Monitoring the synthesis of new pitches from coal tar and its fractions by chromatography and related techniques

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Abstract

The aim of this paper is to study the applications of chromatography and related techniques in the transformation of coal-derived products into pitches for specific uses. Anthracene oil, tar and pitch were thermally treated in the presence of air (and sulfur in the case of anthracene oil) in order to cause the polymerization/condensation of their components. The evolution of the components of the parent materials during the treatments was monitored by gas chromatography–mass spectrometry, gas chromatography–atomic emission detection, probe mass spectrometry and size-exclusion chromatography. From the results obtained, possible mechanisms for the transformation of coal-derived products into new pitches were established.   © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years extensive research into the characterization and thermal behavior of coal tar pitches has been carried out because of the suitability of these products for the manufacture of special carbons [1–3]. However commercial coal tar pitches have certain disadvantages such as their relatively low carbon yield [4] and swelling on pyrolysis [5] which make them inappropriate for the preparation of high-density carbons. These disadvantages, however, can be surmounted by subjecting the pitches to thermal treatment with or without additives, causing polymerization reactions between their components. Air-blowing of the pitches at temperatures over 200°C results in the polymerization of their components with no significant incorporation of oxygen. It is generally accepted that oxygen reacts with aromatics to form oxi and peroxi radicals, which by means of molecular condensation with the removal of most of the oxygen as water, give rise to molecules with a non-planar structure [4,6–8]. Careful control of the air-blowing reactions [4,7] is needed, therefore, to prevent the loss of essential properties, such as wettability, which are dependent on size, structure and functionality of the resultant molecules.

An alternative to the modification of commercial pitches may be the preparation of new pitches from coal tar and its distillation fractions. The catalytic polymerization of pure aromatic hydrocarbons was a promising starting point for the synthesis of special pitches [9]. The preparation of pitches from coal tar

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and its fractions has also been recently undertaken by air-blowing [7] and reaction with sulfur [10].

The study of the reactions which take place between the aromatics and air or elemental sulfur requires the utilization of several techniques of separation and fractionation because of the complexity of the raw materials and resultant products.

This paper reports on the utilization of chromatography and related techniques in the reactions of coal tar and coal tar pitches with air, and also reactions of anthracene oil (AO) with elemental sulfur and air. The reactivity of the main components of AO with sulfur and air was established by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). Studies on the mechanism of the reaction of pure aromatic hydrocarbons with sulfur were carried out by probe MS. Coal tar, before and after reaction with air, was fractionated by liquid chromatography (LC) on alumina. Fractions were characterized by GC–MS and GC with atomic emission detection (AED), selective detectors being used for C, S and N. The polymerization and polycondensation reactions and the size, structure and functionality of the resultant macromolecules were studied by size-exclusion chromatography (SEC), using *N*-methyl-2-pyrrolidone (NMP) as eluent.

2. Experimental

2.1. Materials

For this study several coal-derived products were used: anthracene oil treated with sulfur and air, air-blown tar and, thermally treated and air-blown pitches.

The reaction of AO with sulfur was carried out under reflux conditions at 250, 275 and 300°C for periods of 120 min, using an initial sulfur concentration of 5, 7.5, 10 and 20% (w/w). Samples were taken at different times between 5 and 90 min [10]. The treatment of anthracene oil with air was performed under reflux conditions in the temperature range of 250–300°C for periods of 15 h, using a specific air flow-rate of 112 l h^{-1} kg^{-1}. Samples for analysis were taken at 5 and 10 h.

Tar air-blowing was carried out under gas pressure (0.5 MPa) at a specific air flow-rate of 60 l h^{-1} kg^{-1} at 275°C/20 h and 300°C for 8 and 10 h [7].

The thermal treatment of pitches was performed at 430°C for periods of 2, 3 and 4 h and at 440°C for 2 h. Pitch air-blowing was carried out under a specific air flow-rate of 40 l h^{-1} kg^{-1} at 275°C for periods of 10, 18 and 25 h.

Table 1 summarizes the processing conditions and

Table 1
Experimental conditions and main properties of air-blown tar and air-blown and thermally treated pitch

Sample	Treatment	SP[a]	CY[b]	TI[c]	NMPI[d]
Tar	None	–	21.2	6.7	1.1
	275°C, 20 h, air (60 l h^{-1} kg^{-1})	85	44.0	34.9	14.5
	300°C, 8 h, air (60 l h^{-1} kg^{-1})	117	48.0	38.5	20.3
	300°C, 10 h, air (60 l h^{-1} kg^{-1})	183	49.0	48.5	28.7
Pitch	None	97	34.6	20.0	4.7
	275°C, 10 h, air (40 l h^{-1} kg^{-1})	139	48.0	36.6	13.6
	275°C, 18 h, air (40 l h^{-1} kg^{-1})	168	57.6	44.6	18.9
	275°C, 25 h, air (40 l h^{-1} kg^{-1})	197	61.8	51.8	24.9
	430°C, 2 h, N$_2$	159	56.3	44.4	22.4
	430°C, 3 h, N$_2$	169	61.1	51.5	29.8
	430°C, 4 h, N$_2$	195	67.1	57.4	34.6
	440°C, 2 h, N$_2$	219	74.3	62.4	41.1

[a] Softening point (Mettler, °C).
[b] Carbon yield (900°C; 30 min; %, w/w).
[c] Toluene insolubles (%, w/w).
[d] *N*-Methyl-2-pyrrolidone insolubles (%, w/w).

the main properties of air-blown tar and, air-blown and thermally treated pitches.

2.2. Characterization of anthracene oil and anthracene oil reaction products by GC, GC–MS, probe MS and Fourier transform IR

The GC of the AO and derived reaction products was carried out, using a Hewlett-Packard HP-6890 chromatograph with a flame ionization detector. Toluene-soluble fractions of the samples were analyzed by injection of 1 μl in split mode (24:1 ratio) into an HP-5 capillary column (cross-linked PH ME siloxane, 30 m$\times$0.32 mm I.D.). Hydrogen was used as a carrier gas at a flow-rate of 1.4 ml min^{-1} and a programmed temperature of 4°C min^{-1} to 300°C, this temperature being maintained for 30 min.

