



Application of pyrolysis-gas chromatography-mass spectrometry to the analysis of pitch deposits and synthetic polymers in pulp and pulp mills

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Abstract

Different pitch deposits and impurities, including synthetic polymers occurring in pulps and pulp-mills, have been studied by pyrolysis-GC/MS. Among the samples analyzed, two organic deposits taken from a pulp mill before and after elementary chlorine free (ECF) bleaching, a series of rubber pieces collected from a centri-cleaner unit, and a series of specks occasionally occurring in a total chlorine free (TCF) bleached pulp were selected for this study. Pyrolysis in the presence of a methylating agent, tetramethylammonium hydroxide (TMAH) was required to identify deposits formed by salts of ellagic and fatty acids since these moieties decarboxylate upon conventional pyrolysis. Pyrolysis of the selected rubber pieces allowed the identification of polyisoprene, polystyrene, poly- α -methylstyrene and other synthetic polymers not completely characterized, arising from machine breakage. Likewise, the specks occurring in a TCF pulp were constituted by small fragments of *trans*-poly(isoprene) rubber. The characteristic pyrograms could be used as fingerprints to trace their source. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Pulp; ECF; TCF; Pulp-mill deposits; Synthetic polymers; Pitch; Fatty acid salts; Ellagic acid salts

1. Introduction

Wood extractives are known to cause production problems in the pulp and paper industry. They are difficult to remove in the washing stages and may lead to sticky deposits (the so-called pitch deposits) on process equipments and in pulp and paper

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products. The accumulation of wood extractives in pulp mills can result in blockages, causing a shutdown of operations and are responsible for important economic losses [1]. This problem becomes more severe with the introduction of more environmentally-free chemicals for pulp bleaching that have replaced the gaseous chlorine with chlorine dioxide (the so-called elementary chlorine free, ECF, bleaching) or with chlorine-free chemicals such as oxygen, hydrogen dioxide or ozone (the so-called total chlorine free, TCF, chemicals).

On the other hand, synthetic polymers arising from different parts of the mills are also usually found as impurities in pulp and paper and can impair product quality. They are retained in the different filters along the process; however, if the pieces of rubber are small enough to pass through the filters, they may enter the pulp stream and hence be found as contaminants in pulp [2].

A stoppage or breakdown in production or defects in the final products may be very costly and therefore a rapid characterization of the impurities occasionally occurring in pulp and the deposits occurring in pulp-mills is necessary in order to find solutions to this problem. Analytical pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) enables a rapid characterization of very small amount of material, and is therefore ideally suited to analyzing spots and specks in pulp.

Several papers have successfully used analytical pyrolysis for the identification of commonly found impurities in pulp and paper matrices [2–5]. However, pyrolysis of highly polar samples may yield highly polar products which are difficult to transfer from the pyrolyser and are almost impossible to chromatograph directly by GC. Thus, pyrolysis may underestimate units bearing polar groups. Furthermore, some significant structural moieties can also be heavily modified by unwanted thermal reactions (i.e. decarboxylation), which may lead to incorrect conclusions on the structural composition of certain samples [6,7]. Pyrolysis in the presence of TMAH has been introduced to avoid these limitations. It improves the results gained by conventional pyrolysis by avoiding decarboxylation and producing the methyl derivatives of carboxylic and hydroxyl groups which are more amenable to GC. This procedure is being widely applied to the characterization of bio- and geomacromolecules as well as synthetic polymers [6–17].

In this paper, Py-GC/MS is used to analyze different deposits, synthetic polymers and impurities found in pulp and pulp mills. In certain cases, pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) is used to get more relevant information on their structure.

2. Material and methods

2.1. Description and extraction of the selected samples

Two pitch deposits (deposits 1, 2) accumulated in different parts of pulp-mills, several pieces accumulated in a centri-cleaner unit and presumably corresponding to synthetic polymers (rubbers 1–4), and a set of specks occurring in a TCF pulp

were selected for this study. Details on their origin and location are given in Table 1. The pitch deposits accumulated in pulp mills were taken from the ENCE (Empresa Nacional de Celulosas) pulp mill at Huelva, Spain (Kraft ECF process), while the specks occurring in the TCF pulp and the pieces of rubbers collected from the centri-cleaner unit were taken from the ENCE pulp mill at Pontevedra, Spain, (Kraft TCF process). The pulp mill deposits 1 and 2 and the specks collected from the TCF pulp were previously Soxhlet-extracted with acetone to remove wood extractives.

