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Journal of Chromatography A, 778 (1997) 403–413

JOURNAL OF
CHROMATOGRAPHY A

Characterization of coal-derived pitches as precursors for advanced carbon materials by chromatographic and related techniques

J. Machnikowski^{a,*}, H. Machnikowska^a, M.A. Díez^b, R. Alvarez^b, J. Bermejo^b

^a*Institute of Chemistry and Technology of Petroleum and Coal, Technical University of Wrocław, Gdanska 7/9, 50-344 Wrocław, Poland*

^b*Instituto Nacional del Carbón (INCAR), C.S.I.C., Apartado 73, 33080 Oviedo, Spain*

Abstract

Most applications of pitches involve a thermal treatment with formation of an intermediate liquid crystal phase (mesophase). The nature of the raw material is a crucial factor in the formation, growth and development of mesophase spheres. Hence, better understanding of the pitch constitution is of primary importance for both determining the suitability of a given pitch for a specific application and improving the carbonization behaviour. Differences in chemical composition of two selected pitches derived from coal (coal-tar and coal-hydrogenation pitches) have been evaluated by gas chromatography and probe-mass spectrometry of the extrography fractions. Coal hydrogenation pitch is constituted by a higher amount of neutral polycyclic aromatic hydrocarbons with lower molecular mass and polynuclear aromatic compounds of higher polarity than the coal-tar pitch. These compositional differences can explain the lower residue yield, the higher mesophase formation and the polydispersive size of mesophase spheres as compared to the coal-tar pitch. © 1997 Elsevier Science B.V.

Keywords: Coal; Tars; Extrography; Polynuclear aromatic hydrocarbons

1. Introduction

Pitches from coal-tars produced in high-temperature coke ovens and from coal hydrogenation products are very complex materials consisting of a variety of compounds with different functionality and a wide molecular mass distribution. The more volatile and soluble fractions separated from pitches constitute substituted and unsubstituted aromatic hydrocarbons ranging from one to eight rings, partially hydrogenated aromatics and polar compounds containing oxygen, nitrogen and sulphur [1,2]. The difficulty in pitch characterization due to its complexity can be reduced by an initial fractionation of the different types of compounds. Among all the various techniques which have been used, extro-

graphy has been successfully applied to the fractionation of different materials from coal and petroleum such as coal liquids, coal-tar pitches and the parent tars [3–13]. Extrography is a technique based on a combination of chromatographic and extraction separation. In general, it separates the components of a pitch in fractions that predominantly differ with regard to functionality (polarity). Chromatographic and spectroscopic techniques are generally associated with extrography for the elucidation of the molecular structures in the isolated fractions [8–12].

The early stage of the transformation of coal-tar pitches and coal-liquefaction products into anisotropic coke is the formation of anisotropic lamellar nematic liquid crystals (carbonaceous mesophase) in the isotropic fluid matrix at a temperature between 350 and 450°C. This mesophase can be seen under the polarized light optical microscope as anisotropic

*Corresponding author.

spheres from 1 to 100 μm in diameter. The size developed by these mesophase spheres depends upon the chemical and physical properties of the material being carbonized. The progressive growth and coalescence of the spheres produces an ordered anisotropic structure in semicoke and, finally, in coke [14]. The mesophase spheres isolated from the matrix based on their lower solubility have been named mesocarbon microbeads (MCMBs) [15]. The interest in MCMBs without any adhered particles on the surface of the beads results from the practical use of the material for production of high strength carbon artefacts, adsorbent carbons, ion-exchange material and column packing materials for high-performance liquid chromatography (HPLC) [15,16]. The main requirements for MCMBs as chromatographic fillers are a suitable average size and a narrow size distribution. To achieve these, a close control of chemical composition of pitches is needed since it influences the thermal behaviour.

Direct hydrogenation of coal can be considered as an alternative source of pitch-like material suitable for production of MCMBs as chromatographic fillers. Coal-hydrogenation pitch differs from QI-free coal-tar pitch in carbonization behaviour including kinetics of mesophase formation and average developed size of mesophase spheres [17,18].

The purpose of this work is to evaluate differences in chemical nature between pitches derived from coal tar and coal hydrogenation products which can be relevant to the production and properties of MCMBs by means of chromatographic and related techniques, applied to the extrography fractions.

