A comprehensive study of different types of speck impurities present in bleached eucalypt kraft pulps using PY-GC/MS

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Abstract

Analytical pyrolysis in combination with gas chromatography and mass spectrometry (Py-GC/MS) has been used to characterize a wide set of different speck impurities occurring in total chlorine-free (TCF) kraft pulps made from eucalypt (*Eucalyptus globulus*) wood. The specks included pitch, rubber and plastic impurities and were previously classified by mill technicians upon visual checking. Samples of eucalypt wood chloroform extracts, TCF bleached pulps, as well as a large series of rubber and plastic items taken from different parts of the machinery were also selected for this study. The Py-GC/MS evaluation showed that, except for the impurities classified as plastics, the differentiation made between rubber and pitch by visual checking may give erroneous results. Apart from the presence or absence of wood extractives in some samples, most of the impurities analyzed in this work, even those that were unambiguously classified as pitch by mill technicians upon visual checking, showed to contain synthetic rubbers. Finally, the pyrograms of the specks and those of reference rubbers were used as fingerprints to trace the source of contamination.

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1. Introduction

The presence of impurities in paper pulp can severely impair product quality and is responsible for important economic losses in the pulp industry. The origin of the impurities is mainly due to wood extractives, which are difficult to remove during pulping and bleaching, and may deposit alone or with other components such as inorganic salts, fibers, and defoamers and cause sticky deposits (the so-called pitch) on process equipment and in pulp products [1,2]. On the other hand, synthetic polymers, such as rubbers and plastics, arising from machine breakage in different parts of the pulp mills can also be found in the pulp [3–7]. Most of the rubber and plastic fragments accumulate in the filters along the process and can be thus eliminated, however, if the particles are small enough to pass the cleaners, they may accumulate in the pulp as impurities. The rubber items usually found are polyisoprene, polystyrene, poly- α -methylstyrene and polybutadiene while plastics made up of polyethylene, polypropylene and polyamide can also be found as impurities in pulp.

A gross differentiation of the impurities present in pulp into pitch, rubber and plastics is routinely performed at pulp mills by visual checking of their physical aspects. However, although plastics are easily differentiated from other impurities, this is not the case between pitch and rubber. This differentiation is highly inaccurate and may lead to misinterpretations as some types of rubber could be confused with pitch. A rapid and accurate characterization and differentiation of the impurities present in pulp are necessary so that appropriate measures or treatments can be undertaken.

Analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) enables a rapid characterization of very small amounts of material and is therefore ideally suited to characterize impurities in pulp and hence to distinguish between pitch and different synthetic polymers. Several papers have successfully used Py-GC/MS for the identification of commonly found impurities in pulp and paper matrices [3–8]. In this work, Py-GC/MS has been used to analyze a wide series of speck impurities collected from eucalypt total chlorine-free (TCF)-bleached kraft pulp. On the other hand, wood extractives, cellulose fibers and a large series of reference rubber items from different parts of the pulp mill were also analyzed in order to establish the source of the impurities.

2. Material and methods

2.1. Description of the samples

A total of 56 specks were collected from TCF-bleached kraft pulp made of eucalypt (*Eucalyptus globulus*) wood. The bleaching sequence was OQPoP (pre-bleaching with oxygen, a quelating stage and two hydrogen peroxide stages, one of them under oxygen pressure) and the final TCF pulp had a kappa number 4. The collected impurities were classified by mill technicians according to their usual

procedure upon visual checking into different categories, namely “flexible rubbers”, “perished rubbers”, “green rubbers”, “possible rubbers”, “possible pitch”, “pitch” and “plastics”. At the same time, several pieces of rubber items arising from different parts of the mill were collected and subsequently cooked and bleached before analysis by Py-GC/MS and their pyrograms were used as fingerprints. On the other hand, *E. globulus* wood chloroform extracts (which were extracted in a Soxhlet apparatus with acetone and then the acetone extracts were evaporated to dryness, re-dissolved in chloroform, and evaporated again to dryness before the analysis by Py-GC/MS) and TCF-bleached pulp from Pontevedra pulp mill were also analyzed by Py-GC/MS. All impurities were picked and separated from cellulose fibers with tweezers in a microscope, placed in special quartz tubes, and analyzed by automatic Py-GC/MS without any other treatment.

