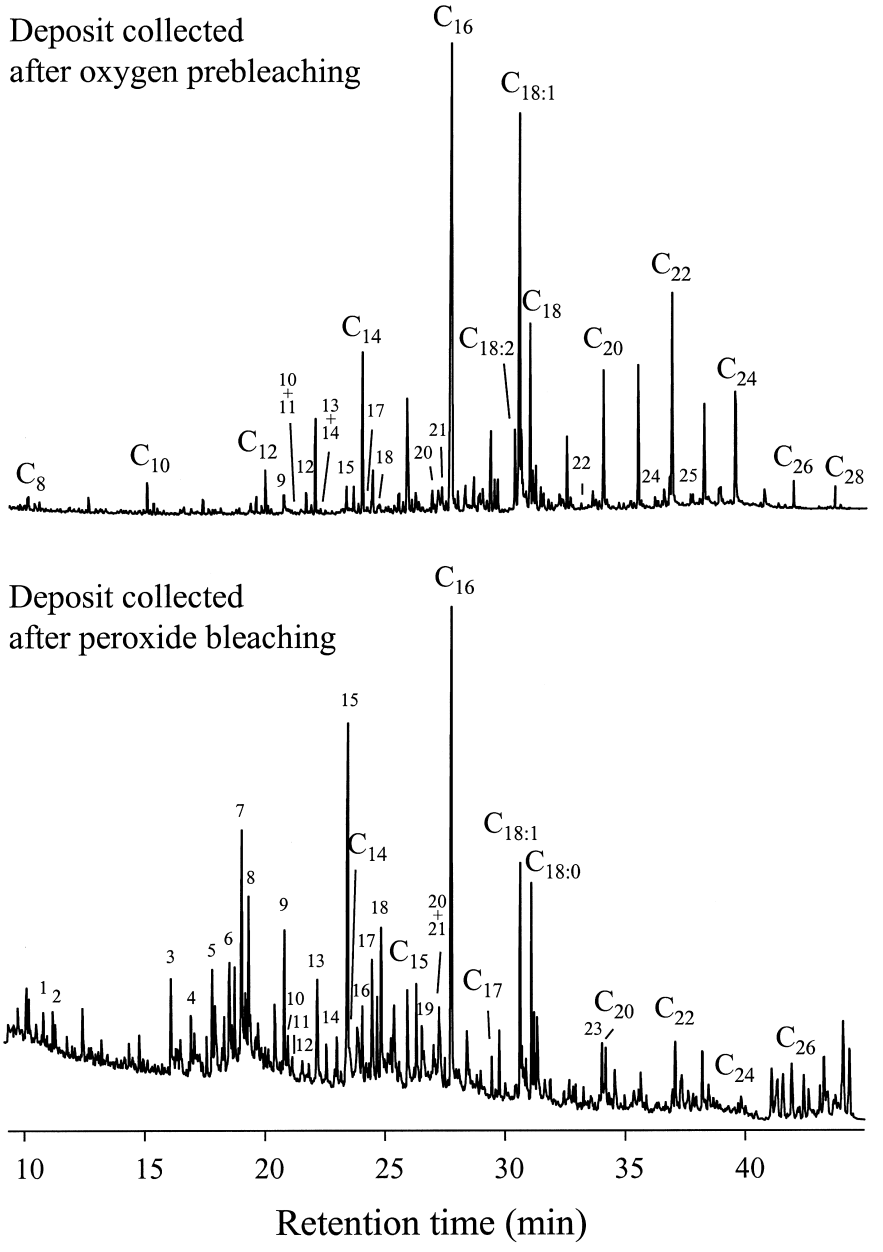

Fig. 4. Py/TMAH–GC–MS of the organic residues left after acetone extraction of the selected deposits. For peak identities refer to Table 4. C_n refers to the chain length of fatty acid methyl esters.

units were detected in the post-oxygen press deposit. However, no further structural information could be obtained on the composition of the post-oxygen press deposit residue due to the inherent limitations of the pyrolysis technique. It is well known that some structural moieties can be heavily modified by unwanted thermal reactions (i.e., decarboxylations) [13,19]. Analytical pyrolysis may also yield highly polar products that are difficult to transfer from the pyrolyser and are not amenable to GC analysis.

