

Monitoring coal-tar pitch composition changes during air-blowing by gas chromatography

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Abstract

A series of air-blown coal-tar pitches was studied by GC and GC-MS in order to achieve a deeper understanding of the behaviour of the different pitch components during air-blowing. Compounds present in the parent pitch were identified and quantified and then compared to those present in the air-blown pitches. The compounds observed were identical before and after the treatments, but the concentration of each compound changed with the treatment to a different extent depending on its molecular structure and consequently its reactivity to oxygen. The most reactive compounds were those with a methylene-bridge in a five member ring, followed by those with a methyl group in their structure. © 2003 Elsevier B.V. All rights reserved.

Keywords: Coal-tar pitch; Air-blowing; Polynuclear aromatic hydrocarbons

1. Introduction

Coal-tar pitches are widely used as precursors of many different carbon materials. Commercial coal-tar pitches meet the requirements of traditional applications such as carbon anodes or graphite electrodes. However, their properties are not suitable for more specific and modern applications such as carbon fibres or carbon-carbon composites. For these applications, the pitch must be subjected to previous treatment so that its properties are improved. Various treatments have been used to modify pitch composition and properties. The main objective of these treatments is to increase pitch carbon yield without undermining other properties such as wettability to carbon substrates or ability to generate graphitizable carbons, i.e. thermal treatment in an inert atmosphere, the use of catalysts (AlCl_3 and BF_3), air-blowing, etc. [1–5]. Air-blowing is one of the most widely studied treatments at present, probably due to its low cost and straightforward application in industrial practice. The mechanisms involved in the pitch air-blowing process have been described by Barr and Lewis [6] and Zeng et al. [7], and then proved by other authors [5]. It has been shown that pitch polymerises by both aromatic condensation and

cross-linking reactions, one or the other being dominant depending on the chemical structure of the pitch components and air-blowing conditions [5]. The effects of air-blowing on the degree of polymerisation and properties are related to the increase in carbon yield, softening point, toluene insoluble content, C/H ratio, viscoelasticity development and variation in the molecular size distribution monitored by size exclusion chromatography [8–10].

Capillary gas chromatography (GC) and capillary gas chromatography with mass spectrometric detection (GC-MS) are generally accepted as two of the most powerful analytical tools available for complex organic mixtures [11–14]. Its widespread use is a direct result of its ability to provide qualitative and quantitative analysis. Useful information on the composition of coal tars and pitches has been obtained by means of these techniques, despite their limitations which are due to the partial solubilization of the sample and volatility problems with certain compounds [15–18]. Another important advantage of GC and GC/MS is their ability to monitor compounds during organic reactions. This feature has been used by several researchers in order to observe the evolution of industrial anthracene oil components during air-blowing under different experimental conditions [19]. The polymerisation of PAHs with AlCl_3 and the synthesis of new pitches from coal tar has also been monitored by GC [20,21].

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This paper focuses on the identification of individual compounds in a commercial coal-tar pitch and monitoring the evolution of these compounds during the air-blowing treatment. The objective was to assess the reactivity of the pitch components under mild oxidation conditions. To this end, both a qualitative and quantitative analysis of the soluble fraction was performed by GC and GC-MS. The different behaviours of the compounds in the air-blowing process were attributed to differences in their molecular structure.

2. Experimental

2.1. Samples

A commercial impregnating coal-tar pitch (P) was selected as the raw material. The pitch air-blowing was carried out at 275 °C under air for 10, 18 and 25 h, and the samples obtained were labelled AB10, AB18 and AB25, respectively.

2.2. Pitch air-blowing

The commercial impregnating coal-tar pitch was air-blown in a 2-l Pyrex reactor. The pitch was stirred at 100 rpm with an L shaped stirrer. The reactor was heated with an electric mantle. The temperature was controlled with a controller connected to a thermocouple immersed in the pitch. A total of 1000 g of coarsely ground pitch (<6 mm particle diameter) was pre-heated to 200 °C at a heating rate of 10 °C min⁻¹ and this temperature was maintained for 30 min. The temperature was then increased to 275 °C, at a rate of 3 °C min⁻¹, and maintained at this temperature for 10, 18 and 25 h, to produce a series of three air-blown pitches (AB10, AB18, and AB25, respectively). An air flow of 40 l h⁻¹ was bubbled into the pitch through an 8 mm glass tube during the experiment.