2.2. 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). 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⁻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 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. Pyrolysis-methylation/gas chromatography-mass spectrometry

Approximately 100 μg of sample of sample in finely divided form, was deposited on a ferromagnetic wire and mixed with approximately 0.5 μl tetramethylammo-

Table 1
Samples selected for this study

Sample	Location	Pulp mill
Deposit 1	Sunds Displacement Press (after O ₂ prebleaching)	ENCE-Huelva ECF process
Deposit 2	3rd Lower Press-Pulp Machine (after ClO ₂ bleaching)	ENCE-Huelva ECF process
Rubber 1	Centri-cleaner head	ENCE-Pontevedra TCF process
Rubber 2	Centri-cleaner head	ENCE-Pontevedra TCF process
Rubber 3	Centri-cleaner head	ENCE-Pontevedra TCF process
Rubber 4	Centri-cleaner head	ENCE-Pontevedra TCF process
Speck	TCF pulp	ENCE-Pontevedra TCF process

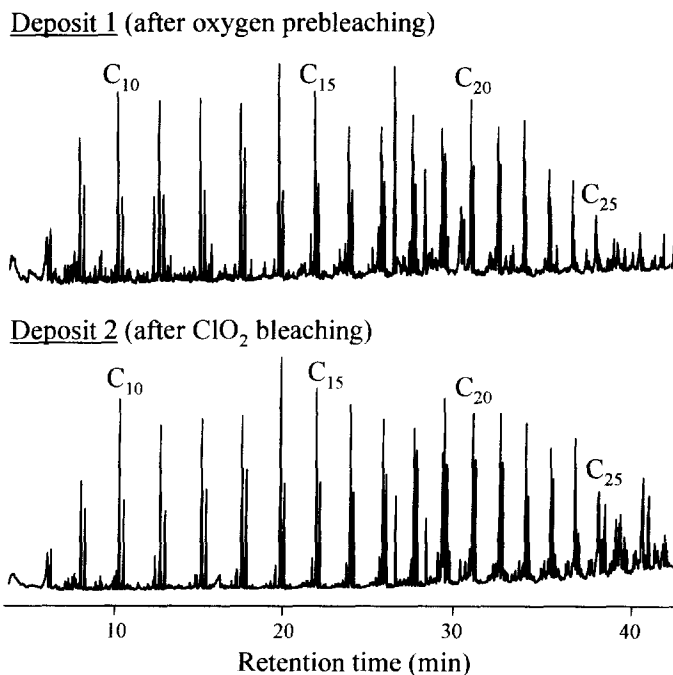


Fig. 1. Py-GC/MS of pitch deposits in pulp-mills. Carbon atoms refer to *n*-alkane/*n*-alkene series.

nium 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

3.1. Characterization of pitch deposits in pulp-mills

The pitch deposits collected in different parts of the pulp-mill consisted of one acetone-soluble and one acetone-insoluble fraction. The insoluble organic fractions accounted for 55% of the total organic matter in the deposit collected after kraft cooking and oxygen prebleaching (deposit 1), and for more than 70% of the total organic matter in the deposit collected after chlorine dioxide bleaching (deposit 2). The organic soluble fractions consisted of a variety of wood extractives that were analyzed by GC and GC/MS [18].

The pyrograms of the insoluble organic fractions isolated from the selected pitch deposits are shown in Fig. 1. A series of C₈ to C₂₈ *n*-alkanes/*n*-alkenes was released, indicating only the highly aliphatic character of the insoluble organic matter. However, no further structural information could be obtained due to the inherent limitations of the technique. It is well known that some structural moieties can be

modified by unwanted thermal reactions (i.e. decarboxylations) which may lead to structural misinterpretation [6,7,11]. Analytical pyrolysis may also yield highly polar products which are difficult to transfer from the pyrolyser and are almost impossible to chromatograph directly by GC.

Some of these analytical limitations can be overcome with the high temperature reaction of macromolecules with tetra-alkylammonium hydroxides. This allows the detection of polar compounds as their alkyl derivatives [6,7,11]. 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 [6,7]. It is thus possible to separate and detect more structurally significant products than those observed by conventional pyrolysis. It has been demonstrated that this procedure consists of a thermally assisted chemolysis rather than a true pyrolysis followed by in situ methylation [6,7,19].