Table 3
List of compounds identified in the Py–GC–MS of the selected pulp-mill deposits[a]

No.	Compound	MS fragments
1	Furan-2-one	55, 84
2	Toluene	91, 92
3	Phenol	66, 94
4	Styrene	78, 104
5	Cyclopenten-1-one,2-hydroxy-3-methyl (t)	55, 69, 112
6	Benzenemethanol	77, 79, 108
7	Guaiacol	81, 109, 124
8	4-Methylguaiacol	95, 123, 138
9	Dihydroxybenzaldehyde (t)	81, 109, 138
10	Dihydroxybenzaldehyde (t)	81, 109, 138
11	Dihydroxybenzoic acid	136, 152
12	Methoxycatechol	97, 140
13	4-Vinylguaiacol	107, 135, 150
14	Syringol	111, 139, 154
15	*cis*-Isoeugenol	103, 149, 164
16	Unknown	111, 154
17	Vanillin	109, 151, 152
18	Unknown	149, 186
19	4-Methylsyringol	125, 153, 168
20	*trans*-Isoeugenol	103, 149, 164
21	Unknown	84, 186
22	Unknown	125, 186
23	Guaiacyl acetone	122, 137, 180
24	4-Vinylsyringol	137, 165, 180
25	4-Allylsyringol	167, 179, 194
26	*cis*-4-Propenylsyringol	151, 179, 194
27	Syringaldehyde	167, 181, 182
28	*trans*-4-Propenylsyringol	151, 179, 194
29	Acetosyringone	153, 181, 196
30	Syringylacetone	123, 167, 210
31	Phytadiene	111, 125, 266
32	Propiosyringone	151, 181, 210
33	C_{18} Isoprenoid ketone	95, 109, 250
34	*trans*-Synapaldehyde	137, 165, 208
35	Hexadecanoic acid	129, 256

[a] (t)=Tentatively.

Some of these limitations can be overcome with the pyrolysis in the presence of a methylating agent, such as TMAH, that allows the detection of polar compounds as their methyl derivatives which are more amenable to chromatographic separation. The use of Py in the presence of TMAH (Py/TMAH) also avoids decarboxylation by protecting the carboxylic groups, which are then converted to their methyl esters [12–17]. Py/TMAH of the residues showed a predominant release of series of fatty acid methyl esters from both deposits (Fig. 4). However, while the deposit collected at the post-oxygen press released almost exclusively fatty acid methyl esters, the pitch deposit collected after peroxide bleaching also released high amounts of lignin-derived compounds, similar to those released after Py/TMAH of lignin [16,17]. The distribution of fatty acid methyl esters ranged from C_8 to C_{28} in the residues of both deposits. The palmitic acid methyl ester (C_{16}) was the major one, with the presence of the unsaturated oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acid methyl esters. The presence of unsaturated fatty acids in the deposits collected after peroxide bleaching evidenced that hydrogen peroxide bleaching does not affect them, in contrast to the bleaching with chlorine dioxide that leads to a complete removal of unsatu-

Table 4
List of compounds identified in the Py/TMAH–GC–MS of the selected pulp-mill deposits

