



ELSEVIER

Journal of Chromatography A, 823 (1998) 457–465

JOURNAL OF
CHROMATOGRAPHY A

Characterization of organic deposits produced in the kraft pulping of *Eucalyptus globulus* wood

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Abstract

The composition of the organic deposits (the so-called pitch deposits) accumulated in different parts of the mills during the kraft pulping of *Eucalyptus globulus* wood using an ECF (elementary chlorine free) bleaching sequence has been studied. Three pitch deposits were selected in the bleaching sequence. The first one was taken just after the kraft pulping and the oxygen prebleaching step, while the other two were taken from different parts of the mill after the chlorine dioxide bleaching step. The pitch deposits were Soxhlet extracted with acetone, and the extracts were redissolved in chloroform and subsequently analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). The composition of *E. globulus* wood extractives was also analyzed for comparison. High temperature short capillary columns were used for the GC and GC–MS analyses, which enabled the elution and separation of compounds with a wide range of molecular mass, with no prior derivatization nor fractionation. Sterols and sterol esters were major compounds in the lipidic extractives of *E. globulus* wood, and hence, contribute to pitch deposition during pulping. The composition of the pitch deposits varied along the bleaching sequence. The kraft cooking and oxygen prebleaching had a minor influence on the composition of the extract of the pitch deposits. These extracts were very similar to those of *E. globulus* wood extractives, but with a higher content of waxes. No structural changes of sterols and sterol esters were observed. In contrast, after chlorine dioxide bleaching (ECF), the deposits were composed of saturated sterols and sterol esters, with the remarkable absence of unsaturated sterols and sterol esters, mainly the β -sitosterol and β -sitosterol esters, which were completely degraded. The insoluble residues left after acetone extraction of the pitch deposits were analyzed by Curie-point flash pyrolysis–GC–MS and by pyrolysis-methylation–GC–MS. Whereas conventional pyrolysis released series of *n*-alkanes/*n*-alkenes, a series of fatty acid methyl esters were released after pyrolysis-methylation, suggesting that the residues left after acetone extraction might be made up of fatty acids salts. Very minor amounts of ellagic acid were also found in all the pitch deposits, probably deposited as magnesium complex. © 1998 Published by Elsevier Science B.V.

Keywords: *Eucalyptus globulus*; Wood extractives; Kraft pulp; Pitch; ECF

1. Introduction

A variety of chemical pulping processes has been developed, together with improved bleaching meth-

ods to meet growing demands for paper of increasing quality and in greater yields. Practically the entire production of chemical pulps in the world today is based on the kraft process [1], which is done with a solution composed of sodium hydroxide and sodium sulfide, named ‘white liquor’. A subsequent bleach-

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ing step results in a high and reasonably permanent brightness of the pulp. Common bleaching chemicals are gaseous chlorine, chlorine dioxide and oxygen. Because of environmental reasons, gaseous chlorine is being replaced today either with chlorine dioxide (the so-called elementary chlorine free, ECF, bleaching) or with chlorine-free chemicals such as oxygen, hydrogen peroxide and ozone, (the so-called total chlorine free, TCF, bleaching) [1].

However, regardless of pulping and bleaching procedures, wood extractives, a term that refers to a large number of wood compounds which are soluble in organic solvents, cause production and environmental problems in the pulp and paper industry. Wood extractives are difficult to remove in the washing stages and may lead to sticky deposits (the so-called pitch deposits) on process equipments. The accumulation of small amounts of wood extractives can result in blockages causing shutdowns. These blockages have long been a serious problem in the industry and are responsible for reduced production levels, higher equipment maintenance costs, higher operational costs, and increased incidence of quality defects. The use of certain pulping procedures with some species can lead to particularly serious deposits that will coat the surfaces of various pieces of equipment of both the pulp and paper mill, as well as becoming entwined in the pulp. The increasing need for recirculation and conservation of water in some parts of pulp and paper mills and the increasingly stringent controls of the composition of effluents to meet environmental protection requirements is also leading to an increase in pitch concentrations which likewise results in higher deposition.

Traditionally, pitch deposits in pulping processes have been reduced by debarking and seasoning logs and wood chips [2–8]. However, during such storage, microbial stain and decay can decrease the value of the wood fiber. Recent pressures to keep wood inventories and the shortage of wood supplies small, have also tended to curtail seasoning which enhances pitch problems at pulp mills. As alternatives to the above, biological removal of wood extractives by treatment with enzymes [9–11] or microorganisms [12–14] have been suggested in recent years for pitch control.