2.2. Pyrolysis-gas chromatography/mass spectrometry

Analytical pyrolysis was performed using a CDS Pyroprobe AS-2500 Autosampler. The AS-2500 provides hand-free analysis of up to 36 samples. The sample was placed in a quartz tube of 2 mm × 40 mm and put into the sample tray. The pyrolysis was carried out at 610 °C for 10 s. The pyrolysis chamber was kept at 265 °C and purged with helium in order to transfer the pyrolysis products as quickly as possible to GC column. The pyrolyser was connected to an Agilent 6890 gas chromatograph equipped with an on-column injector and a fused silica capillary column (DB5 MS, 30 m × 0.25 mm ID, 0.25 µm film thickness) coupled to an Agilent 5973N mass spectrometer. 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 was programmed from 47 to 300 °C at 200 °C min⁻¹, while GC/MS interface was kept at 300 °C. The compounds were identified by comparing the mass spectra thus obtained with those of Wiley computer libraries, and by mass fragmentography.

3. Results and discussion

3.1. Pyrolysis of reference materials

Prior to the analysis of the speck impurities, a series of reference materials, such as *E. globulus* wood chloroform extracts, a TCF-bleached pulp and a wide set of rubber items arising from different parts of the mill were analyzed by Py-GC/MS.

3.1.1. Pyrolysis of *E. globulus* wood chloroform extracts

As one of the possible sources of the speck impurities in pulp could be deposits of lipophilic wood extractives (pitch), a sample of *E. globulus* wood was extracted and analyzed by Py-GC/MS. The pyrogram of the chloroform extracts is shown in Fig. 1 and the identities of the lipophilic compounds released are given in Table 1. Fatty acids, including tetradecanoic, hexadecanoic, 9,12-octadecadienoic, 9-octadecenoic, octadecanoic and eicosanoic acids, as well as squalene and several steroid

Fig. 1. Py-GC/MS analysis of the chloroform extracts of *E. globulus* wood. For peak identity, see Table 1.

Table 1

Main lipophilic compounds identified in the analysis of chloroform extracts of *E. globulus* wood by Py-GC/MS

No.	Compounds	MS fragments (m/z)
1	<i>n</i> -Tetradecanoic acid	60/73/129/185/228
2	9-Hexadecenoic acid	55/69/83/97/236/254
3	<i>n</i> -Hexadecanoic acid	60/73/129/256
4	9,12-Octadecadienoic acid	55/67/81/95/280
5	9-Octadecenoic acid	55/67/81/97/264/282
6	<i>n</i> -Octadecanoic acid	60/73/129/284
7	<i>n</i> -Eicosanoic acid	60/73/129/312
8	Squalene	69/81/95/137/410
9	Steroid hydrocarbon C _{29:2}	145/213/255/275/381/396
10	Steroid hydrocarbon C _{29:1}	147/215/257/383/398
11	Steroid hydrocarbon C _{29:2}	145/255/381/396
12	Steroid hydrocarbon C _{29:3}	135/143/394
13	Steroid hydrocarbon C _{29:2}	145/147/213/275/381/396

hydrocarbons with a C₂₉ skeleton, were among the lipophilic compounds released upon Py-GC/MS [9]. Sitosterol and sitosterol esters, which are also important lipophilic compounds from eucalypt wood responsible for pitch deposition during pulp manufacturing [3,10–13], are out of Py-GC/MS analytical window because of their high molecular weight. Therefore, in this work, we focussed only on the lipophilic compounds that are released upon Py-GC/MS and observed in the analytical conditions used here in order to confirm the presence of deposits of wood

extractives (pitch) in the speck impurities. It should be noted here that TCF bleaching with hydrogen peroxide has a minor influence on the composition of wood extractives [12]. Therefore, the composition of the lipophilic extractives in the eucalypt TCF kraft pulp is very similar to that of *E. globulus* extractives, except for the triglycerides that are hydrolyzed during cooking [12]. Other compounds released from the chloroform extracts were lignin-derived phenols with guaiacyl and syringyl structures and compounds arising from carbohydrates such as furfural, furfuryl-alcohol and levoglucosan.

3.1.2. Pyrolysis of eucalypt TCF kraft pulp

Since in some cases it was difficult to completely separate the impurities from the cellulose fiber, it was necessary to pyrolyze TCF pulp in order to distinguish the compounds arising from the pyrolysis of the pulp from those arising from the impurities. The pyrogram of a TCF pulp is shown in Fig. 2 and the identities of the released compounds are listed in Table 2. The main compounds identified were hydroxypropanone, furfural, several furanones and levoglucosan. The content of wood extractives in the pulp was very low (0.07%) and therefore they could not be detected upon Py-GC/MS.