No.	Compound	MS fragments
1	1,2-Dimethoxybenzene	95, 123, 138
2	Dimethoxybenzene	95, 123, 138
3	1,2,3-Trimethoxybenzene	110, 153, 168
4	3,4,5-Trimethoxytoluene	139, 167, 182
5	Tetramethoxybenzene	183, 198
6	Permethylated monosaccharide	101, 129
7	Unknown	163, 222
8	Permethylated monosaccharide	101, 129
9	3,4-Dimethoxybenzoic acid methyl ester	165, 181, 196
10	*cis*-1-(3,4-Dimethoxyphenyl)-methoxyprop-1-ene	165, 193, 208
11	3,4-Dimethoxybenzeneacetic acid methyl ester	107, 151, 210
12	1-(3,4-Dimethoxyphenyl)-2-methoxyethylene	151, 179, 194
13	*trans*-1-(3,4-Dimethoxyphenyl)-methoxyprop-1-ene	165, 193, 208
14	3,4,5-Trimethoxyacetophenone	139, 195, 210
15	3,4,5-Trimethoxybenzoic acid methyl ester	195, 211, 226
16	3,4,5-Trimethoxybenzeneacetic acid methyl ester	121, 181, 240
17	*cis*-1-(3,4,5-Trimethoxyphenyl)-2-methoxyethylene	181, 209, 224
18	*trans*-1-(3,4,5-Trimethoxyphenyl)-2-methoxyethylene	181, 209, 224
19	1-(3,4,5-Trimethoxyphenyl)-1,3-dimethoxyprop-1-ene	151, 207, 238
20	1-(3,4,5-Trimethoxyphenyl)-1,2,3-trimethoxypropane	181, 211, 300
21	1-(3,4,5-Trimethoxyphenyl)-1,2,3-trimethoxypropane	181, 211, 300
22	2,3,4,2′,3′,4′-Hexamethoxy-1,1′-diphenyl	273, 288, 334
23	Dehydroabietic acid methyl ester	239, 299, 314
24	2-(2,3,4-Trimethoxyphenyl),2,3,4-trimethoxybenzoic acid methyl ester	239, 361, 392
25	2,3,4,2′,3′,4′-Hexamethoxy-6,6′-dicarbomethoxy-1,1′-diphenyl	239, 419, 450

rated fatty acids [4]. Presumably, these fatty acids are mainly salts of ferric, calcium or magnesium ions, coming from the additives used for pulping and/or pitch control as well as from the wood and water. High amounts of these cations were found in all the pitch deposits analyzed in this work (Table 1). Conventional pyrolysis of the fatty acid salts would yield the *n*-alkene/*n*-alkane series detected previously due to decarboxylation process [12,19].

Minor amounts of compounds arising from ellagic acid were identified in the post-oxygen press deposit upon Py/TMAH (peaks 15, 22, 24 and 25 in Fig. 4 and Table 4), but, except peak 15, they were absent in the deposit after peroxide bleaching. The chemical structures of these compounds are shown in Fig. 5. Peak 15 corresponds to the fully methylated gallic acid derivative but may also arise from oxidized lignin moieties [16,17]. Py/TMAH has proven to be specially indicated for the characterization of salts of ellagic acid in pitch deposits since these moieties can

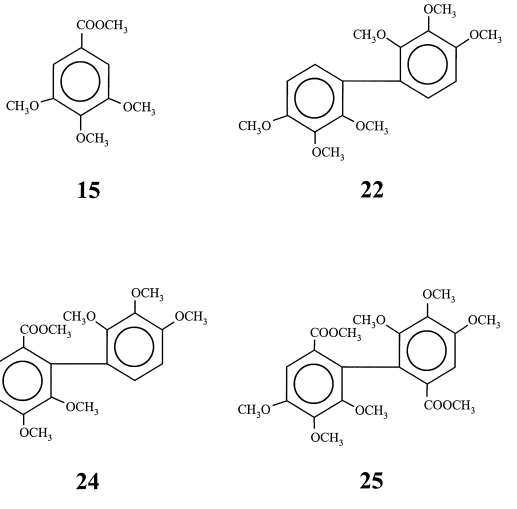

Fig. 5. Chemical structures of the compounds released after Py/TMAH of ellagic acid salts.

be biased upon conventional pyrolysis due to the high polarity of the compounds produced and/or decarboxylation processes [12,14]. Gallic and ellagic acids, as well as their glucose derivatives gallo- and ellagitannins, are typical extractives in the wood of *Eucalyptus* species [20]. During alkaline pulping, hydrolyzable tannins yield gallic and ellagic acids. While gallic acid oxidizes rapidly in alkaline solution, ellagic acid is stable in alkaline pulping liquors, especially in the presence of magnesium ions, but precipitates on cooling as metal complexes, preferably with magnesium and sodium ions, yielding deposits on the surface of pulp washing equipment, and occasionally some specks in pulp [21,22].