GC–MS was performed with a Finnigan MAT CGQ ion trap spectrometer with ionization occurring by electron impact (EI), using an HP-5 capillary column (30 m$\times$0.32 mm I.D.) and a programmed temperature of 5°C min^{-1} from 50 to 270°C for 20 min. Probe MS was performed in a Finnigan MAT 95 spectrometer by heating the samples in a vacuum from 20 to 300°C at 5°C min^{-1}.

Fourier transform infrared (FT-IR) spectra were obtained on KBr pellets in a Perkin-Elmer 1750 spectrometer. Two pellets of each sample (sample/ KBr=1/100) were used to minimize experimental errors.

2.3. Characterization of tar and air-blown tar products by GC–AED and GC–MS

Before performing GC–AED and GC–MS analyses, parent tar and air-blown tar products were extracted by Soxhlet for 24 h with dichloromethane (DCM). The DCM-soluble fraction was then fractionated by liquid chromatography [11] according to the following procedure: 0.3 g of the extract was mixed with 3 g of neutral alumina. The mixed material was placed at the top of a column containing 6 g of packed neutral alumina. The sample was eluted from the column using a sequence of four solvents: *n*-hexane, toluene, chloroform and tetrahydrofuran (THF). Four fractions were obtained: A-1 (aliphatic hydrocarbons), A-2 (neutral polycyclic aromatic compounds), A-3 (nitrogen polycyclic aro-

matic compounds and oxygen-polar compounds), and A-4 (hydroxy polycyclic aromatic compounds).

DCM solutions (10 g l^{-1}) of the A-1, A-2 and A-3 fractions were analyzed by GC–AED using a Hewlett-Packard 5890 Series II gas chromatograph coupled via a heated transfer line to a Hewlett-Packard 5921A atomic emission detector for elemental carbon, nitrogen and sulfur. A 1-μl volume of each DCM extract was injected in splitless mode into a BPX5 capillary column, using argon as carrier gas at a flow-rate of 1 ml min^{-1}, and a programmed temperature of 280°C/30 min at 5°C min^{-1}.

GC–MS analyses were carried out in a GC–MS Finnigan MAT spectrometer, using a CP-Sil 8 CB.MS capillary column (0.25 mm I.D.), and a programmed temperature of 320°C at 5 °C min^{-1}. A 1-μl volume of the DCM extracts of the A-1, A-2 and A-3 fractions of each sample was injected in splitless mode at 250°C. The transfer line between the GC and the MS was heated at 250°C. A mass scan was performed at 1 scan s^{-1}.

2.4. Characterization of anthracene oil, tar, pitch and their reaction products by SEC

The SEC analysis was carried out employing a Plgel Mixed E column (30 cm$\times$7.5 mm I.D., polystyrene–divinylbenzene, 3 μm) and NMP as mobile phase. A Kontron Instruments HPLC pump (Model 422) was used to maintain a 0.5 ml min^{-1} flow-rate. The column was preheated to 80°C in a thermostatic oven (Pickstone). The detector was a Jasco 875-UV (UV–Vis detector) with a 280 nm wavelength. The samples were injected with a 6-ports injector equipped with a 20-μl loop. Samples were solubilized in NMP (1/400 conc.) in an ultrasonic bath and filtered before injection.

3. Results and discussion

3.1. Reaction of anthracene oil with sulfur and air – reactivity and mechanisms

The composition of the AO was obtained by GC–MS, the main components being phenanthrene, fluoranthene, pyrene, anthracene, acenaphthene and fluorene (Fig. 1).
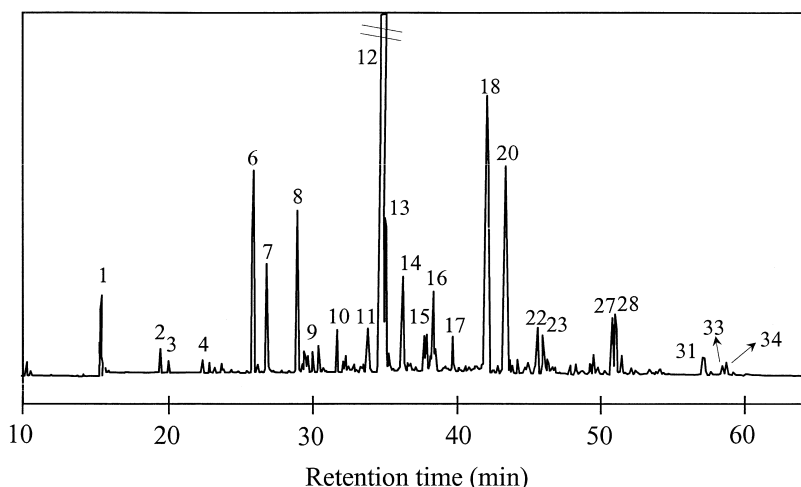
Fig. 1. GC–MS chromatogram of anthracene oil. Numbers refer to compounds listed in Table 2.

The reactivity of the main components of AO was monitored by GC analysis of the toluene-soluble fraction of the samples. The concentration of the components was determined, approximately, from the area of the respective peaks in the chromatograms of the toluene extracts, according to the following equation:

$$\text{Conversion (\%, w/w)} = \frac{C_0 - C'}{C_0} \cdot 100$$

$$\text{where } C' = C \cdot \frac{100 - R_{350}}{100} \tag{1}$$

where C_0 and C are the percentage of the peak area in the original AO and the reaction product, respectively. R_{350} is the residue of the reaction products at 350°C determined by thermogravimetry (R_{350} for AO is 0), which was taken as a measure of AO conversion [10]. Fig. 2 shows the reactivity of the main components of AO with air at 300°C. Components with methylene-bridges are the most reactive. Components without aliphatic hydrogen, such as phenanthrene, anthracene, fluoranthene and pyrene, which account for 47% (w/w) of AO, scarcely react at 300°C with air at times <5 h.