Effective deposit control in a pulp-mill system requires a thorough understanding of the system and

the analysis of all components of a deposit. The knowledge of the chemical nature of these organic deposits will assist the development of suitable methods for their removal. In this work, we are reporting the analysis and the composition of the organic deposits accumulated in different parts of the mills during the kraft pulping of *Eucalyptus globulus* wood in an ECF bleaching sequence. Three pitch deposits were selected in the bleaching sequence: the first one was taken just after the kraft pulping and the oxygen prebleaching step, while the other two were taken from different parts of the mill after the chlorine dioxide bleaching step. The composition of *E. globulus* wood extractives was also analyzed for comparison. The acetone extracts of the deposits were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS), whereas the insoluble fractions were analyzed by pyrolysis-methylation followed by analysis using GC and GC–MS.

2. Material and methods

2.1. Description and extraction of the deposits

The selected pitch deposits were taken from the ENCE (Empresa Nacional de Celulosas) pulp mill at Huelva, Spain (Kraft ECF 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 for 24 h. The acetone extracts were evaporated to dryness and redissolved in chloroform 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 [15].

2.2. Gas chromatography and gas chromatography–mass spectrometry

The GC analyses of the extracts were performed in

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

Sample	Location	Moisture content	Ash	Acetone extracts	Insoluble organic residue	Fe	Mn	Ca	Mg	K	Na
1	Sunds displacement press (after oxygen prebleaching)	25	35	18 (45)	22 (55)	0.30	0.81	3.92	12.25	0.05	0.42
2	3rd lower press-pulp machine (after ClO ₂ bleaching)	7	14	24 (30)	55 (70)	0.11	0.03	1.72	2.08	0.02	0.07
3	Vacuum boxes-pulp machine (after ClO ₂ bleaching)	7	17	26 (34)	50 (66)	0.09	0.01	2.80	1.56	0.01	0.10

^a Values in parenthesis refer to the percentage of organic content.

a Hewlett-Packard HP-5890 using a short fused-silica capillary column (DB-5HT, J&W; 5 m×0.25 mm I.D., 0.1- μ m film thickness). 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 detector (flame ionisation) 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 (ion trap detector), equipped with a fused-silica capillary column (DB-5HT, J&W; 15 m×0.25 mm I.D., 0.1- μ m 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.

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

The residue analysis was performed with a Varian Saturn 2000 GC–MS system, using a 30 m×0.25 mm DB-5 column (film thickness 0.25 μ m), coupled to Curie-point pyrolyzer (Horizon Instruments). Approximately 100 μ g 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 μ g of sample of residues in finely divided form, was deposited on a ferromagnetic wire and mixed with approximately 0.5 μ l tetramethylammonium hydroxide (TMAH) (25% w/w, aqueous solution). The wire was then inserted into the glass liner, which was subsequently placed in the pyrolyzer. The pyrolysis was carried out as described above.

3. Results and discussion

All the pitch deposits selected for this study had a high organic content (Table 1). Two organic fractions were observed: a fraction soluble in acetone and an insoluble fraction. The proportion of both fractions were similar for the sample after the oxygen prebleaching step, whereas the insoluble organic fractions had three times the amount of the soluble fraction for the sample taken after the ECF bleaching with chlorine dioxide.

3.1. Composition of the pitch deposits extracts in relation with the composition of the extractives of *E. globulus* wood

The acetone extracts were analyzed by a gas chromatographic procedure using high temperature short capillary columns that has been developed in our laboratories for the rapid analysis of wood extractives [16]. The method enables elution and separation in a wide range of molecular masses (from fatty acids to sterol esters and triglycerides),

with no prior derivatization nor fractionation steps, and in a short time.

Fig. 1 shows the total ion chromatograms (TIC) of the extractives from *E. globulus* wood and the pitch deposit extracts. The two deposits taken from different parts of the mill, just after ECF bleaching with chlorine dioxide, gave identical composition (only one is shown). The relative composition of the main compounds identified in the *E. globulus* wood extractives and in the extracts of the different pitch deposits are listed in Table 2. It is apparent from the