Pyrolysis-methylation of the insoluble residues showed a completely different pattern, with the release of series of fatty acid methyl esters (Fig. 2). In deposit 1, the distribution of fatty acids 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. Deposit 2 released fatty acids in the range from C_{12}

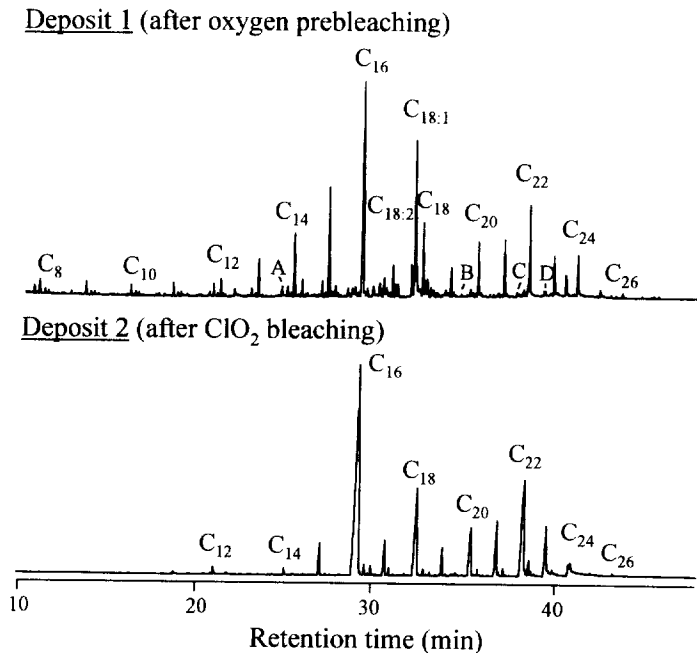


Fig. 2. Py(TMAH)-GC/MS of pitch deposits in pulp-mills. Carbon atoms refer to fatty acid methyl ester series. Labels A, B, C and D correspond to compounds arising from the Py(TMAH) of ellagic acid (their structures and mass spectra are shown in Fig. 3).

to C₂₆, with the palmitic acid methyl ester (C₁₆) as the highest. The remarkable absence of unsaturated fatty acids evidenced that chlorine dioxide bleaching leads to a complete removal of unsaturated fatty acids.

These results clearly indicate that fatty acids exist in the selected pitch deposits. 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 [18]. Previous studies have demonstrated that the IR spectrum of similar deposits showed signals attributable only to acid salts and not to free acids [1].

It is apparent from these results that the presence of fatty acid moieties in the insoluble organic residues of the pulp mill deposits have been biased upon conventional pyrolysis due to decarboxylation processes. In conventional pyrolysis, fatty acid salts decarboxylate, mainly producing series of alkanes and alkenes, in accordance with previous reported results [20,21]. The use of pyrolysis-methylation makes evident the presence of high amounts of fatty acid salts in the pitch deposits.

On the other hand, it is well known that pulp mills using eucalypt wood are often plagued with pitch deposition problems caused by the precipitation of ellagic acid soaps of magnesium and sodium ions [22–24]. Gallic and ellagic acids, as well as their glucose derivatives gallo- and ellagitannins, are typical extractives in the wood of *Eucalyptus* species [25]. During alkaline pulping, tannins are hydrolyzed into 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 [1]. The identification of ellagic acid deposits has been usually carried out by FT-IR [23]. However, if low amounts of ellagic acid soaps are present in the deposits, it is very difficult to assess its presence in the deposits by FT-IR. As in the case of fatty acid salt deposits, the presence of ellagic acid salts can be easily and rapidly assessed by Py(TMAH)-GC/MS.

While Py-GC/MS of ellagic acid salts did not result in any significant structural peaks due to the high polarity of the compounds produced and/or decarboxylation processes, Py(TMAH) released several compounds arising from the ellagic acid moiety (peaks A, B, C and D in Fig. 2). The mass spectra of these compounds and their structures are shown in Fig. 3 and similar compounds have been released after Py(TMAH) of an ellagic acid standard [26]. Low amounts of these compounds have been found in the deposits studied here, showing that in this particular case the problems associated with the deposition of ellagic acid soaps are minor. Pyrolysis-methylation has thus demonstrated to be very useful in identifying ellagic acid salts in pitch deposits, even when very low amounts of these moieties are present.