The reaction rate of AO with sulfur is much more rapid than with air. However, the relative reactivity of the components follows the same trend.

The considerable differences between the reactivities of the AO components suggest the existence of different mechanisms of reaction. It has been suggested that several mechanisms coexist in the air oxidation of mixtures of aromatic hydrocarbons and that they contribute to different extents depending on the structure and functionality of the components. However, the reaction of sulfur with AO has never been studied. To gain an insight into the reaction mechanisms involved in the treatment of AO with sulfur, two pure aromatic compounds were studied
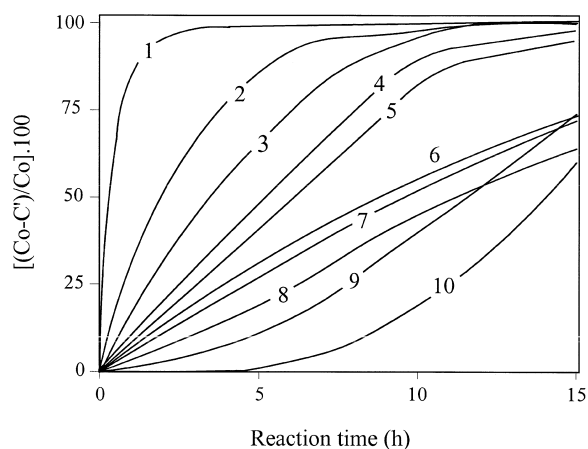

Fig. 2. Conversion degree of main anthracene oil components with reaction time for air-blowing at 300°C: dihydroanthracene (1), acenaphthene (2), benzo[b]fluorene (3), fluorene (4), benzo[a]fluorene (5), dibenzothiphene + dibenzofuran (6), pyrene (7), chrysene + fluoranthene + benzo[a]anthracene (8), carbazole (9), and phenanthrene + anthracene (10).
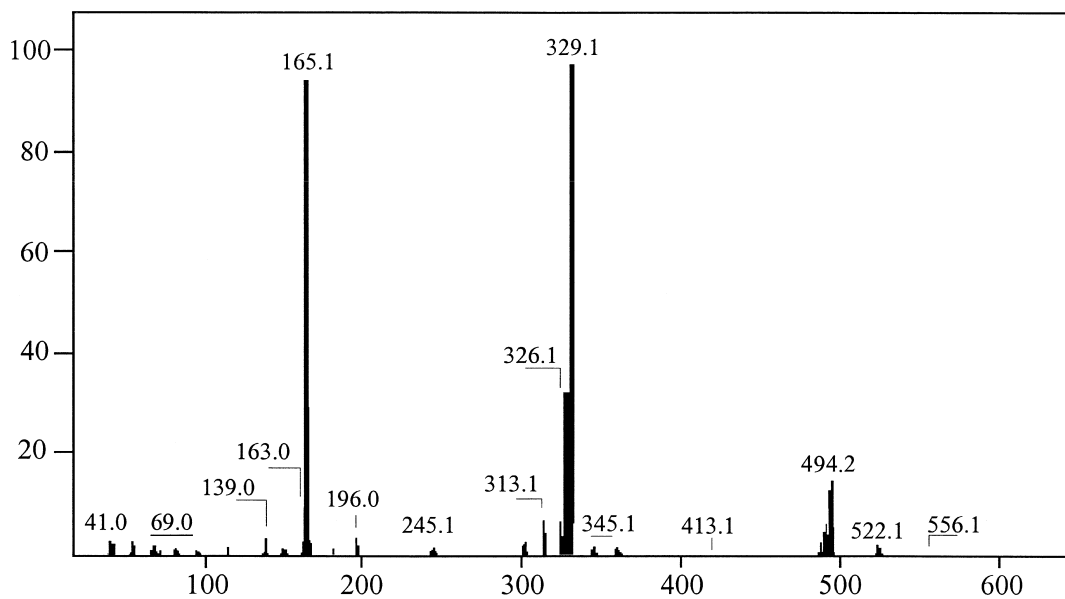
Fig. 3. Probe mass spectrum of fluorene treated at 250°C for 360 min with 10% (w/w) of sulfur.
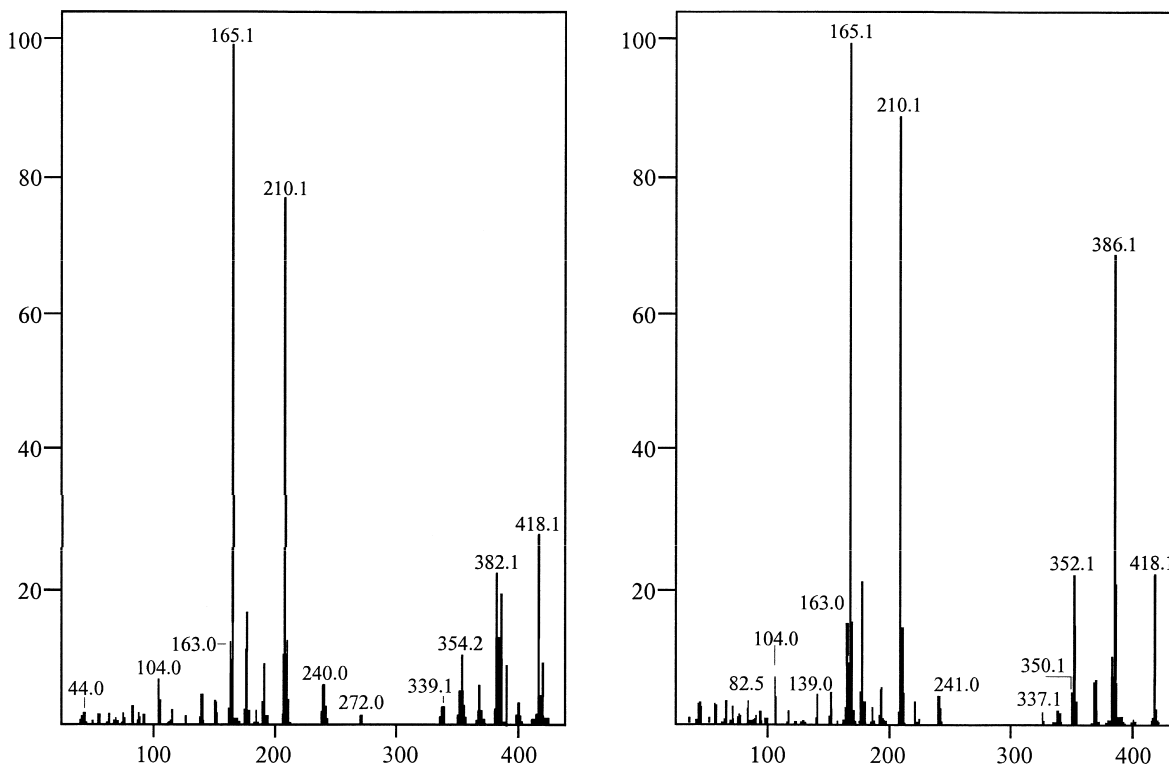
Fig. 4. Probe mass spectra of phenanthrene treated at 300°C for 120 min with 20% (w/w) of sulfur.