3.1.3. Pyrolysis of selected rubber items from different parts of the pulp mill

A series of 19 reference rubber items (R01–R19) were collected at different locations along the pulp mill. Details on their location are given in Table 3. These samples were analyzed by Py-GC/MS after being cooked and bleached in a similar manner as TFC pulp. Table 4 summarizes the results obtained in this study (only characteristic compounds were considered). The different rubber items collected were basically composed of polyisoprene, polystyrene, poly- α -methylstyrene, poly-

Fig. 2. Py-GC/MS of a TCF pulp sample. For peak identity, see Table 2.

Table 2

Main compounds released after pyrolysis of TCF eucalypt kraft pulp

No.	Compounds	MS fragments (<i>m/z</i>)
1	Hydroxyacetaldehyde	42/56/58/60
2	Hydroxypropanone	43/74
3	(3H) Furan-2-one	55/84
4	3-Hydroxypropanal	43/57/73/74
5	Butanedial	43/57/58
6	Methylpyruvate	43/102
7	(2H) Furan-3-one	54/84
8	Furfural	95/96
9	Furfuryl alcohol	53/69/81/97/98
10	(5H) Furan-2-one	55/84
11	Hydroxycyclopentenone	42/55/69/98
12	Methylfurfural	53/81/109/110
13	4-Hydroxy-5,6-dihydro(2H)pyran-2-one	58/114
14	2-Hydroxy-3-methyl-2-cyclopenten-1-one	55/69/83/97/112
15	2,3-Dihydro-5-methylfuran-2-one	44/57
16	Dihydrohydroxypyran-1-one	56/84/114
17	Dianhydro- α -D-glucopyranose	57/69/85/98/114/144
18	Hydroxymethylfurfural	69/97/126
19	Levogluconan	60/73/98/144

Table 3

List of reference rubbers collected at different locations at ENCE pulp mill in Pontevedra, Spain

Reference rubbers	Location at the mill
R01	Insulation from drying machine ventilation shaft
R02	Baffle seal
R03	Chipper belt conveyor
R04	From drying machine No. 2 press support platform
R05	Andritz filter compartment seal
R06	Upper seal on C350 pulp centricleaner
R07	Chip feed belt conveyor
R08	Digester feed belt conveyor
R09	Lower seal O20 (perished rubber)
R10	Press rubber No. 2 catwalk
R11	No. 1 B11 seal (perished rubber)
R12	Flexible motor coupling
R13	Soft miner sheathing on electric cables
R14	Hard outside sheathing on electric cables
R15	B70 fiber-box seal
R16	Twin Nip press safety box
R17	B11/O20 lower door seal
R18	Digester box conveyor belt
R19	L80 filter seal No. 1

Table 4

Relative abundance (percent of total peak area in the pyrogram) of characteristic compounds obtained in the analysis by Py-GC/MS of reference rubbers collected at different locations at ENCE pulp mill in Pontevedra, Spain