2.3. Softening point

The SP of each pitch was measured using a Mettler Toledo FP90 following the ASTM D3104 standard procedure. A small cup (with a pierced bottom) was filled with approximately 0.5 g of pitch. The cup was placed in the Mettler furnace and pre-heated to 20 °C below the expected SP. Then, the oven temperature was increased at a rate of 2 °C min⁻¹ until a drop of pitch passed through the hole, this point representing the softening temperature of the pitch.

2.4. Carbon yield

Four grams of pitch, <0.4 mm particle diameter, was poured into a ceramic cup (42 mm internal diameter and 11 mm height) which was then placed in a horizontal tube furnace. The pitch was carbonised under nitrogen flow (62 ml min⁻¹) by increasing the furnace temperature to 900 °C at a rate of 5 °C min⁻¹, this temperature being main-

tained for 30 min. Pitch CY was calculated from the weight of the carbonaceous residue.

2.5. Solubility

The solubility of the pitch in toluene was determined using a standard procedure. Two grams of pitch, <0.4 mm particle diameter, and 100 ml of toluene were placed in a 500 ml flask. The solution was heated to boiling point, and maintained under reflux for 30 min. Filtering was performed with a No. 4 porous ceramic plate. The residue was washed with hot toluene and acetone.

2.6. Elemental analysis

The carbon, hydrogen, sulphur and nitrogen contents were determined with a LECO-CHNS-932 microanalyzer. The oxygen content was measured using a LECO-VTF-900 furnace coupled to the same microanalyzer.

2.7. Gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS)

The samples analysed were the obtained by extraction of the coal tar pitches in an ultrasonic bath for 2 h using carbon disulphide as solvent (1 g of sample: 20 ml of CS₂). The extraction procedure has been described in detail elsewhere [22].

The GC analysis was carried out on a Hewlett Packard 5890 chromatograph with a flame ionisation detector and an OV 1701 capillary column (25 mm × 0.22 mm i.d.). Hydrogen was used as a carrier gas at a flow rate of 2 ml min⁻¹ and a splitting ratio of 1:87. The oven temperature was programmed at a rate of 4 °C min⁻¹, from 50 to 260 °C, this temperature being maintained for 10 min. The injector and detector temperature was 300 °C. 1-Methylfluorene was used as an internal standard for the quantitative analysis of the compounds.

GC-MS was performed with a Finnigan MAT CGQ ion trap spectrometer, ionisation occurring by electron impact (EI), employing the same capillary column and temperature program as used in the GC analysis. The ion source and transfer line temperatures were 230 and 250 °C, respectively. The data were acquired in the full scan mode between *m/z* 50–550 and a solvent delay of 6 min was used. The most probable compounds were identified by comparing their mass spectra to the mass spectra contained in the NIST library in the MS database and from their retention time, standard compounds being used when available.

3. Results and discussion

The main characteristics of the parent pitch (P) and the pitches obtained after the air-blowing treatment (AB10, AB18 and AB25) are shown in Table 1. Air-blowing caused

Table 1
Main properties of the parent pitch (P) and of the pitches obtained after air blowing treatment (AB10, AB18 and AB25)

Pitch	SP (°C) ^a	TI ^b	CS ₂ I ^c	CY (%) ^d	O (%) ^e	C/H ^f
P	97	20.0	19.0	34.6	1.8	1.64
AB10	139	36.6	32.1	48.0	1.78	1.82
AB18	168	44.6	38.3	57.6	1.81	1.83
AB25	197	51.8	43.8	61.8	1.89	1.86

^a Softening point.

^b Toluene insoluble.

^c Carbon disulfide insoluble.

^d Carbon yield.

^e Oxygen content.

^f Atomic ratio.

the softening point, carbon yield and content of the insoluble fractions to increase in accordance with the severity of the conditions used. The hydrogen content decreased significantly during the initial hours of air-blowing (from 4.65 for P to 4.26 for AB10) but it remained constant thereafter. The C/H ratio therefore was lower for the parent pitch (1.6) than for the air blown pitches (1.8).