separately by probe MS. One of them, fluorene, is representative of the most reactive compounds, whereas phenanthrene represents the least reactive.

The mass spectra at different scans of the reaction product of fluorene with sulfur (10%, w/w) at 250°C and 360 min, show even peaks at m/z 166, 330 and 494, m/z 330 being the dominant peak. The molecular ion at m/z 330 was identified as 9,9′-bi-9H-fluorene ($C_{26}H_{18}$), by comparing a spectrum in

Table 2
Main components identified by GC–MS in A-1 and A-2 parent tar fractions

No.	Compound	m/z
1	Naphthalene	128
2	2-Methylnaphthalene	142
3	1-Methylnaphthalene	142
4	Biphenyl	154
5	Acenaphthylene	152
6	Acenaphthene	154
7	Dibenzofuran	168
8	Fluorene	166
9	Methylfluorenes	180
10	Dihydroanthracene	180
11	Dibenzo[b,d]thiophene	184
12	Phenanthrene	178
13	Anthracene	178
14	Carbazole	167
15	Methylphenanthrene/anthracene	192
16	Cyclopenta[def]phenanthrene	190
17	1-Phenylnaphthalene	204
18	Fluoranthene	202
19	Benzoacenaphthene	204
20	Pyrene	202
21	Methylfluoranthene/pyrene	216
22	Benzo[a]fluorene	216
23	Benzo[b]fluorene	216
24	Methylfluoranthene/pyrene	216
25	Benzo[c]phenathrene	228
26	Benzo[ghi]fluoranthene	226
27	Benzo[a]anthracene	228
28	Chrysene/tryphenilene	228
29	Methylchrysene	242
30	Cyclopenta[def]chrysene	240
31	Benzofluoranthene	252
32	Benzofluoranthene	252
33	Benzo[e]pyrene	252
34	Benzo[a]pyrene	252
35	Perylene	252
36	Methylbenzofluoranthene	266
37	Cyclopenta[ghi]perylene	264
38	Indene[1,2,3-cd]pyrene	276
39	Benzo[ghi]perylene	276

which the only significant even mass peak was that at 330 with the library spectrum of 9,9′-bi-9H-fluorene. The spectrum obtained by measuring the difference between the spectrum of the spectrometer library for the pure compound and the one registered suggests the presence of small amounts of compounds at m/z 328 and 326, which could belong to dibenzo[a,c]triphenylene and rubicene, respectively, products from the dehydrogenation and rearrangement of 9,9′-bi-9H-fluorene [12]. Fig. 3 shows that the compound with a molecular mass of 494 is a trimer of the fluorene.

In contrast, phenanthrene, when treated with 20% (w/w) of sulfur at 300°C for 120 min gives a mass spectrum characterized by a series of m/z ions which differ by 32 and 64 units (Fig. 4). This suggests the formation of compounds involving one or two sulfur atoms. Spectra obtained at different scans indicate that ions of the 418, 386 and 354 series are independently formed. On the other hand, the 382 ion was identified as dibenzo[2,3:10,11]perylo[1,12-bcd]thiophene, by comparing with the library spectrum. The compound with a molecular mass of 210 is probably phenanthrenethiol ($C_{14}H_{9}SH$), which is formed by addition of S to phenanthrene. This compound is an intermediate in the formation of the 418 and 382 series. These results reveal the existence of at least three different condensation reactions with the incorporation of zero, one or two sulfur atoms, followed by a dehydrogenative cyclization. Furthermore, low scan spectra reveal the presence of elemental sulfur, the peaks of 64, 96, 128, 160, 192 and 256 corresponding to the mass spectrum of S_8. This is in agreement with the low reactivity of phenanthrene observed by GC.

3.2. Monitoring of tar air-blowing – influence of the experimental conditions

A commercial tar, with the characteristics shown in Table 1, was air-blown under several experimental conditions, which are summarized in the Table. In order to obtain a deeper insight into the influence of air-blowing on composition, the parent tar and its air-blown products were fractionated by LC and the fractions analyzed by GC–AED according to the procedure described in Experimental. The A-4 frac-

tion was not analyzed because it had not been solubilized by DCM.