Compounds	R01	R02	R03	R04	R05	R06	R07	R08	R09	R10	R11	R12	R13	R14	R15	R16	R17	R18	R19
Butadiene	n.d.	8	6	2	n.d.	n.d.	6	11	3	2	8	n.d.	n.d.	n.d.	n.d.	tr.	n.d.	8	9
Toluene	7	8	8	2	n.d.	1	7	7	11	4	1	5	5	4	n.d.	7	7	8	1
4-Vinylcyclohexene	5	7	7	2	n.d.	n.d.	6	7	5	2	2	n.d.	n.d.	n.d.	n.d.	2	2	7	2
Isoprene	tr.	tr.	2	23	n.d.	n.d.	9	7	tr.	23	10	n.d.	n.d.	n.d.	n.d.	26	16	6	17
Isoprene dimers	n.d.	n.d.	2	37	n.d.	n.d.	12	5	n.d.	36	n.d.	n.d.	n.d.	n.d.	n.d.	34	38	5	n.d.
Isoprene trimers/tetramers	n.d.	n.d.	n.d.	4	n.d.	n.d.	tr.	n.d.	n.d.	4	n.d.	n.d.	n.d.	n.d.	n.d.	5	10	n.d.	n.d.
Styrene	4	29	21	3	n.d.	1	30	34	36	4	1	4	4	4	n.d.	7	1	29	1
α -Methylstyrene	n.d.	7	7	20	n.d.	n.d.	6	5	7	19	1	n.d.	n.d.	n.d.	n.d.	3	n.d.	5	tr.
Diphenylpropane	n.d.	2	2	n.d.	n.d.	n.d.	2	1	2	n.d.	n.d.	tr.	n.d.	n.d.	n.d.	1	n.d.	2	n.d.
Indene	4	1	tr.	tr.	n.d.	n.d.	tr.	tr.	tr.	tr.	20	1	2	1	n.d.	1	n.d.	tr.	24
Indene derivatives	9	2	4	n.d.	n.d.	n.d.	n.d.	2	3	n.d.	3	1	2	2	n.d.	1	tr.	2	5
Naphthalene and derivatives	8	2	2	tr.	n.d.	n.d.	1	tr.	2	n.d.	n.d.	2	7	5	n.d.	n.d.	n.d.	2	n.d.
Phthalates	25	6	6	1	48	79	n.d.	1	3	1	25	32	40	34	74	3	5	4	1
Dibutylsebacate	n.d.	n.d.	n.d.	n.d.	16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
N-compounds	n.d.	2	2	tr.	n.d.	n.d.	2	1	n.d.	n.d.	13	n.d.	n.d.	n.d.	n.d.	n.d.	tr.	2	15
Fluorine compounds	n.d.	n.d.	n.d.	n.d.	28	18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	n.d.	n.d.	n.d.	n.d.
Total diagnostic compounds ^a	62	74	68	94	92	99	81	80	72	95	84	45	60	50	98	90	79	80	75

tr., trace amounts; n.d., not detected; all rubbers were cooked and bleached in the same manner as TCF pulp.

^a The rest corresponded to non-diagnostic compounds such as other alkylbenzenes.

butadiene and fluororubber (viton). The pyrograms of these reference rubbers were used as characteristic fingerprints for the identification of the rubber impurities that appear in pulps in order to trace their source from different parts of the machinery.

3.2. Characterization of speck impurities occurring in chlorine-free pulp

A wide set (56 samples) of speck impurities found in chlorine-free pulps were collected and analyzed by Py-GC/MS. Attending to their physical aspects, they were previously classified by mill technicians upon visual checking into different categories, namely rubbers (“flexible rubbers”, “perished rubbers”, “green rubbers”, “possible rubbers”), pitch (“possible pitch”, “pitch”) and plastics (“plastics”). However, this differentiation is highly inaccurate and a detailed characterization of the chemical composition of the impurities among the different categories is needed. For that purpose, Py-GC/MS was used. Figs. 3–6 show some examples of representative pyrograms of the studied impurities. The list of the main compounds identified is in Table 5.

3.2.1. Py-GC/MS of impurities classified as rubbers (“flexible rubbers”, “perished rubbers”, “green rubbers” and “possible rubbers”)

The Py-GC/MS analysis of all these samples, which were classified as rubber impurities by mill technicians, corroborated that all they contained rubbers. However, different types of synthetic polymers were identified and their origin could be easily traced by comparison with the reference materials already analyzed. The Py-GC/MS results are summarized in Table 6, where only the most representative and characteristic compounds have been considered.

Fig. 3. Py-GC/MS of a selected impurity in TCF pulp classified as “flexible rubber” (4). For peak identities, see Table 5.

Fig. 4. Py-GC/MS of a selected impurity in TCF pulp classified as “pitch” (52). For peak identities, see Table 5.

3.2.1.1. Flexible rubbers. A total of five samples (1–5) included in this group was analyzed by Py-GC/MS. Fig. 3 shows an example of Py-GC/MS of an impurity classified as flexible rubber. The Py-GC/MS results shown in Table 6 indicated that the impurities in this category did not correspond to a unique type of rubber. Two samples (3 and 5) released, after pyrolysis, predominantly dipentene, a compound with a similar structure to limonene, and consisting of two isoprene units, which is characteristic of the pyrolysis of polyisoprene rubber [14]. Several other dimers, trimers and tetramers of isoprene, were also detected in the pyrograms, and so these two samples were made of polyisoprene rubber. Another two samples (2 and 4) produced upon pyrolysis of styrene, butadiene, and α -methylstyrene, and so these pieces of rubber were made up of a copolymer of these three compounds. Finally, one of the samples (1) of this category released compounds derived from polystyrene and polyisoprene together. Besides the rubber fragments, steroid hydrocarbons occurred in the pyrograms of four of these samples but in trace amounts, indicating the contribution of pitch to these samples.