3.2. Identification of synthetic polymers in pulp-mills

Synthetic polymers arising from rubber items from different parts of the mills may enter the pulp stream. Most of these fragments accumulate in the filters along the process and can be thus eliminated, however, if the particles of rubber are small

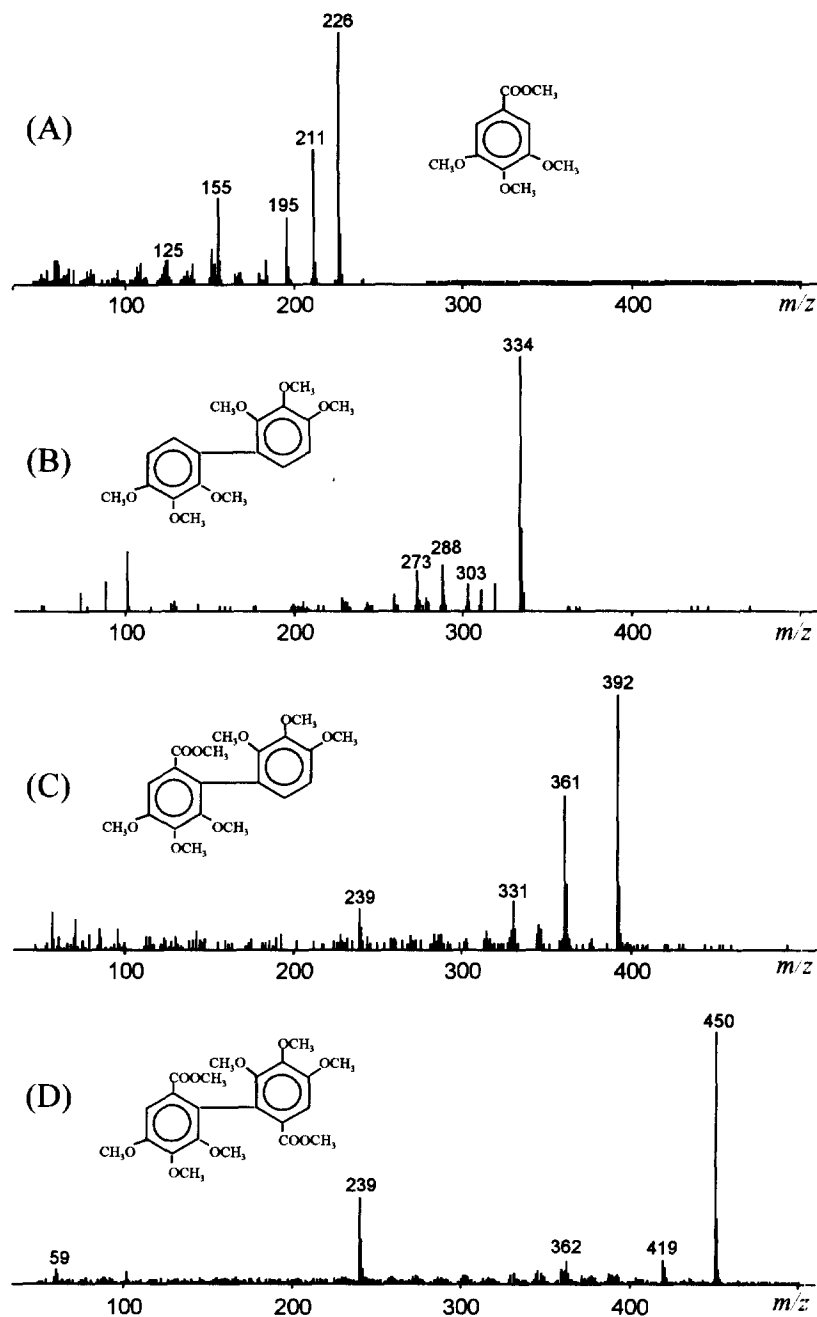


Fig. 3. Mass spectra and structures of the compounds released after pyrolysis-methylation of ellagic acid salts.

enough to pass the filters, they may accumulate in the pulp as impurities impairing product quality and originating important economic losses. A gross differentiation between pitch and rubber occurring in pulp and pulp-mills is routinely performed at the mills by checking visually. However, this differentiation is highly inaccurate and may lead to erroneous misinterpretations and some types of rubber can be confounded with pitch.