The main components of the A-1 and A-2 fractions of the parent tar are listed in Table 2. Changes in the chemical composition caused by air-blowing are evident from the comparison of the chromatograms of the A-2 fractions of the parent tar (Fig. 5a) and air-blown tar at 275°C/20 h (Fig. 5b). All the methylene-bridged and alkyl-substituted components

of the parent tar have disappeared with air-blowing, providing further proof that they have a higher reactivity, as found in the reaction of AO with air (Fig. 2) and sulfur.

The GC–MS of the A-1 and A-2 fractions, with the help of the specific S detector, can be used to identify 14 thiophenic compounds with a molecular mass ranging from benzothiophene to benzo[*b*-]naphthothiophene, all in very low concentrations,
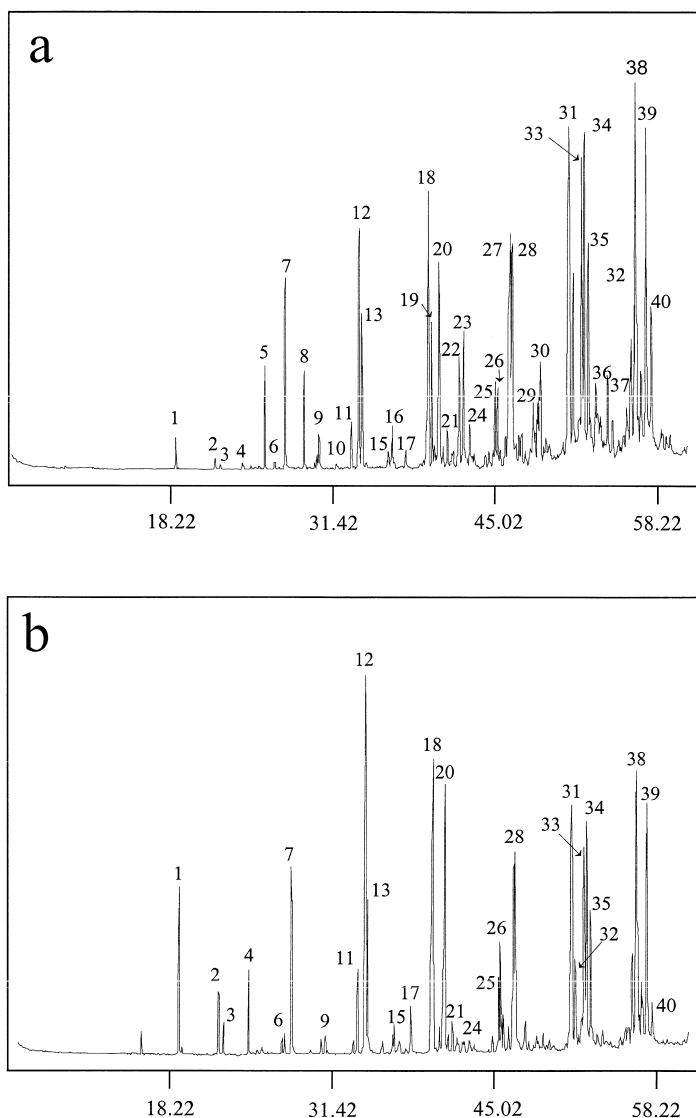

Fig. 5. A-2 fraction GC–MS chromatograms of (a) parent tar and (b) air-blown tar at 275°C for 20 h. Numbers refer to compounds listed in Table 3.

except for dibenzothiophene. The effect of air-blowing on this kind of compound seems to be minimal.

The A-3 fraction, made up of polar aromatic nitrogen compounds together with residual amounts of the main aromatic hydrocarbons (Table 3), represents about 5% (w/w) of the parent tar and air-blown coal tar. N-Compounds were identified by GC–MS with the aid of a specific N detector. A-3 fraction chromatograms of the parent tar, before (Fig. 6a) and after air-blowing for 20 h (Fig. 6b), show the changes in the composition of the A-3 fraction caused by air-blowing, revealing that the N-compounds also react with air in spite of their low concentration in the parent tar. The main components of the A-3 fraction in air-blown tar (Fig. 6b) are aromatic ketones, which are referred to by letters in Table 3 and Fig. 6b. However, apart from ketones other C=O groups may be present in very low concentrations in condensed molecules, as Fig. 7 shows, this figure representing an enlarged region of the FT-IR spectrum (1600–1800 cm^{-1}) of the air-blown anthracene oil. At least five different kinds of carbonyl groups are detected, and can be assigned to aliphatic and aromatic carboxylic acids, aryl and alkyl esters, ketones, quinones, etc. [13,14]. The presence of these functionalities suggests that they are involved in the condensation reactions induced by air-blowing. They are also interesting from a mechanistic point of view. However, the small IR absorption bands (Fig. 7), and the insignificant increase in the oxygen content determined by elemental analysis show that the incorporation of oxygen is small.

3.3. Monitoring anthracene oil, tar and pitch air-blowing by SEC

Pitch properties are dependent on the size, structure and functionality of molecules resulting from air-blowing. This is especially true of those properties required for industrial applications. Parameters commonly used for the characterization of commercial pitches, such as softening point, carbon yield and solubility tests, are not suitable for the characterization of air-blown pitches, because of the cross-linked structures and oxygen functionalities arising from air-blowing. It would be of great interest therefore to find techniques able to measure the extent of cross-linking and functionality and determine their effects on pitch properties.

Recently, SEC with UV detection, using polystyrene–divinylbenzene as stationary phase and NMP at 80°C as mobile phase, was described as the best chromatographic technique for molecular mass determination in complex mixtures derived from coal [15]. When the samples contain a wide range of molecular masses, like coal tar pitches, molecules with a size above a critical value, elute at the exclusion limit of the column (excluded material), whereas the smaller species are separated by the column eluting before the permeation limit (separated material) is reached.