4. Conclusions

The composition of two organic pitch deposits produced during the Kraft pulping of *E. globulus* wood throughout a TCF bleaching sequence was characterized. The analysis of the acetone soluble fractions was performed by GC and GC–MS using short and medium length high temperature capillary columns, respectively, while the composition of the acetone insoluble residue was characterized by Py–GC–MS. Steroid compounds (hydrocarbons, alcohols, ketones and fatty acyl esters) were the major lipophilic components in all the samples (wood and pitch deposits). This confirms that these compounds survive the cooking and bleaching processes and produce pitch depositions. The similar composition of sterols and sterol esters in the deposits collected before and after peroxide bleaching indicates that TCF bleaching caused no structural changes in the sterols and sterol esters, in contrast to the ECF process. On the other hand, Py/TMAH has proven to be useful in the characterization of fatty acids salts and ellagic acid moieties in the pitch deposits since these moieties can be biased upon conventional pyrolysis due to decarboxylation processes. The deposit at the post-oxygen press was composed of fatty acid salts and minor amounts of ellagic acid salts, while the deposit after peroxide bleaching showed fatty acids salts and high amounts of phenolic compounds arising from lignin-derived moieties.

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References

[1] J. Koistinen, J. Paasivirta, T. Nevalainen, M. Lahtiperä, Chemosphere 28 (1994) 2139.
[2] S. Sinkkonen, E. Kolehmainen, J. Paasivirta, J. Koistinen, M. Lahtiperä, R. Lammi, Chemosphere 28 (1994) 2049.
[3] J.C. del Río, A. Gutiérrez, F.J. González-Vila, J. Chromatogr. A 830 (1999) 227.
[4] J.C. del Río, A. Gutiérrez, F.J. González-Vila, F. Martín, J. Romero, J. Chromatogr. A 823 (1998) 457.
[5] R.P. Evershed, V.L. Male, L.J. Goad, J. Chromatogr. 400 (1987) 187.
[6] F. Örså, B. Holmbom, J. Pulp Paper Sci. 20 (1994) J361.
[7] B.B. Sitholé, J.L. Sullivan, L.H. Allen, Holzforschung 46 (1992) 409.
[8] A. Gutiérrez, J.C. del Río, F.J. González-Vila, F. Martín, J. Chromatogr. A 823 (1998) 449.
[9] J. Ralph, R.D. Hatfield, J. Agric. Food Chem. 39 (1991) 1426.
[10] O. Faix, D. Meier, I. Fortman, Holz Roh-Werkst. 48 (1990) 281.
[11] J. Rodrigues, D. Meier, O. Faix, H. Pereira, J. Anal. Appl. Pyrol. 48 (1999) 121.
[12] J.C. del Río, A. Gutiérrez, F.J. González-Vila, F. Martín, J. Anal. Appl. Pyrol. 49 (1998) 165.
[13] J.C. del Río, F. Martín, F.J. González-Vila, Trends Anal. Chem. 15 (1996) 70.
[14] G.C. Galletti, P. Bocchini, Rapid Commun. Mass Spectrom. 9 (1995) 250.
[15] J.M. Challinor, J. Anal. Appl. Pyrol. 20 (1991) 15.
[16] F. Martín, J.C. del Río, F.J. González-Vila, T. Verdejo, J. Anal. Appl. Pyrol. 35 (1995) 1.
[17] D.J. Clifford, D.M. Carlson, D.E. McKinney, J.M. Bortiatynski, P.G. Hatcher, Org. Geochem. 23 (1995) 169.
[18] M.B. Jansson, P. Wormald, O. Dahlman, Pulp Paper Can. 96 (1995) 134.
[19] W.A. Hatgers, J.S. Sinninghe Damsté, J.W. de Leeuw, J. Anal. Appl. Pyrol. 34 (1995) 191.
[20] D. Fengel, G. Wegener, Wood Chemistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin, 1984.
[21] E. Sjöström, Wood Chemistry – Fundamentals and Applications, Academic Press, San Diego, CA, 1993.
[22] W.E. Hillis, M. Sumimoto, in: J.W. Rowe (Ed.), Natural Products of Woody Plants II, Springer-Verlag, Berlin, 1989, pp. 880–920.