A set of rubber pieces presumably arising from machine breakage were collected from a centri-cleaner unit, where they accumulate, and were analyzed by Py-GC/MS. Different and distinctive chromatograms were obtained from the several pieces collected, suggesting that they belong to different synthetic polymers. Fig. 4 shows some examples of pyrograms obtained from selected synthetic polymers (rubbers 1–4) collected from the pulp-mill centri-cleaner unit, and Table 2 lists the compounds identified. The identification of the pyrolysis products provided valuable information about the nature of the polymer.

Rubber 1 released predominantly styrene (peak 5) after pyrolysis, as well as characteristic fragments corresponding to diphenylpropane (peak 49) and styrene trimer (peak 55). Additional aromatic compounds (peaks 4, 7, 13, 14, 17, 22, 23) were also detected in small quantities. Therefore, this piece corresponded to a polystyrene rubber.

The main compound released from rubber 2 corresponded to dipentene (peak 24), a compound with a similar structure to limonene, and consisting of two isoprene units. Several other dimers were also present (peaks 10, 16, 18, 21, 33), as well as their aromatic counterparts (peaks 29, 31). Peaks corresponding to trimers (peaks 45, 46) and tetramers (peaks 53, 54) were also detected in the pyrogram. Similar pyrograms and mass spectra were reported by Roussis and Fedora [27] for *trans*-poly(isoprene) or natural rubber.

The main compounds produced in the pyrolysis of rubber 3 were isopropenylbenzene (α -methylstyrene, peak 17) and a dimer of 1,3-butadiene-2-chloro (chloroprene dimer, peak 39). Minor peaks corresponding to a dimer made up of a moiety of butadiene and α -methylstyrene (peak 44) and two trimers composed of a moiety of α -methylstyrene and two moieties of butadiene (peaks 47, 50), were also detected. Therefore, this piece of rubber was made up of poly- α -methylstyrene and polychloroprene (neoprene).

Finally, rubber 4 released a series of compounds (peaks 2, 6, 11, 12, 15, 20, 26, 30, 41, 48) with similar mass spectra and characteristic fragments at m/z 113 and 163. The structures of these compounds have not been identified so far, and the identity of this synthetic polymer remains unknown.

In general terms, the total ion chromatograms or selected ions in the chromatograms can be used as characteristic fingerprints for the identification of synthetic polymers in order to trace its source from the different parts of the machinery. In this sense, comparison with pyrograms of known synthetic polymers would help to determine the composition of rubber 4.