From this, it seems that separations are mainly produced by a size-exclusion mechanism induced by the high polarity of the NMP, the latter preventing effects of molecular association and solute adsorption on the stationary phase. On the other hand, NMP has the advantage of a high solubilization capacity which makes it possible to analyze a larger amount of samples than by means of the other usual solvents [16]. However, Lafleur and Nakagawa have demonstrated that small highly polar compounds also elute at the exclusion limit of the column [17]. It is possible that compounds with a non-planar structure

Table 3

Main compounds identified by GC–MS in A-3 air-blown tar fractions

| No./Letter	Compound	m/z
1	Quinoline	129
2	Naphthalene	128
3	Acenaphthylene	152
4	Naphthalene carbonitrile	153
5	Naphthalene carbonitrile	153
a	1H-Phenalen-1-one	170
6	Phenanthrene	178
7	Benzoquinoline	179
8	Carbazole	167
b	9,10-Anthracenedione	208
c	Cyclopenta[*def*]phenanthrenone	204
9	Fluoranthene	202
10	Azafluoranthene	203
11	Pyrene	202
d	7H-Benzo[*de*]anthracene-7-one	230
12–14	Benzoacridines	229
e	Benzo[*a*]anthracene-7,12-dione	258
15–16	Benzoazafluoranthene/benzoazapyrene	253
17	Dibenzoacridine	279
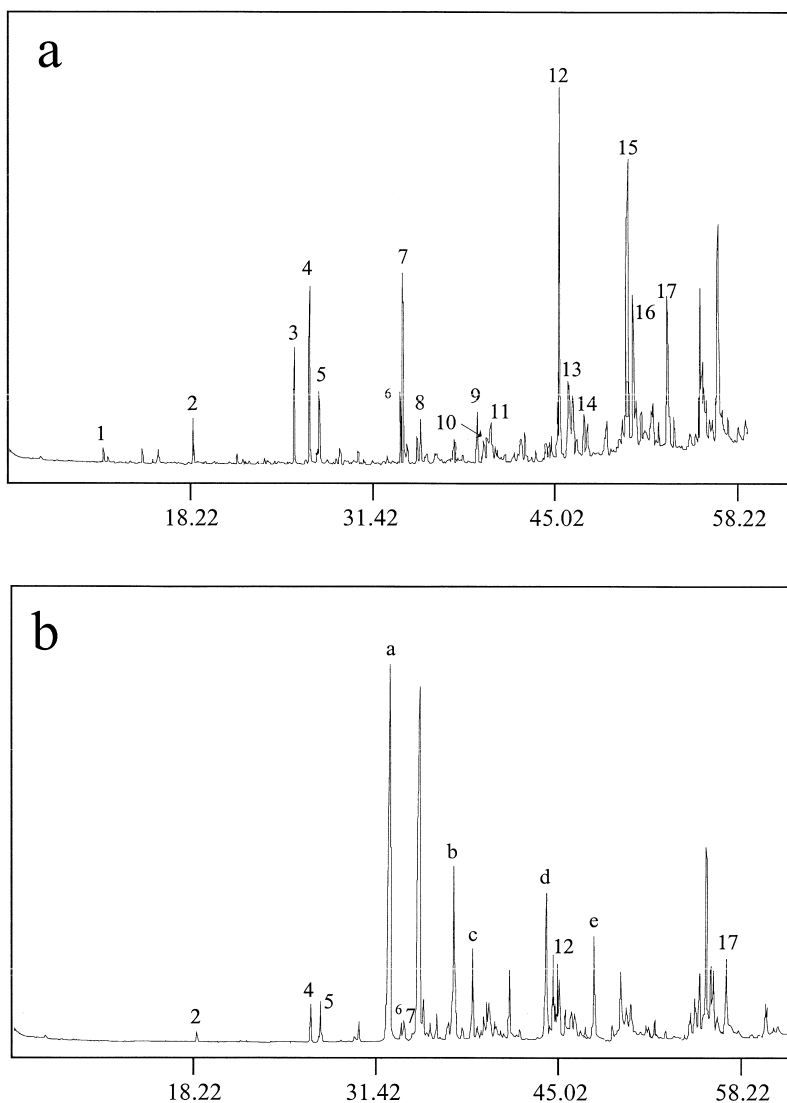
Fig. 6. A-3 fraction GC–MS chromatograms of (a) parent tar and (b) air-blown tar at 275°C for 20 h. Numbers refer to compounds listed in Table 3.

elute in the same short time even though their molecular mass is not excessively large, e.g., fullerenes [18]. In this way, SEC of air-blown products could be useful, at least for determining the extent of the air-blowing reactions.

Products from the air-blowing of parent tar and pitch, obtained under several experimental conditions (Table 1), as well as those obtained by air-blowing and sulfur reaction of AO, were studied by SEC in order to find differences in their SEC chromato-

grams, which could be attributed to differences in chemical composition and structure.

Air-blowing brings about the formation of insoluble material in NMP (Table 1) in amounts which increase with the severity of the treatment. This non-chromatographable material is obviously composed of the largest and most highly polar compounds present in the reaction products. In spite of this, SEC chromatograms of the air-blown products show a significantly higher amount of excluded
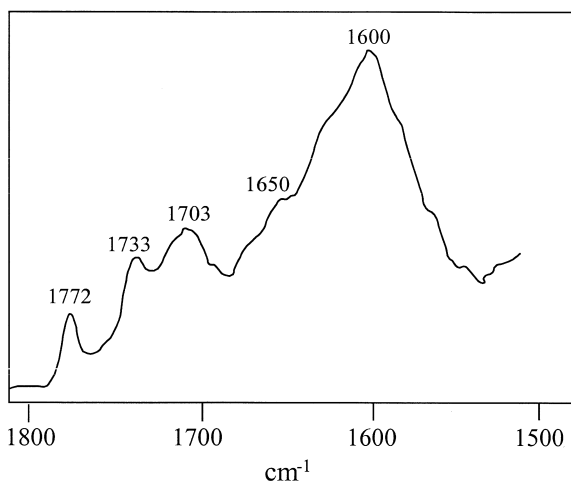
could be made up of compounds of an intermediate molecular mass. On the other hand, the elemental analysis reveals that air-blowing of the parent tar does not produce any significant increase in oxygen content, which rules out the possibility that highly polar oxygen compounds could be the main constituents of the excluded material.