These results indicate that an increase in the average size of the components occurs during air-blowing. This could be due either to the distillation of light compounds or the polymerisation. In a previous work [8], the effect of the thermal treatment at 275 °C was studied with the same parent pitch but under a nitrogen atmosphere. In that work, it was concluded that in the absence of oxygen, SP and CY increase only slightly after heat treatment up to 30 h. This indicates that the increase in these parameters during air blowing (Table 1) is mainly due to the polymerisation of the pitch components, caused by the oxygen in the air, and not to the removal of volatile compounds. These results are also in agreement with the SEC studies of the samples [10].

Table 1 also shows how the oxygen content of the original coal tar pitch was not significantly affected by air-blowing, which seems to indicate that the main effect of the oxygen was to induce the polymerisation of the pitch compounds without itself being significantly incorporated into the products.

Changes in pitch composition during the air-blowing treatment were monitored by GC and GC-MS. An appropriate characterisation of both the parent pitch and the air blown pitches could be valuable for a more detailed understanding of the air-blowing process, as the analysis of the chromatographic fraction has proven to be a suitable approach for understanding pitch behaviour [23]. In this work the composition of the chromatographic fraction has been related to the bulk properties of the pitches.

Fig. 1 shows the chromatograms of the CS₂ extracts of the parent pitch (P) and the air-blown pitch (AB25). The structures of the main PAHs have been included. The chromatograms of air blown pitches AB10 and AB18 present the

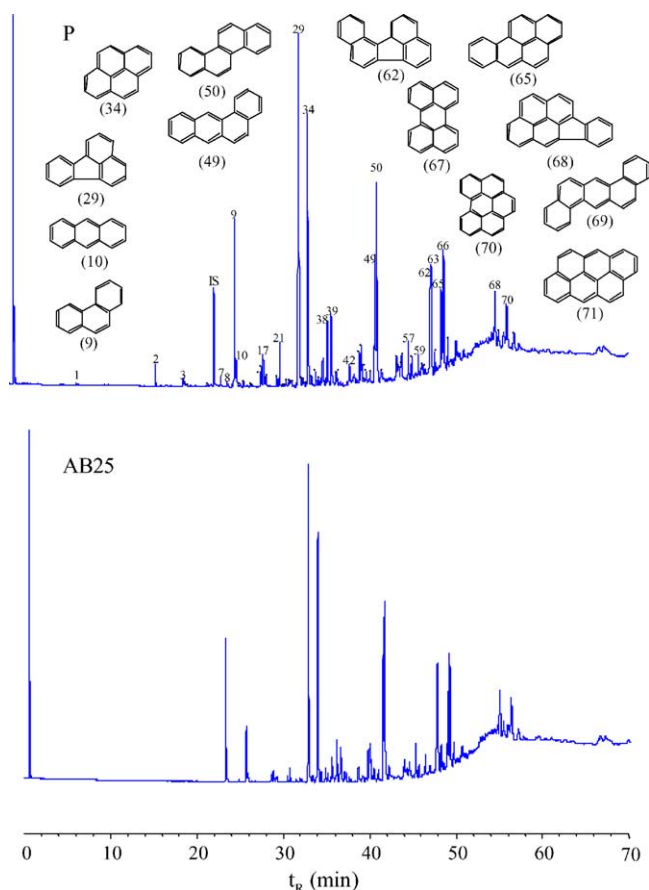


Fig. 1. Chromatograms of the CS₂ extracts of the parent pitch (P) and air-blown pitch AB25. Numbers refer to compounds listed in Table 3.

same peaks as that of AB25. The absence of new peaks in the chromatograms indicates that pitch P and the air-blown pitches have a similar qualitative chromatographic fraction composition, there being only slight differences at the beginning of the chromatogram. Peak assignments are reported in Table 3.

In agreement with the previous results [17], the extracts studied are composed of a large variety of polynuclear aromatic compounds (PACs) which can be classified into: polycyclic aromatic hydrocarbons (PAHs), alkyl and phenyl derivatives, partially hydrogenated PAHs, PAHs with a –CH₂– group in their structure such as 4H-cyclopenta(def)-phenanthrene, fluorene and its benzoderivatives and benzoderivative compounds that contain sulphur, nitrogen and oxygen. Nevertheless, the different profiles of the chromatograms in Fig. 1 reveal quantitative differences between the parent pitch and the air blown pitches.