3.2.1.2. Perished rubbers. Four samples included in this group (6–9) were analyzed by Py-GC/MS. As in the previous category, the samples grouped here did not correspond to a unique type of rubber polymer. According to Py-GC/MS results (Table 6), one sample (6) was classified as being made up of polyisoprene, while the rest (7, 8 and 9) corresponded to polyisoprene/polybutadiene/polystyrene copolymers. Steroid hydrocarbons, which arise from wood extractives, were detected in all of them albeit in trace amounts, indicating the contribution of some amounts of pitch in these samples.

Fig. 5

Fig. 5

Fig. 6. Py-GC/MS of a selected impurity in TCF pulp classified as “plastic” (53).

3.2.1.3. Green rubbers. Two samples classified within this group (10 and 11) were analyzed. In this case, both samples have similar composition as revealed by Py-GC/MS (Table 6). The main compounds produced in the pyrolysis were isoprene monomer and dimers (e.g. dipentene), trimers and tetramers of isoprene, as well as styrene and therefore corresponded to a rubber made up of a polyisoprene–polystyrene copolymer. In addition, relatively high amounts of steroid hydrocarbons arising from wood extractives were also present in the pyrogram of sample 11 indicating the contribution of pitch to this rubber sample.

3.2.1.4. Possible rubbers. Five samples classified into this group (12–16) were analyzed upon Py-GC/MS. These samples were specially difficult to separate from the fiber, and therefore a considerable number of peaks arising from the cellulose pulp appeared in the pyrograms. The pyrolysis data (Table 6) showed that all samples in this category corresponded to a polyisoprene–polystyrene copolymer. The samples in this category had been previously classified into the rubber groups upon visual checking although with a high uncertainty as being mixtures of pitch and rubber. Interestingly, no traces of steroid hydrocarbons and/or fatty acids could be detected in any of these samples upon Py-GC/MS.

3.2.2. Py-GC/MS of impurities classified as pitch (“possible pitch” and “pitch”)

These categories include those impurities that have been unambiguously classified by mill technicians as being pitch (“pitch”), and those that are very likely to be

Fig. 5. Py-GC/MS of selected impurities in TCF pulp classified as “pitch” (31, 34, 44, 51). For peak identities, see Table 5. Note the high amounts of compounds arising from synthetic polymers in these samples.

Table 5

List of the main compounds released from the impurities collected in TCF eucalypt kraft pulps upon Py-GC/MS

No.	Compounds	Main fragment ions (m/z)
1	Butadiene	50/53/54
2	Isoprene	53/67/68
3	Methylcyclopentadiene	77/79/80
4	Hydroxypropanone	43/74
5	Toluene	91/92
6	Furfural	95/96
7	4-Vinylcyclohexene	54/66/79/93/108
8	Furfuryl alcohol	53/69/81/97/98
9	Ethylbenzene	91/106
10	Xylene	91/106
11	Styrene	78/103/104
12	(5H) Furan-2-one	55/84
13	Isoprene dimer	105/121/136
14	Hydroxycyclopentenone	42/55/69/98
15	C3-alkylbenzene	91/120
16	C3:1-alkenylbenzene	91/115/117/118
17	Isoprene dimer	107/121/136
18	Isoprene dimer	107/121/136
19	Methylfurfural	53/81/109/110
20	C3-alkylbenzene	105/120
21	α -Methylstyrene	78/91/103/117/118
22	Methylstyrene	91/103/117/118
23	Methylstyrene	91/103/117/118
24	Isoprene dimer	105/121/136
25	2-Hydroxy-3-methyl-2-cyclopenten-1-one	55/69/83/97/112
26	C3-alkylbenzene	105/120
27	Methylisopropylbenzene	91/105/119/134
28	Isoprene dimer (Dipentene)	107/121/136
29	Indene	115/116
30	Methylisopropenylbenzene	91/117/132
31	Methylindene	115/129/130
32	Unknown	57/58/69/70/82/85/96/116/128
33	Dianhydro- α -D-glucopyranose	57/69/85/98/114/144
34	Hydroxymethylfurfural	69/97/126
35	C2-indene	115/129/130
36	Phthalic acid	76/104/148
37	C2-indene	115/129/144
38	C3-indene	115/128/143/158
39	α -Methylstyrene-butadiene dimer	117/118/157/172
40	2-Vinylnaphthalene	76/128/154
41	Isoprene trimer	119/161/175/189/204
42	Isoprene trimer	121/161/175/189/204
43	Isoprene trimer	119/161/175/189/204
44	Isoprene trimer	119/161/189/189/204
45	Isoprene trimer	119/161/175/189/204
46	Levoglucozan	60/73/98/144
47	Isoprene trimer	119/161/175/189/204
48	Ethylphthalate	149/177/222