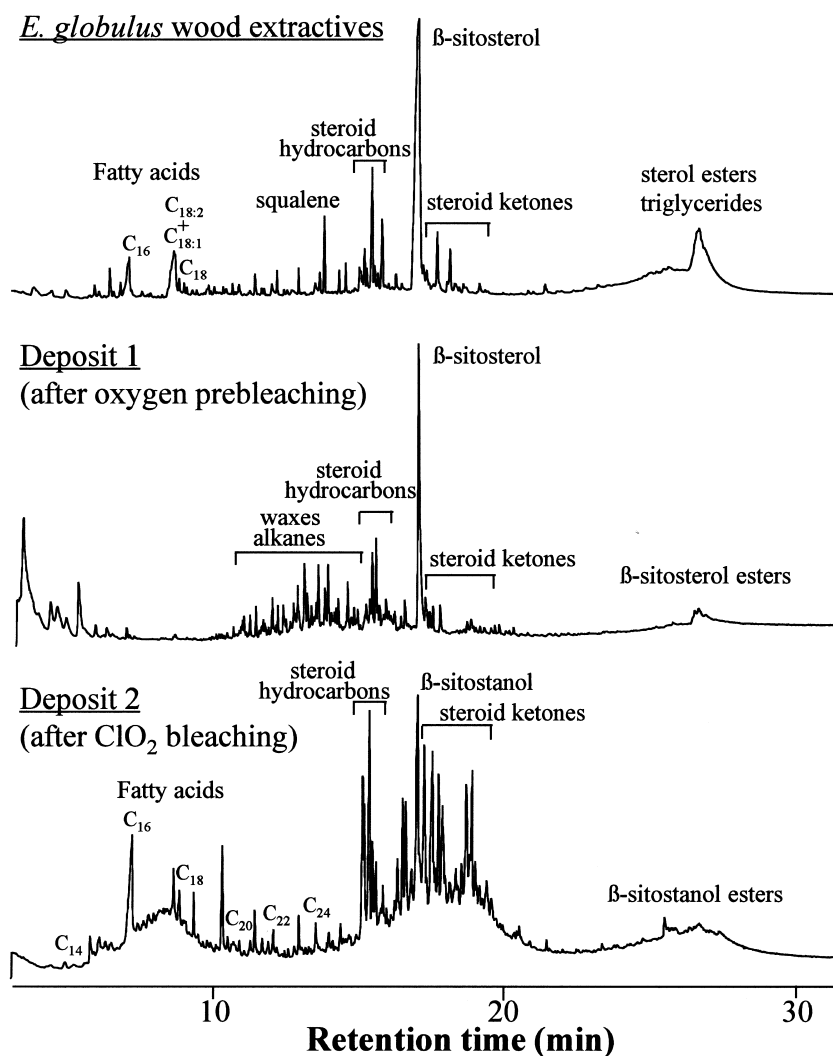


Fig. 1. Total ion chromatogram of *Eucalyptus globulus* wood extractives and pitch deposit extracts.

Table 2

Relative composition of the main compounds identified in the extracts of the selected pitch deposits, and *E. globulus* wood extractives

Compounds	<i>E. globulus</i> wood	Pitch deposit 1 (after oxygen prebleaching)	Pitch deposit 2 (after chlorine dioxide bleaching)
Hydrocarbons			
<i>n</i> -Alkanes C ₁₂ –C ₃₃	1.0	<0.1	<0.1
Squalene	2.0	N.i.	N.i.
Ketones			
C ₁₀ –C ₂₂	N.i.	2.0	0.2
Isoprenoid C ₁₈	N.i.	0.7	0.9
Fatty acids			
C ₆ –C ₂₆	7.6	0.2	13.3
C _{18:1}	2.0	<0.1	N.i.
C _{18:2}	3.8	<0.1	N.i.
Waxes			
C ₂₀ –C ₄₀	3.0	43.3	<0.1
Sterols			
Cholesterol	0.5	<0.1	N.i.
Campesterol	0.6	<0.1	N.i.
Campestanol	0.1	<0.1	<0.1
β-Sitosterol	24.6	21.6	N.i.
β-Sitostanol	3.0	8.0	20.8
Fucoesterol	1.2	3.0	N.i.
Cycloartenol	0.8	1.0	N.i.
24-Methylenecycloartenol	0.5	0.4	N.i.
Citrostadienol	0.7	0.4	N.i.
Steroid hydrocarbons			
Stigmasta-3,5-diene	4.0	2.6	1.7
Others	1.3	2.0	18.5
Steroid ketones			
Stigmastan-3-one	0.6	0.2	10.7
Stigmast-4-en-3-one	4.8	1.0	7.9
Stigmasta-3,5-dien-7-one	4.4	1.2	12.6
Stigmastane-3,6-dione	1.0	0.6	7.9
Sterol esters			
β-Sitosterol esters	21.5	8.1	N.i.
β-Sitostanol esters	4.5	3.6	5.5
Triglycerides			
	6.5	N.i.	N.i.