The percentages of compounds (wt.%), which elute in the different regions of the chromatogram are reported in Table 2. R1 includes PACs with a molecular weight lower than phenanthrene (peak no. 9, Mw = 178); R2 compounds with a molecular weight between phenanthrene and fluoranthene (peak no. 29, Mw = 202); R3 PACs from fluoranthene to benzo(a)anthracene (peak n° 49, Mw = 228); R4 ranges

Table 2
Percentages of pitch compounds (wt.%) eluting in different chromatographic regions

	P	AB10	AB18	AB25	P/AB25
R1	0.33	0.00	0.00	0.00	–
R2	2.46	1.00	0.55	0.59	4.17
R3	8.71	5.77	4.03	4.10	2.12
R4	4.83	3.22	2.69	2.69	1.80
R5	7.61	6.39	5.64	4.71	1.62
^a CM	23.94	16.38	12.91	12.09	1.98

^a CM, proportion of pitch detected by gas chromatography.

from benzo(a)anthracene to benzo(j)fluoranthene (peak no. 62, Mw = 252); finally, R5 contains the heavier PACs, from benzo(j)fluoranthene to the end of the chromatogram.

It must be pointed out that all the peaks in these regions have been included and not only the identified peaks. Thus, the sum of the percentages of the five regions provides an estimation of the proportion of pitch detected by gas chromatography (CM). The quantitative values shown in Table 2 have been calculated as mentioned in the experimental section, using 1-methylfluorene as internal standard, the total area of each region and the values of pitch solubility in CS₂ given in Table 1. The results shown in Table 2 indicate that an increase in the air-blowing time causes a decrease in the amount of the compounds in the different regions of the chromatogram, and in the concentration of CM. The largest differences were found for air-blowing times <18 h while slight changes were observed when the reaction time was increased from 18 to 25 h. Table 2 also shows that the decrease in the concentration of the compounds with air-blowing time depends on their molecular weight. This behaviour is reflected by the values of the ratio between the concentration of the compounds in pitch P and those in the AB25 pitches (P/AB25). This ratio decreases as the molecular weight increases, the highest values corresponding to the lightest compounds (R2) and the lowest values to the heaviest (R5). On the other hand, the concentration of CM in the original pitch (23.94%) is approximately two times higher than in the pitch after 25 h of air-blowing treatment (12.09%).

Bearing in mind that the distillation of volatiles does not occur to a high degree during air-blowing, the results obtained seem to indicate that the decrease observed for CM is mainly due to the polymerisation of these pitch components in air, giving rise to an increase in the molecular weight of the pitch components. In general, the polymerisation process induced by air is more marked in the lighter compounds than in the heavier ones. However, the structure of the compounds also plays an important role in their behaviour during air-blowing i.e. compounds with the same molecular weight showed a different reactivity towards oxygen and some heavy hydrocarbons were even more reactive than the lighter ones.

Table 3 shows the concentration of the main PACs (mg/g pitch) in the parent coal tar pitch and in the pitches ob-

tained after the air blowing treatment as evaluated by GC. The total amount of identified material ranges from 20.37% for the parent pitch to 10.01% for AB25. These percentages indicate that the identified material represents approximately 78–80% of the proportion of pitch detected by GC (CM).

In general, a decrease in the concentration of the identified compounds was observed as the duration of the air-blowing treatment increased, although the extent of this decrease varied depending on the structure of the polycyclic aromatic compounds. This influence is evidenced by the values of the P/AB25 ratio which are higher than 1 for all the evaluated compounds (see Table 3). Compounds with a methyl or –CH₂– group, PAHs of a different size and topology [24] (alternant and non-alternant pericondensed hydrocarbons and catacondensed hydrocarbons) and compounds with N, O and S were compared.