2. Experimental

Two pitches were subjected to extrographic separation, one is derived from commercial coke oven tar (CTP95) produced at high carbonization temperature and the other from the product of coal hydrogenation performed in a continuous bench scale unit at 455°C under 20 MPa hydrogen pressure (CHP98). Both pitches with a similar Kramer–Sarnow softening point (95°C for CTP95 and 98°C for CHP98) were obtained on a laboratory distillation process under reduced pressure. The main characteristics of the pitches are given in Table 1. The pitches were

Table 1
Main characteristics of the pitches

	CTP95	CHP98
Ash (% w/w, db)	0.1	<0.1
Coking value (% w/w)	44.0	39.1
QI (% w/w)	5.9	0.1
TI (% w/w)	32.6	31.6
C/H ratio ^a	1.78	1.41
N (% w/w, db)	0.99	1.42
S (% w/w, db)	0.64	0.54
O (% w/w, db)	1.03	2.79
<i>FTIR indices</i> ^b		
I_{Ar}	0.87	0.52
I_C	0.32	0.48
¹ H NMR data ^c		
H_{Ar}	86.6	60.6
H_F	2.9	3.2
H_N	0.3	6.7
H_m	9.8	17.8
$H_{\beta+\gamma}$	0.4	11.7

^a Carbon:hydrogen atomic ratio from elemental analysis.

^b Aromatic index defined as: $I_{Ar} = \text{Area } 900\text{--}700 / (\text{Area } 900\text{--}700 + \text{Area } 2980\text{--}2800)$; Condensation index, $I_C = \text{Area } 1600 / \text{Area } 900\text{--}700$.

^c H_{Ar} : aromatic hydrogen (9–6 ppm); H_F : aliphatic hydrogens in methylene groups to α to two aromatic rings —fluorene type— (4.5–3.3 ppm); H_m : aliphatic hydrogens in methyl or methylene groups in α -position to an aromatic ring (3.3–2.0 ppm); H_N : naphthenic hydrogen (2.0–1.4 ppm); $H_{\beta+\gamma}$: aliphatic hydrogens in methyl or methylene groups in β - and γ -position to an aromatic ring (1.4–1.0 and 1.0–0.5 ppm, respectively).

carbonized isothermally in a conventional vertical retort at 450°C with soaking time from 15 to 60 min. The residues produced at several soaking times were analyzed by optical microscopy using polarized light in conjunction with a half-wave retarder plate in order to quantify the total mesophase content, the proportion of mesophase spheres as well as the size distribution of mesophase spheres.

Pitches were fractionated by extrography (sample:gel ratio of 1:10) into six fractions, using a sequence of six solvents of increasing polarity [6,7,11–13]. Briefly, 4 g of each pitch (<200 μm in particle size), solubilized in dichloromethane, were mixed with 40 g of silica gel which was previously activated by heating at 120°C and its activity adjusted by adding an appropriate amount of water. After removing the solvent in a rotary evaporator, the residue was dried under nitrogen and placed in a glass column. At the bottom of the column, 20 g of

unloaded silica gel was also placed to avoid overlapping of fractions. The separation was performed into six fractions using the following sequence of solvents: F1 eluted with *n*-hexane (150 ml); F2 with *n*-hexane–benzene (64:36, v/v; 220 ml); F3 with chloroform (225 ml); F4 with chloroform–dimethyl ether (95:5, v/v; 300 ml); F5 with chloroform–ethanol (93:7, v/v; 325 ml) and F6 with pyridine (325 ml). An additional fraction (F7) was obtained by soxhlet extraction of the material remaining on the silica gel with 300 ml of pyridine. Further experimental details, efficiency and reproducibility of this method were described elsewhere [6,7,11–13]. All the resulting fractions were characterized by Fourier transform infrared (FTIR) spectroscopy and vapour pressure osmometry. The fractions F2, F3 and F4 were also analysed by GC–flame ionization detection (FID), GC–MS and probe–MS.

GC analyses were carried out with a Perkin–Elmer 8320 gas chromatograph equipped with a FID system. A fused-silica capillary column (25 m×0.25 mm) loaded with chemically bonded cross linked methyl 50% phenyl silicone, OV-17, was used with temperature programmed from 50 to 270°C at 4°C/min and H₂ as carrier gas (flow rate, 1.5 ml min⁻¹); splitter ratio, 1:50; injector and detector temperature 275°C. Identification of major components of fractions was carried out by comparing retention data of available standards, data from the literature in GC–FID [19–24] and acquired mass spectra in GC–MS analysis with the published spectra. From GC–FID analysis, the ratios of the peak areas of some major representative compounds were calculated [24]. For F4, probe–MS experiments were performed by direct injection in the spectrometer of the GC–MS Hewlett–Packard 5987A instrument. Experiments were carried out by sample heating up 260°C at 7 K/min in vacuum.