N.i.: not identified.

chromatograms that the composition of the pitch deposits varied throughout the bleaching sequence.

The extractives from *E. globulus* wood consisted mainly of hydrocarbons, fatty acids, waxes, steroids (hydrocarbons, alcohols, ketones and esters) and triglycerides. Many of these species survive the pulping and bleaching processes and hence may be found as pulp extractives, which in turn can also

deposit and accumulate on different parts of the mill, causing pitch deposits.

3.1.1. Pitch deposits produced after oxygen prebleaching

Just after the kraft pulping of *Eucalyptus* wood, the pulp is subjected to oxygen prebleaching or delignification. As shown in Fig. 1 and Table 2, the

composition of the acetone extract of the pitch deposit produced after kraft cooking and oxygen prebleaching was very similar to that of the extractives from *E. globulus* wood. This indicates that kraft pulping and oxygen prebleaching have a minor influence on the extract composition of the deposits formed in this part of the pulp mill. Similar results have been found in pulp extracts [17].

The main compounds present in this deposit were waxes, sterols and sterol esters. Triglycerides are hydrolyzed and fatty acids dissolved during the kraft cooking. Trace amounts of fatty acids were found, including unsaturated oleic and linoleic acids. The composition of sterols, accounting for 34.4% of the deposit extract, was similar to that found in the *E. globulus* extractives, with β -sitosterol predominant. Minor amounts of other sterols, such as campesterol, cycloartenol, citrostadienol (α -sitosterol), 24-methyl-encycloartenol, fucosterol, β -sitostanol and campestanol, were also identified. Sterol esters were also important components of this deposit (8.7% of the deposit extract) and were composed mainly of β -sitosterol esters, of which the major compound was β -sitosterol linoleate, with minor amounts of β -sitostanol esters, as also found in the *E. globulus* wood extractives. The same steroid ketones (stigmastan-3-one, stigmast-4-en-3-one, stigmasta-3,5-dien-7-one and stigmastane-3,6-dione) and steroid hydrocarbons (the main compound was tentatively identified as stigmasta-3,5-diene), present in the *E. globulus* wood, were also identified in this deposit. The hydrocarbon squalene, found among the *E. globulus* extractives, could not be identified in this deposit, suggesting that this highly unsaturated compound was affected by the kraft cooking and oxygen prebleaching. Series of *n*-alkanes from C_{12} to C_{31} and series of methyl ketones from C_{10} to C_{22} were also found in this deposit. The isoprenoid ketone 6,10,14-trimethylpentadecan-2-one, probably arising from the oxidation of phytol, was also present.

The main difference between the composition of the *E. globulus* wood extractives and the deposits produced after kraft cooking and oxygen prebleaching, was the accumulation of waxes, which accounted for 43.3% of the deposit extract. This series was found in the range from C_{20} to C_{40} , and consisted of a complex mixture of many different compounds. Several waxes of same molecular mass

coelute in a single chromatographic peak. The analysis by mass spectrometry of the different peaks confirmed that the waxes were formed by esters of C_{10} to C_{20} fatty alcohols and fatty acids. Series of waxes of unsaturated oleic acid and esters of dicarboxylic acids and hydroxy fatty acids were also found. Finally, minor amounts of anthraquinone, an additive of the pulping process, were also detected in this deposit.

3.1.2. Pitch deposits produced after bleaching with chlorine dioxide

The pulp is subsequently bleached with chlorine dioxide after the kraft cooking and oxygen prebleaching. The composition of the extracts of the pitch deposits produced after chlorine dioxide bleaching was quite different to those produced after the oxygen prebleaching (Fig. 1, Table 2). The main compounds identified in these deposits were steroid ketones, sterols, steroid hydrocarbons and sterol esters (representing 39.1, 20.9, 20.2, and 5.5% of the deposit extract, respectively). Only the saturated sterols β -sitostanol and campestanol, which are more resistant to oxidation, remained in the deposits taken after chlorine dioxide bleaching, from the original sterols present in *E. globulus* wood and in the deposits taken after oxygen prebleaching. No traces of β -sitosterol were found in any of the deposits taken after chlorine dioxide bleaching. Björlund Jansson et al. [17] also found that the amount of β -sitosterol in pulp samples decreased more than 99% after bleaching with chlorine dioxide to full brightness, whereas the amount of β -sitostanol only decreased about 30%. Likewise, the series of sterol esters identified in these pitch deposits after chlorine dioxide bleaching corresponded to the β -sitostanol esters and no traces of β -sitosterol esters were identified. On the other hand, the same steroid ketones and steroid hydrocarbons present in the *E. globulus* wood and the pitch deposit taken after oxygen prebleaching, were also present in the deposits taken after chlorine dioxide bleaching.