When AO and its air-blown derivatives were analyzed by SEC, similar results were obtained. Fig. 9 shows that the formation of the excluded material is directly related to the air-blowing temperature. Although in the air-blowing of AO, a slight increase in oxygen content is produced [19], this increase is similar for all the chromatographed products. The increase in the P_{ex}/P_{se} ratio, therefore, is not due to highly polar oxygen compounds.

In order to obtain a deeper knowledge of the nature of the excluded material, the parent tar and its air-blown products, were fractionated by solvent extraction with n-hexane, toluene, chloroform and THF. The extracts were analyzed by SEC. Fig. 10 shows the chromatograms of the parent tar fractions (a) and the air-blown tar fractions (b). The only significant difference between the SEC chromatograms of the respective fractions is the shift to
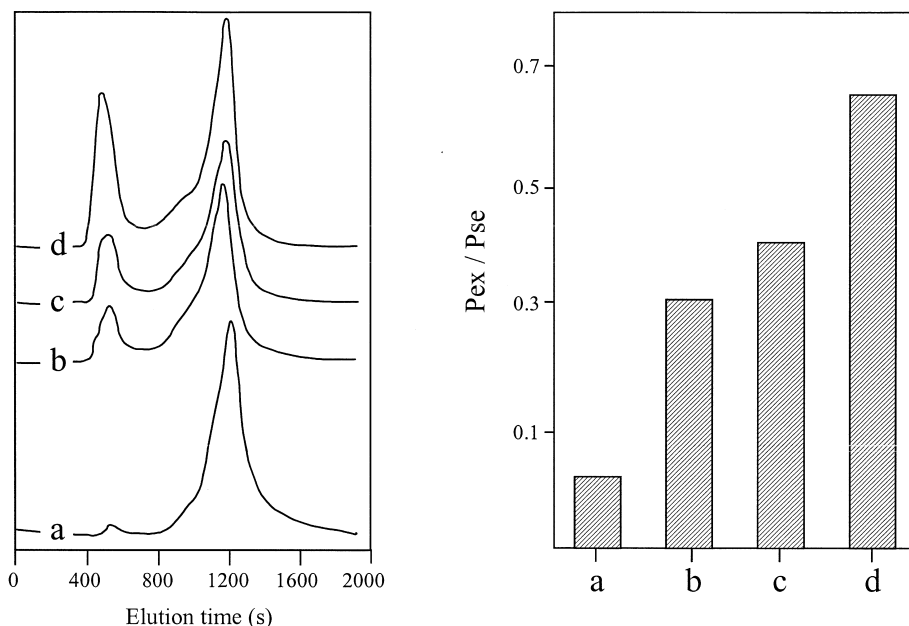

Fig. 7. FT-IR spectrum between 1600–1800 cm^{-1} of air-blown anthracene oil.

material than in the parent tar (Fig. 8). Furthermore, the ratio between the peak heights of the excluded (P_{ex}) and the separated (P_{se}) material increases with the severity of air-blowing (Fig. 8).

These results suggest that the excluded material

Fig. 8. SEC chromatograms of (a) tar, and air-blown tar at (b) 300°C/8 h, (c) 300°C/10 h and (d) 275°C/20 h, and P_{ex}/P_{se} ratios.
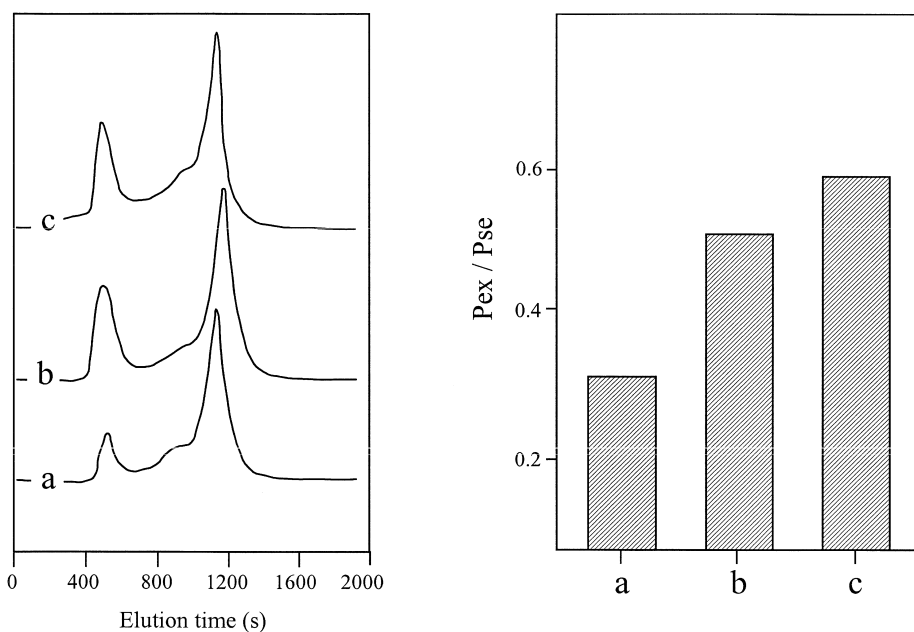
Fig. 9. SEC chromatograms of air-blown anthracene oil at (a) 250°C/15 h, (b) 275°C/15 h and (c) 300°C/15 h, and P_{ex}/P_{se} ratios.