The values of the P/AB25 ratio for a PAH and for the corresponding hydrocarbon with a CH₂ or CH₃ group are shown in Fig. 2. High P/AB25 ratio values were found for compounds belonging to the R2 region such as phenanthrene [9] and anthracene [10], their methyl derivatives [15,16,18,19] and 4H-cyclopenta(def)phenanthrene [17]. Given that aromatics with alkyl side chains are more reactive than unsubstituted ones [25], the highest P/AB25 values for phenanthrene and anthracene could be attributed to a certain degree of volatilisation of these compounds during the air-blowing treatment. The higher ratio value for 4H-cyclopenta(def)phenanthrene (Mw = 190) with respect to the methyl phenanthrenes (Mw = 192) indicates that a CH₂ group in a five member ring increases the reactivity of a PAH more than a methyl group. The influence of a CH₂ group on reactivity was evaluated by comparing the values of P/AB25 for fluoranthene (29), benzo(a)anthracene (49) and chrysene (50) with those obtained for benzofluorenes (38,39), 11H-benz(bc)aceanthrylene (54) and 4H-cyclopenta(def)chrysene (55), respectively (see Fig. 2). The higher ratio value obtained for the hydrocarbons with a CH₂ bridge indicates that they have a higher reactivity than the corresponding PAH without the CH₂ group. On the other hand, the average P/AB25 ratio value for the methylbenzo(a)anthracenes (51–53) shows that a methyl group also increases the reactivity of the parent PAH, although this effect is more marked in the case of a methylene bridge (see Fig. 2). Other examples of the influence of methyl groups can be observed in Table 3. Thus, methylpyrene (41) and dimethylbenzo(def)carbazole (60) show a much higher P/AB25 value than pyrene and 4H-benzo(def)carbazole (42), respectively.

In accordance with their topology a number of differences have been observed in relation with their reactivity towards oxygen. Table 3 shows that the alternant pericondensed PAHs like pyrene (34) and benzo(ghi)perylene (70) have higher P/AB25 ratio values and, therefore, are more reactive than the non-alternant PAHs of the same size, such as fluoranthene (29) and indenopyrene (68). Similarly, the

Table 3
Concentration of PACs (mg/g pitch) in the parent coal tar pitch and in those obtained after the air blowing treatment