Table 5 (Continued)

No.	Compounds	Main fragment ions (<i>m/z</i>)
49	1,3-Diphenylpropane	91/105/196
50	1,3-Diphenylpropene	91/115/179/193/194
51	1,4-Diphenylbutane	91/92/104/117/210
52	Isoprene tetramer	121/175/229/272
53	Isobutylphthalate	149/167/223
54	Isoprene tetramer	91/107/121/175/229/272
55	<i>n</i> -Hexadecanoic acid	60/73/129/256
56	Isoprene tetramer	93/107/119/175/229/272
57	Butylphthalate	149/205/223
58	9,12-Octadecadienoic acid	55/67/81/95/280
59	9-Octadecenoic acid	55/67/81/97/264/282
60	<i>n</i> -Octadecanoic acid	57/60/73/129/284
61	Styrene trimer	91/117/194/297/312
62	Isooctylphthalate	149/167/279
63	Squalene	69/81/137/410
64	Steroid hydrocarbon C _{29:2}	145/213/255/275/381/396
65	Steroid hydrocarbon C _{29:1}	147/215/257/344/383/398
66	Steroid hydrocarbon C _{29:2}	145/213/255/342/381/396
67	Steroid hydrocarbon C _{29:3}	135/143/394
68	Steroid hydrocarbon C _{29:2}	145/213/255/275/288/381/396

composed of wood extractives but with some uncertainty as being mixed with rubber (“possible pitch”). However, as shown below, Py-GC/MS results indicate that the classification of the impurities in these two categories have been erroneously assigned by visual checking. Due to the high importance in the mill to distinguish between pitch and rubber impurities in the pulp, a large set of samples (28 samples) included among the “pitch” category by visual checking, were collected and analyzed in detail.

3.2.2.1. Possible pitch. Although eight samples were classified as being “possible pitch” (17–24), characteristic compounds of wood extractives (pitch), such as steroid hydrocarbons and/or fatty acids, could only be detected by Py-GC/MS in two of those samples (18 and 24), although in trace amounts (Table 7). All the samples released predominantly dipentene (dimer of isoprene) together with isoprene and several other dimers, trimers and tetramers of isoprene. Therefore, according to the results, we could conclude that all these impurities in this category were made of polyisoprene rubber.

3.2.2.2. Pitch. Twenty-eight samples (25–52), which were unambiguously classified by mill technicians as being pitch by visual checking of their physical aspect, were selected for this study. However, detailed analysis by Py-GC/MS (see Table 8) showed that only sample 52 released, besides compounds arising from the cellulose fiber, high amounts of compounds characteristics of the presence of wood extractives (pitch), namely fatty acids and steroid hydrocarbons (Fig. 4). Characteristic

Table 6

Results obtained in the analysis by Py-GC/MS of the impurities in TCF pulp, previously classified by mill technicians as “flexible rubbers”, “perished rubbers”, “green rubbers” and “possible rubbers”

	Flexible rubbers					Perished rubbers				Green rubbers		Possible rubbers				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sterol hydrocarbons	tr.	tr.	tr.	tr.	n.d.	tr.	tr.	tr.	tr.	tr.	1.1	n.d.	n.d.	n.d.	n.d.	n.d.
Fatty acids	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Isoprene	25	3	30	n.d.	30	28	22	25	28	25	23	22	25	28	22	19
Isoprene dimers	35	5	41	2	46	48	35	41	44	34	35	12	29	36	14	20
Isoprene trimers and tetramers	4	n.d.	2	n.d.	2	6	3	3	5	2	1	1	1	1	n.d.	n.d.
Styrene	12	35	n.d.	38	5	1	7	10	6	9	9	2	4	3	9	4
α -Methylstyrene	3	3	n.d.	3	2	n.d.	6	2	2	2	2	n.d.	tr.	2	n.d.	n.d.
Methylstyrene	n.d.	n.d.	n.d.	1	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Vinylcyclohexene	4	10	n.d.	10	2	n.d.	4	3	2	4	5	n.d.	n.d.	3	n.d.	n.d.
Carbohydrate compounds	3	3	5	2	2	7	3	2	3	3	3	29	18	7	21	29
Phthalates	1	2	1	3	2	3	2	1	3	1	2	12	1	tr.	6	tr.
Total diagnostic compounds ^a	87	61	79	59	92	93	82	87	93	80	80	78	78	80	72	72