Waxes were only very minor components and squalene was absent in these deposits. Series of fatty acids in the range from C_{14} to C_{20} were also present, with the remarkable absence of the unsaturated ones. Finally, no chlorinated compounds were identified in these deposits, in agreement with the work done by

Björklund Jansson et al. [17] who could not identify chlorinated compounds in extracts of an ECF pulp.

3.2. Composition of the insoluble organic residues

The residues left after Soxhlet extraction with acetone were very organic in nature. These insoluble organic residues represented a significant fraction of the pitch deposits. The insoluble residue accounted for 22% of the whole deposit after kraft cooking and oxygen prebleaching, whereas it accounted for more than 50% of the whole pitch deposit after chlorine dioxide bleaching.

The conventional pyrolysis of the insoluble residues (shown in Fig. 2) released a series of C_8 to C_{28} *n*-alkanes/*n*-alkenes, indicating the highly aliphatic character of the organic matter. No further structural information can be obtained due to the inherent

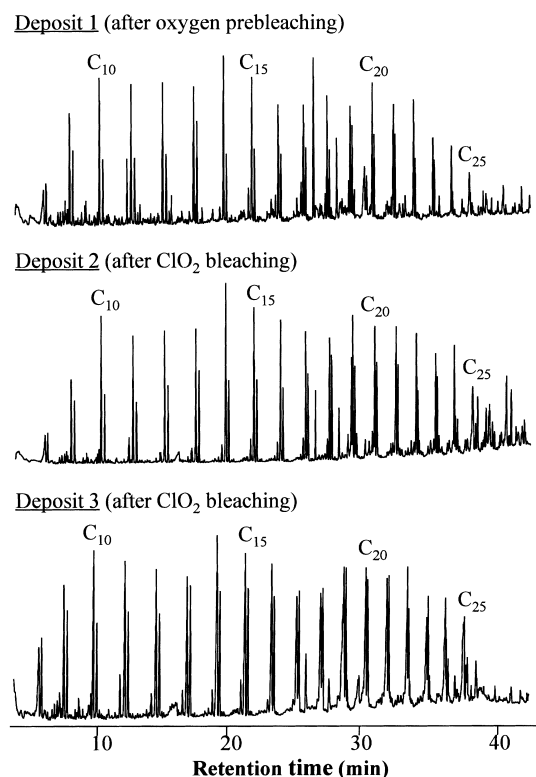


Fig. 2. Total ion chromatograms of the products released after Curie-point (610°C) pyrolysis of the organic residues left after acetone extraction of the different pitch deposits. The carbon numbers refer to the chain-length of the alkane/alkene pairs.

limitations of the technique. It is well known that some structural moieties can be modified by unwanted thermal reactions which may lead to structural misinterpretation [15,18].

Some of these analytical limitations can be overcome with the high temperature reaction of macromolecules with tetraalkylammonium hydroxides. This allows the detection of polar compounds as their alkyl derivatives [15,18,19]. The gaseous methylating agent, TMAH, at the point of pyrolysis assists in converting polar products to less polar derivatives, which are more amenable to chromatographic separation. The use of pyrolysis in the presence of TMAH (the so-called pyrolysis-methylation) also avoids decarboxylation by protecting the carboxyl groups which are converted to methyl esters [15,19]. It is thus possible to separate and detect more structurally significant products than those observed by conventional pyrolysis.

Series of fatty acid methyl esters were released from all the insoluble organic residues after pyrolysis-methylation (Fig. 3). In the pitch deposit taken after kraft cooking and oxygen prebleaching, the distribution of fatty acids released ranged from C_8 to C_{26} . The palmitic acid methyl ester (C_{16}) was the major one, with the presence of high amounts of the unsaturated oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids. On the other hand, the deposits taken after chlorine dioxide bleaching released fatty acids in the range from C_{12} to C_{26} , with the palmitic acid methyl ester (C_{16}) as the highest one, and the remarkable absence of unsaturated fatty acids. As in the case of the sterols present in the extracts, the chlorine dioxide bleaching led to complete removal of the unsaturated fatty acids.