shorter time observed in peaks corresponding to the retained material. This is due to the increase in the molecular mass of the fractions as the solvent

strength increases. The excluded material formed during the air-blowing of the parent tar (Fig. 8), therefore, is not soluble in the solvents used. So
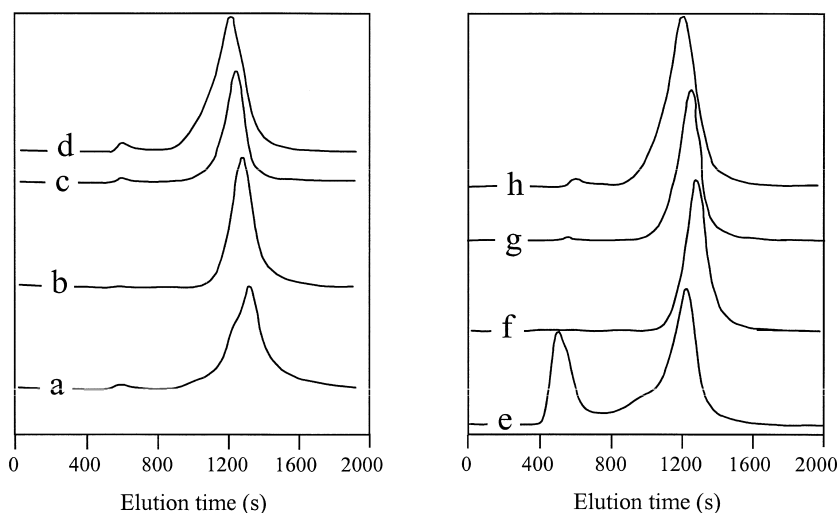

Fig. 10. SEC chromatograms of (a) tar, (b) A-1, (c) A-2 and (d) A-3 tar fractions; and (e) air-blown tar at 275°C/20 h, (f) A-1, (g) A-2 and (h) A-3 air-blown tar fractions.

highly polar oxygen compounds of low molecular mass found in the A-3 air-blown tar fraction, which is soluble in chloroform, do not belong to the excluded material. Again, it seems that the excluded material is made up of high-molecular-mass compounds or molecules with a non-planar structure instead of highly polar compounds.

To discriminate between the two possibilities, pitches obtained by air-blowing and by thermal treatment of a commercial pitch (Table 1) were also analyzed by SEC and the results shown in Fig. 11. For the air-blown pitches, the excluded material increases with the severity (time) of the treatment, as observed previously for the AO and for the parent tar. For pitches obtained by thermal treatment, the excluded material seems to decrease in spite of the increase in the conventional parameters (Table 1) and the presence of mesophase (10, 25 and 37%, v/v), which ensure the presence of planar compounds with high molecular mass. The small shift of the peak corresponding to the retained material to a shorter time is now due to the progressive loss of light components during air-blowing or thermal treatment.

These results suggest that the excluded material formed by the air-blowing of AO and tar is mainly composed of cross-linked molecules generated by the condensation of oxi and peroxi radicals of the aromatic constituent of the mixtures.

4. Conclusions

Chromatography and related techniques used in this work are shown to be suitable techniques for studying complex mixtures, such as coal-derived products, from the standpoint of the reactivity of their components and mechanisms involved in their transformation into new pitches for special uses.

GC–MS and probe MS were successfully used to determine the reactivity and condensation mechanism of the different anthracene oil components during air-blowing and thermal treatment with sulfur. Reaction with sulfur, however, took place more rapidly than with air. In both treatments, compounds containing aliphatic hydrogen were more reactive than those compounds that did not contain aliphatic hydrogen. The condensation mechanisms were also different depending on the structure of the compounds. While fluorene produced oligomers, phenanthrene mainly gave thiophenic compounds.

By means of the sequential fractionation of tar and its air-blown products, and further analysis of the fractions by GC–MS and GC–AED, it was possible
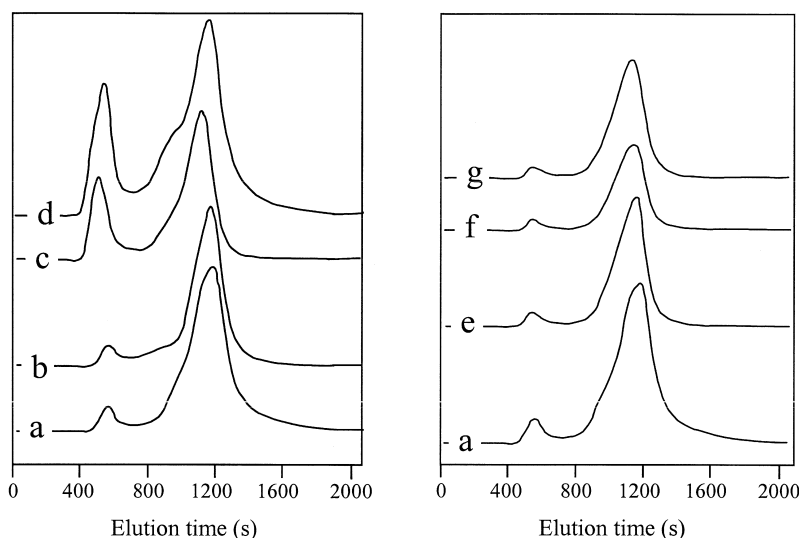

Fig. 11. SEC chromatograms of (a) pitch, air-blown pitch at (b) 275°C/10 h, (c) 275°C/18 h, (d) 275°C/25 h, and thermally treated pitch at 430°C for (e) 2 h, (f) 3 h and (g) 4 h.

to identify different carbonylic compounds. The presence of these functionalities suggested that air-blowing caused condensation reactions, which led not only to large molecules but also to the formation of carbonyl-containing molecules. However, the influence of the large molecules was much greater than that of the carbonyl groups.

The monitoring of anthracene oil, tar and pitch air-blowing by SEC, using NMP at 80°C as eluent, showed that the ratio between excluded and separated material increased with air-blowing severity, which supports the view that air-blowing caused condensation reactions, thereby producing large molecules. A comparison of the size-exclusion chromatograms of both, air-blown and thermally treated pitches, indicates that the excluded material generated during air-blowing is mainly composed of cross-linked molecules (oligomers).

Acknowledgements

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