The results are expressed as percentage of the total area of the pyrogram. n.d., not detected; tr., detected in trace amounts.

^a The rest corresponded to non-diagnostic compounds such as alkylbenzenes and alkylindenes.

Table 7

Results obtained in the analysis by Py-GC/MS of the impurities in TCF pulp, previously classified by mill technicians as “possible pitch”

	Possible pitch							
	17	18	19	20	21	22	23	24
Sterol hydrocarbons	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	tr.
Fatty acids	n.d.	tr.	n.d.	n.d.	n.d.	n.d.	n.d.	tr.
Isoprene	25	12	27	23	18	29	25	26
Isoprene dimers	31	7	35	27	18	39	32	36
Isoprene trimers and tetramers	1	n.d.	1	1	n.d.	1	1	1
Styrene	3	tr.	2	5	tr.	2	n.d.	n.d.
α -Methylstyrene	tr.	n.d.	tr.	tr.	n.d.	tr.	n.d.	n.d.
Methylstyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Vinylcyclohexene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carbohydrate compounds	20	44	16	17	34	12	20	17
Phthalates	1	1	tr.	3	1	3	2	2
Total diagnostic compounds ^a	81	64	81	76	71	86	80	82

The results are expressed as the percentage of the total area of the pyrogram. n.d., not detected; tr., detected in trace amounts.

^a The rest corresponded to non-diagnostic compounds such as alkylbenzenes and alkylindenes.

compounds of the presence of pitch were also observed in appreciable amounts in six other samples (31, 33, 34, 38, 48 and 51) while in some others were present in very minor or trace amounts. No traces of wood extractives were released from the rest of the samples upon Py-GC/MS, indicating the absence of pitch in these samples. In contrast, all samples in this category, except sample 52, released high amount of compounds arising from synthetic polymers. Fig. 5 shows some examples of impurities classified as pitch but that released compounds from synthetic polymers. Most samples in this category released predominant compounds arising from polyisoprene rubber, such as isoprene, dipentene and other dimers, trimers and tetramers of isoprene. Compounds arising from the pyrolysis of polystyrene were also detected in the pyrograms although only in seven samples (31, 34, 38, 39, 40, 41 and 44) the amounts of styrene, methylstyrene and α -methylstyrene were significant. Finally, one of the samples (34) released high amounts of butadiene (accounting for 13.4% of the released compounds) pointing out to the presence of polybutadiene.

3.2.3. Py-GC/MS of impurities classified as “plastics”

Four samples (53–56) belonging to the plastics group were analyzed by Py-GC/MS. The results showed that all the samples in this category were correctly classified as plastics upon visual checking. No steroid hydrocarbons and/or fatty acids were found in any of them upon Py-GC/MS indicating the absence of pitch. In one sample (53), two characteristic components from polyamide fiber (nylon-6), caprolactam ($C_6H_{11}NO$) and cyclopentanone (C_5H_8O) [15,16] were detected (Fig. 6). The caprolactam proportion was 45%. Another 43% of this sample corresponded to a series of alkenes and alkanes, which occurs after the breaking up of the polyethylene

Table 8

Results obtained in the analysis by Py-GC/MS of the impurities in TCF pulp, previously classified by mill technicians as “pitch”