These results indicate that the fatty acids may exist in salt form in the selected pitch deposits. Previous studies have demonstrated that the IR spectrum of similar deposits showed signals attributable only to acid salts and not free acids [20]. Presumably, these fatty acids are mainly salts of ferric, calcium or magnesium ions, coming from the additives used for pulping and/or pitch control. High amounts of these cations were found in all the pitch deposits analyzed in this work (Table 1).

It is clear that the presence of fatty acid moieties in the insoluble organic residues have been biased upon conventional pyrolysis due to decarboxylation

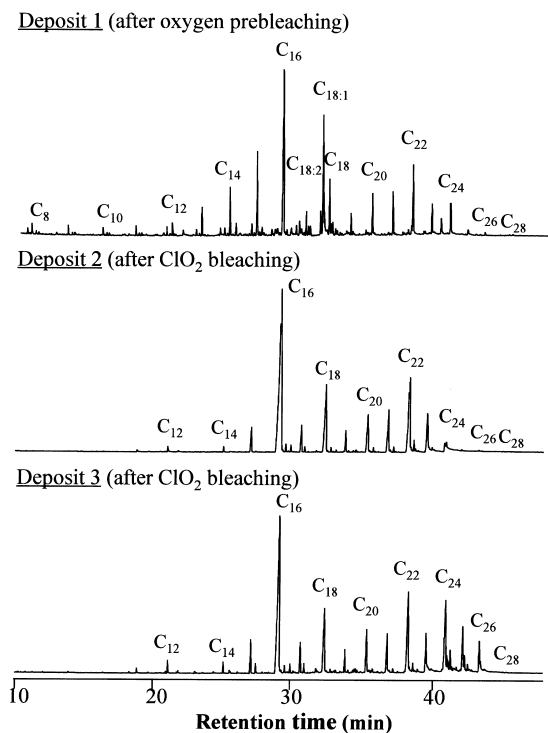


Fig. 3. Total ion chromatograms of the products released after thermally-assisted hydrolysis-methylation of the organic residues left after acetone extraction of the different pitch deposits. The carbon numbers refer to the chain-length of fatty acid methyl esters.

processes. In conventional pyrolysis, fatty acid salts decarboxylate, producing predominantly series of alkanes and alkenes, as shown in Fig. 2. The use of pyrolysis-methylation makes the presence of high amounts of fatty acid salts in the pitch deposits clear.

Minor amounts of compounds arising from the pyrolysis-methylation of ellagic acid were found in all the pitch deposits. Previous studies have confirmed that ellagic acid had deposited as a magnesium complex [1]. Under pulping conditions, the ellagic acid present in the wood or resulting from hydrolysis of the ellagitannins also forms nearly insoluble complexes with inorganic ions such as magnesium, calcium, sodium and aluminum [20]. Mills that pulp eucalypt wood are often plagued with pitch deposition problems caused by precipitation of ellagic acid soaps of magnesium and sodium ions [21,22]. However, in the pitch deposits studied here,

the problems associated with the deposition of ellagic acid soaps seemed to be minor.

4. Conclusions

The composition of the organic deposits accumulated during the kraft pulping of *E. globulus* wood using an ECF (elementary chlorine free) bleaching sequence, was studied. Sterol esters and sterols were the major compounds in the lipidic extractives of *E. globulus* wood, and contributed to pitch deposition during pulping. After kraft cooking and oxygen prebleaching, the main compounds found in the deposits were sterols (mainly β -sitosterol), waxes and β -sitosterol esters. In contrast, after chlorine dioxide bleaching, unsaturated sterols and sterol esters were degraded and the main compounds present were saturated sterols and sterol esters, and series of steroid ketones and hydrocarbons. The residues left after the acetone extraction of the pitch deposits were also analyzed. A series of fatty acid methyl esters were released from the residues after pyrolysis-methylation, suggesting that the residues were composed of fatty acids salts. Minor amounts of ellagic acid were found in all the pitch deposits, probably deposited as magnesium complex.

The identification of the compounds responsible for pitch deposition will lead to the design of effective biotechnological or physicochemical solutions for their removal. Among these solutions, the biological elimination of wood extractives prior to pulping and the enzymatic treatment of pulp, represent promising approaches to control pitch problems in pulp and paper manufacture. Significant improvement can be expected after the careful identification of the key compounds causing pitch, which will provide criteria for a more selective screening and optimization of biotechnological approaches.

Acknowledgements

We thank the EU Commission (Contract FAIR CT95-0560) for financial support. Mrs. T. Verdejo is also acknowledged for her technical support.

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