Peak no.	Compounds	P	AB10	AB18	AB25	P/AB25
1	Quinoline	0.11	0.00	0.00	0.00	
2	Acenaphthene	1.09	0.00	0.00	0.00	
3	Fluorene	0.44	0.00	0.00	0.00	
4	Methylacenaphthene	0.14	0.00	0.00	0.00	
5	Methylacenaphthene	0.07	0.00	0.00	0.00	
6	9,10-Dihydroanthracene	0.07	0.00	0.00	0.00	
7	Tetrahydroanthracene	0.50	0.00	0.00	0.00	
8	Dibenzo(b,d)thiophene	0.40	0.00	0.00	0.00	
9	Phenanthrene	9.90	4.66	1.93	2.22	4.45
10	Anthracene	1.80	0.97	0.47	0.42	4.29
11	Benzoquinoline	0.19	0.00	0.00	0.00	
12	Benzoquinoline	0.38	0.00	0.00	0.00	
13	Benzoquinoline	0.15	0.00	0.00	0.00	
14	Benzoquinoline	0.19	0.00	0.00	0.00	
15	Methylphenanthrene	0.78	0.39	0.19	0.21	3.69
16	Methylphenanthrene	1.36	0.76	0.40	0.42	3.24
17	4H-Cyclopenta(def)phenanthrene	2.18	1.07	0.56	0.50	4.38
18	Methylphenanthrene	0.60	0.35	0.19	0.21	2.88
19	Methylphenanthrene	0.70	0.41	0.25	0.25	2.79
20	Phenylanthralene	0.61	0.38	0.23	0.26	2.31
21	Carbazole	2.66	1.04	0.63	0.63	4.24
22	Dimethylphenanthrene-anthracene	0.08	0.00	0.00	0.00	
23	Dimethylphenanthrene-anthracene	0.18	0.00	0.00	0.00	
24	Dimethylphenanthrene-anthracene	0.61	0.00	0.00	0.00	
25	Dimethylphenanthrene,-anthracene	0.15	0.00	0.17	0.24	0.65
26	Dimethylphenanthrene-anthracene	0.43	0.00	0.17	0.18	2.34
27	Dimethylphenanthrene-anthracene	0.36	0.00	0.17	0.16	2.21
28	Dimethylphenanthrene-anthracene	0.66	0.00	0.13	0.13	5.12
29	Fluoranthene	23.31	17.10	11.76	12.57	1.85
30	Methylcarbazole	0.85	0.00	0.00	0.00	
31	Phenanthro[4,5-bcd]thiophene	0.61	0.71	0.41	0.33	1.85
32	Azafluoranthene, pyrene	0.29	0.00	0.00	0.00	
33	Benzonaphthofuran	0.35	0.00	0.12	0.14	2.51
34	Pyrene	21.79	14.93	10.28	10.79	2.02
35	Benzonaphthofuran	0.87	1.05	0.56	0.50	1.75
36	Benzonaphthofuran	1.35	1.02	0.67	0.70	1.92
37	Benzo(kl)xantene	0.75	0.57	0.38	0.40	1.86
38	Benzo(a)fluorene	5.03	3.30	2.25	2.14	2.34
39	Benzo(b)fluorene	7.94	4.30	2.81	2.51	3.17
40	Methylbenzonaphthofuran	1.17	0.87	0.64	0.64	1.82
41	Methylpyrene	1.25	0.68	0.48	0.46	2.68
42	4H-Benzo(def)carbazole	2.25	1.49	1.08	0.94	2.41
43	Benzo(b)naphtho(2,1-d)thiophene	2.39	1.71	1.32	1.37	1.75
44	Tetrahydroanthracene	2.75	1.99	1.54	1.90	1.45
45	Benzo(ghi)fluoranthene	1.51	1.24	0.95	0.97	1.55
46	Benzo(b)naphtho(1,2-d)thiophene	0.62	0.42	0.32	0.29	2.18
47	Dibenzoquinoline	1.06	0.80	0.62	0.60	1.77
48	Benzo(a)naphtho(2,3-d)thiophene	1.39	1.24	0.76	0.80	1.74
49	Benzo(a)anthracene	9.34	8.48	6.65	6.92	1.35
50	Chrysene	16.60	11.37	8.67	9.04	1.84
51	Methylbenzo(a)anthracene	1.78	1.35	1.18	1.13	1.58
52	Methylbenzo(a)anthracene	2.49	1.96	1.50	1.35	1.84
53	Methylbenzo(a)anthracene	1.04	0.62	0.47	0.65	1.60
54	11H-Benzo(bc)aceanthrylene	1.12	0.91	0.69	0.55	2.02
55	4H-Cyclopenta(def)Chrysene	1.19	0.73	0.50	0.38	3.12
56	4H-Cyclopenta(def)triphenylene	2.33	1.69	1.26	1.23	1.90
57	11H-Benzo(a)carbazole	2.60	1.74	1.37	1.45	1.79
58	7H-Benzo(c)carbazole	1.55	0.82	0.64	0.59	2.62
59	5H-Benzo(b)carbazole	1.76	1.22	0.82	0.87	2.02
60	Dimethylbenzo(def)carbazole	1.77	0.78	0.47	0.45	3.91
61	Dihydrobenzofluoranthene	0.81	0.58	0.45	0.44	1.84
62	Benzo(j)fluoranthene	8.58	6.62	5.29	4.92	1.74
63	Benzo(b)fluoranthene	10.08	7.94	6.11	6.09	1.66

Table 3 (Continued)

Peak no.	Compounds	P	AB10	AB18	AB25	P/AB25
64	Benzo(k)fluoranthene	2.11	1.99	1.51	1.30	1.62
65	Benzo(e)pyrene	5.92	5.53	4.35	4.04	1.47
66	Benzo(a)pyrene	9.68	8.27	6.65	5.99	1.62
67	Perylene	2.41	1.99	1.57	1.32	1.83
68	Indenopyrene	5.82	3.88	2.96	2.81	2.07
69	Dibenzo(a,h)anthracene	1.86	1.44	1.28	1.18	1.57
70	Benzo(ghi)perylene	6.12	3.45	2.89	2.46	2.48
71	Anthanthrene	2.45	2.15	1.37	1.05	2.34
	Sum (wt.%)	20.37	13.90	10.11	10.01	2.04
	Identified material (%)	85.10	84.85	78.31	82.79	1.03

P/AB25 ratio shown in Table 3 for perylene (67) (alternant pericondensed hydrocarbon) indicates that it has a higher reactivity than other PAHs with five rings such as benzo(k)fluoranthene (62), benzopyrenes (65) and dibenzo(a,h)anthracene (69). On the other hand, pyrene is more reactive than benzo(a)anthracene (49) and chrysene (50), which are catacondensed hydrocarbons with the same number of rings as pyrene (see Fig. 1 for structures). It is clear also from Table 3 that the PAHs with the highest molecular weight and six rings, such as benzo(ghi)perylene, indenopyrene and anthanthrene (alternant pericondensed hydrocarbons), show greater decreases in concentration than the other hydrocarbons without aliphatic groups or heteroatoms in their structure. This indicates that such PAHs have a higher reactivity to air.