	Pitch																											
	25	26	27	28	29	30	31	32	33	34 ^a	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52
Sterol hydrocarbons	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2	n.d.	2	4	tr.	tr.	tr.	4	tr.	tr.	tr.	tr.	n.d.	tr.	n.d.	tr.	tr.	1	tr.	tr.	2	9
Fatty acids	n.d.	n.d.	n.d.	n.d.	n.d.	tr.	tr.	tr.	tr.	n.d.	n.d.	tr.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	tr.	n.d.	n.d.	n.d.	tr.	tr.	tr.	tr.	tr.	10
Isoprene	39	34	36	53	38	1	27	26	29	12	27	25	33	21	30	27	32	38	26	23	22	29	20	26	31	30	24	n.d.
Isoprene dimers	24	31	25	18	19	10	29	20	25	7	32	9	23	27	23	20	24	18	14	21	14	33	13	32	30	25	27	n.d.
Isoprene trimers and tetramers	1	3	1	1	1	n.d.	2	1	1	n.d.	tr.	n.d.	1	n.d.	1	n.d.	n.d.	n.d.	1	1	n.d.	tr.	1	tr.	tr.	n.d.	tr.	n.d.
Styrene	4	4	6	5	2	4	9	tr.	2	15	tr.	6	6	9	4	4	5	5	4	5	4	n.d.	3	2	2	3	n.d.	n.d.
Methylstyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2	tr.	tr.	tr.	1	tr.	1	1	1	n.d.	1	1	tr.	1	1	1	1	1	1	1	n.d.	n.d.
α -Methylstyrene	tr.	tr.	tr.	1	tr.	n.d.	2	n.d.	tr.	3	n.d.	tr.	1	1	7	5	1	tr.	1	7	tr.	n.d.	tr.	tr.	tr.	1	n.d.	n.d.
4-Vinylcyclohexene	tr.	tr.	tr.	1	tr.	tr.	2	n.d.	n.d.	5	n.d.	n.d.	2	4	2	tr.	tr.	tr.	tr.	2	tr.	n.d.	tr.	n.d.	n.d.	tr.	n.d.	n.d.
Carbohydrate compounds	12	10	11	tr.	16	38	6	19	12	11	12	25	11	8	6	23	14	19	16	10	22	8	29	15	16	21	28	79
Phthalates	2	1	2	2	2	1	1	1	1	2	1	6	1	8	2	2	5	5	11	8	11	10	6	6	tr.	1	tr.	1
Total diagnostic compounds ^b	82	83	81	81	78	54	82	67	72	73	73	71	79	83	76	81	82	86	73	78	74	81	73	83	80	82	81	99

The results are expressed as the percentage of the total area of the pyrogram. n.d., not detected; tr., detected in trace amounts.

^a Butadiene was also identified representing 14% of the total compounds identified.^b The rest corresponded to non-diagnostic compounds such as alkylbenzenes and alkylindenes.

at high temperatures [17]. So, the speck was possibly a mixture of polyamide and polyethylene. The same set of alkenes and alkanes, but in higher amounts (70%), was identified in the rest of the samples indicating their polyethylene nature.

Taking into account all these results, it is obvious that the differentiation made in the mill by visual checking is highly inaccurate, except for the impurities classified as plastics. Apart from the presence or absence of pitch in some samples, all impurities analyzed, even those unambiguously classified as pitch (except 52), contained small fragments of synthetic rubbers. This suggests that small rubber pieces arising from machine breakage are a major source of pulp contamination in the mill. A rapid characterization of the impurities and the determination of their source are important in order to undertake appropriate measures. In this sense, the pyrograms of different reference rubbers collected from the machinery can be used as fingerprints to trace back the source of contamination. Therefore, comparing Py-GC/MS data of the impurities with those of the reference materials, it was possible to form five different groups: (A) impurities with important amount of polyisoprene similar to reference rubber R17; (B) impurities with important amounts of polyisoprene and polystyrene and similar to reference rubber R16; (C) impurities with important amounts of polyisoprene and poly- α -methylstyrene, similar to R04 and R10 reference rubbers; (D) impurities with important amounts of polystyrene similar to R09 reference rubber and (E) impurities with important amounts of polyisoprene, polystyrene and polybutadiene, similar to R7, R8 and R18 reference rubbers.

4. Conclusions

Py-GC/MS has proven to be an effective analytical technique to characterize small impurities in pulp, without sample treatment, and to distinguish between different synthetic polymers. Taking into account the results obtained in this study, almost all impurities analyzed in this work and collected from chlorine-free pulps had fragments of synthetic rubbers arising from machine breakage from different parts of the mill. In addition, most of them also had compounds that come from wood extractives (pitch) in its composition. However, inherent limitations of this technique have made it impossible to quantify the proportion of pitch and rubbers in mixed samples. The identification of the composition of the impurities in pulp will help to trace them back to their source, and define strategies for their control.

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