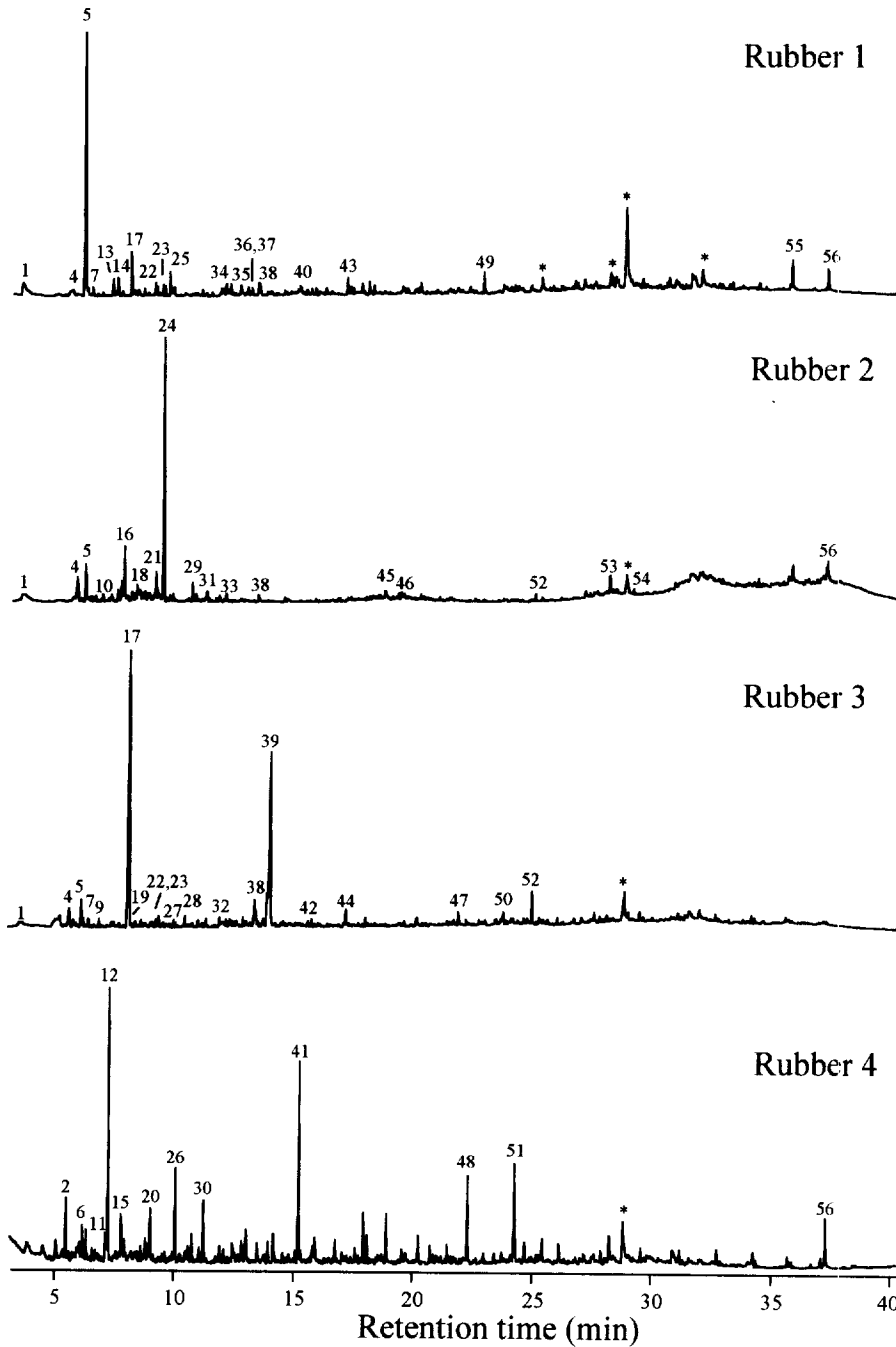


Fig. 4. Py-GC/MS of selected synthetic polymers collected from the pulp-mill centri-cleaner unit. Numbers refer to the compounds listed in Table 2. (* Denotes compounds arising from wood extractives).

Table 2
List of compounds identified in the pyrolysis-GC/MS of synthetic polymers

Number	Scan number	MS fragments	Compound
1	354	91, 92	Toluene
2	550	113, 163	
3	564	91, 106	Ethylbenzene
4	580	91, 106	Xylene
5	619	78, 104	Styrene
6	620	113, 163	
7	628	91, 106	Xylene
8	650	91, 106	Xylene
9	694	105, 120	C3-alkylbenzene
10	695	121, 136	C ₁₀ H ₁₆ (isoprene dimer)
11	717	113, 163	
12	728	113, 163	
13	734	105, 117, 118	Methylstyrene
14	756	91, 120	C3-alkylbenzene
15	784	113, 163	
16	785	121, 136	C ₁₀ H ₁₆ (isoprene dimer)
17	821	103, 117, 118	α -Methylstyrene
18	840	121, 136	C ₁₀ H ₁₆ (isoprene dimer)
19	846	91, 117, 118	C3-alkenylbenzene
20	904	113, 163	
21	916	121, 136	C ₁₀ H ₁₆ (isoprene dimer)
22	932	91, 117, 118	C3-alkenylbenzene
23	944	115, 116	Indene
24	951	121, 136	Dipentene (C ₁₀ H ₁₆) (isoprene dimer)
25	973	51, 77, 105, 134	Propiophenone
26	1007	113, 163	
27	1007	77, 103, 138, 140	Chlorostyrene
28	1052	105, 140	Chloro-C2-benzene
29	1069	117, 132	Methylisopropenylbenzene
30	1125	113, 163	
31	1129	119, 134	Methylisopropylbenzene
32	1197	115, 129, 130	C1-Indene
33	1209	121, 136	C ₁₀ H ₁₆ (isoprene dimer)
34	1226	115, 129, 130	C1-Indene
35	1268	77, 128	Naphthalene
36	1268	129, 144	C2-indene
37	1297	129, 144	C2-indene
38	1341	108, 135	Benzothiazole
39	1409	105, 141, 143, 176, 178	1,3-butadiene-2-chloro dimer
40	1516	115, 141, 142	Methylnaphthalene
41	1525	113, 163	
42	1565	115, 141, 142	Methylnaphthalene
43	1720	51, 63, 76, 128, 154	2-Vinylnaphthalene
44	1722	117, 118, 172	α -Methylstyrene-butadiene dimer
45	1877	121, 189, 204	Isoprene trimer C ₁₅ H ₂₄
46	1945	189, 204	Isoprene trimer C ₁₅ H ₂₄
47	2198	117, 118, 211, 226	α -Methylstyrene-butadiene trimer
48	2231	113, 163	