Fig. 3 shows the P/AB25 ratio values for PACs with and without heteroatoms but of the same size and topology. The ratio values for dibenzoquinoline (47) and for benzocarbazoles (BC) (average peak values n° 57, 58, 59), indicate that the PAC with nitrogen have a higher reactivity to air than the corresponding PAH, benzo(a)anthracene (49) and fluoranthene (29), respectively. The average P/AB25 values for benzonaphthofurans (BF) (peaks no. 33, 35, 36) and benzonaphthothiophenes (BT) (peaks no. 43, 46, 48) show that they have a similar reactivity to the corresponding PAH (fluoranthene) but a lower one than the nitrogen compounds (BC). A similar tendency was observed for 4H-benzo(def)carbazole (42) and phenanthro(4,5-bcd)thiophene (31) ($R_2 = \text{NH}$ and S , respectively) (Fig. 3). The P/AB25 values show once again that the nitrogen compounds are more reactive than

PAHs	P/AB25	PAHs with CH_2	P/AB25	PAHs with CH_3	P/AB25
	4.45		4.38		3.15
	1.85		2.34		
			3.17		
	1.35		2.02		1.67
	1.84		3.12		

Fig. 2. P/AB25 ratio values for a PAH and for the corresponding hydrocarbon with a CH_2 or CH_3 -group. P/AB25 is the ratio between the concentration of a given compound in P and its concentration in the AB25 pitch (see Table 3).

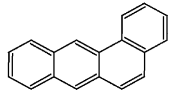
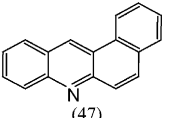
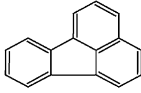
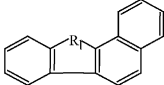
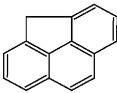
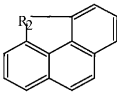
PAHs	P/AB25	Heteroaromatics	P/AB25
 (49)	1.35	 (47)	1.77
 (29)	1.85	 BC (57,58,59) R ₁ = NH 2.14 BF (33,35,36) R ₁ = O 1.82 BT (43,46,48) R ₁ = S 1.89	
 (17)	4.38	 (42) R ₂ = NH 2.41 (31) R ₂ = S 1.85	

Fig. 3. P/AB25 ratio values for PACs with and without heteroatoms. P/AB25 is the ratio between the concentration of a given compound in P and its concentration in the AB25 pitch (see Table 3).

the sulphur compounds in the air blowing treatment of pitches.

In all the cases studied the P/AB25 ratio values were lower than those obtained for R_1 and $R_2 = \text{CH}_2$, i.e. benzo(a) and benzo(b)fluorene (38, 39) and 4H-cyclopenta(def)phenanthrene (17).

4. Conclusions

GC and GC-MS are powerful techniques for monitoring the changes that occur in pitch composition during air-blowing treatment, providing valuable information for understanding the possible mechanisms involved in the polymerisation of pitch components. The proportion of pitch detected by GC is approximately two times higher in the original pitch than in the pitch after 25 h of air-blowing treatment. This indicates that the molecular weight of the pitch components increases during the process due to polymerisation in air. The most reactive compounds are those with methylene-bridges in five member rings. Nitrogen compounds are more reactive than the corresponding PAH without nitrogen or with S or O, while alternant pericondensed hydrocarbons show a higher reactivity than non-alternant pericondensed and catacondensed hydrocarbons. Alternant pericondensed PAHs with the highest molecular weight were found to be the most reactive of the hydrocarbons, with the exception of the PACs with aliphatic groups or heteroatoms as just mentioned.

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