Table 2 (continued)

List of compounds identified in the pyrolysis-GC/MS of synthetic polymers

Number	Scan number	MS fragments	Compound
49	2287	91, 105, 196	1,3-Diphenylpropane
50	2385	117, 118, 211, 226	α -Methylstyrene-butadiene trimer
51	2425	251, 320	
52	2505	69, 111, v125	
53	2820	121, 134, 229, 272	Isoprene tetramer C ₂₀ H ₃₂
54	2925	107, 121, 175, 272	Isoprene tetramer C ₂₀ H ₃₂
55	3574	91, 117, 194, 297, 312	Styrene trimer
56	3726	149, 167, 279, 390	Phtalate di-isooctyl

3.3. Analysis of specks in pulp

A set of specks that appeared occasionally in a TCF pulp were collected and studied. They were previously solvent-extracted to remove wood extractives and analyzed by pyrolysis. Py-GC/MS of several different specks yielded the same results, showing an uniformity in their composition and suggesting that they all arise from a common source. A representative pyrogram is shown in Fig. 5, and the identification of the compounds is listed in Table 2. The pyrogram is similar to that observed previously for *trans*-poly-(isoprene) rubber, dipentene and several aromatic compounds with related structure being the main compounds identified. The specks seemed therefore to be composed by small particles of this synthetic polymer arising from different parts of the mills that had got into the pulp stream.

Although the specks analyzed in this particular case were all made up of the same synthetic polymer (*trans*-poly(isoprene) rubber), this does not exclude the fact that other synthetic polymers may occasionally occur as impurities in pulp. Analysis by Py-GC/MS will provide a rapid means to identify the offending polymer and thus to trace back the source of the contamination.

4. Conclusions

Analytical pyrolysis, with or without TMAH, proves to be a powerful analytical technique to characterize pitch deposits in pulp and pulp-mills as well as impurities arising from synthetic polymers. In particular, pyrolysis-methylation has demonstrated to be especially indicated for the characterization of pitch deposits made up of ellagic or fatty acid salts since these moieties can be biased upon conventional pyrolysis due to decarboxylation processes. Different pieces of rubber arising from machine breakage were collected from a centri-cleaner unit and were identified by Py-GC/MS as being made up of polyisoprene, polystyrene, poly- α -methylstyrene, polychloroprene and other synthetic polymers not completely characterized. Likewise, the series of specks occurring in a TCF

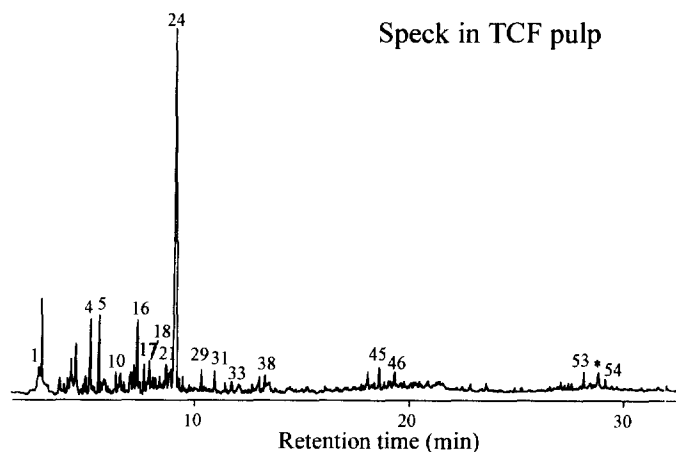


Fig. 5. Py-GC/MS of a speck occurring in a TCF pulp. Numbers refer to the compounds listed in Table 2. (* Denotes compounds arising from wood extractives).

pulp resulted to be composed by small fragments of trans-poly(isoprene) rubber. In general terms, the pyrograms of the synthetic polymers can be used as fingerprints to trace the source of contamination.

Acknowledgements

We thank Dr Javier Romero (ENCE, Pontevedra) for providing the samples used for this study. This research has been carried out with financial support from the Commission of the European Communities, Agriculture and Fisheries (FAIR) specific RTD programme, CT95-0560, Wood Extractives in Pulp and Paper Manufacture: Technical and Environmental Implications and Biological Removal.

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