The number of average molecular masses of the fractions were determined by vapour pressure osmometry (VPO) in CHCl₃ at 40°C for fractions F1–F5 and in pyridine at 60°C for fractions F6 and F7. Measurements were carried out using four solutions with different concentrations for each sample with the results being extrapolated to infinite dilution.

FTIR spectra of pitches and their extrographic fractions were recorded on a Perkin–Elmer 1750

spectrometer attached to a Perkin–Elmer 7500 computer by the co-addition of 50 interferograms at a resolution of 4 cm⁻¹. The spectra of the different fractions were recorded on KBr pellets (1 mg per 100 mg KBr) in the case of original pitches and solid fractions (F3–F7) and on thin films between KBr windows in the case of fractions F2. All spectra were normalized to a sample mass of 1 mg prior to the determination of the band areas [25].

¹H NMR spectra of pitches were recorded at 80 MHz with a Tesla spectrometer. Tetramethylsilane (TMS), as an internal standard, and C₅H₅N as solvent were used [25].

3. Results and discussion

3.1. Pitch characterization

Table 1 summarizes the main characteristics of the pitches used. In the most general terms, atomic C/H ratio can be related to the degree of aromaticity of the pitches. Then, the lower C/H ratio of CHP98 and the greater content of heteroatoms (N, S and O) can be consistent with a lower aromatic and more polar nature of this pitch.

FTIR and ¹HNMR analysis showed structural differences between these pitches. CHP98 is characterized by a lower aromaticity and a higher condensation degree than CTP95. Furthermore, CHP98 contains long alkyl side-chains and hydroaromatic systems [25].

The two pitches differ in their carbonization behaviour evaluated by kinetics of transformation and development of the mesophase at 450°C and different soaking time (Table 2). CHP98 showed a lower residue yield and a higher carbonization rate

Table 2
Mesophase development on thermal treatment at 450°C

Pitch		Soaking time (min)		
		15	30	60
CTP95	Residue yield (% w/w)	n.d.	76.9	74.8
	Total mesophase (% v/v)	n.d.	34.1	52.8
	Mesophase spheres (% v/v)	n.d.	33.8	48.0
CHP98	Residue yield (% w/w)	66.5	62.1	58.8
	Total mesophase (% v/v)	18.8	39.0	80.0
	Mesophase spheres (% v/v)	18.8	27.5	10.2

which is reflected by the higher content of total mesophase in the residue (anisotropic carbon) and the lower percentage of mesophase spheres in the total mesophase content. It is noticed that CTP95 requires a longer soaking time to form the same amount of total mesophase (Table 2). Both pitches also differ in the size distribution of spheres. A characteristic of CTP95 is a narrow distribution of the diameter of mesophase spheres (Fig. 1). Units of diameter between 2.5 and 7.5 μm constitute about 80% of the total mesophase volume. On the contrary, mesophase produced on carbonization of CHP98 shows a polydisperse distribution of spherical unit size over the range up to 15 μm (Fig. 1). The different characteristics of the two pitches could be the key of the different behaviour during the early stages of the carbonization process for the mesophase formation. Indeed, these data clearly suggest that mesophase formation is deeply influenced by the chemical composition of the pitches. The scope of such influence requires a deep study on pitch composition that it can be assessed by the combination of several chromatographic techniques.

3.2. Extrographic separation and qualitative characterization of fractions

Fig. 2 displays the distribution of extrography fractions as weight percentages of the original pitch. The absence of compounds eluted with *n*-hexane as

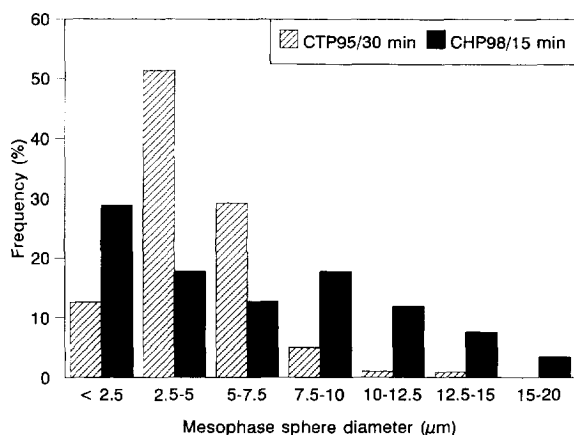


Fig. 1. Size distribution of mesophase spheres in the residues of pitches obtained at 450°C and a soaking time of 30 min for CTP95 and 15 min for CHP98.

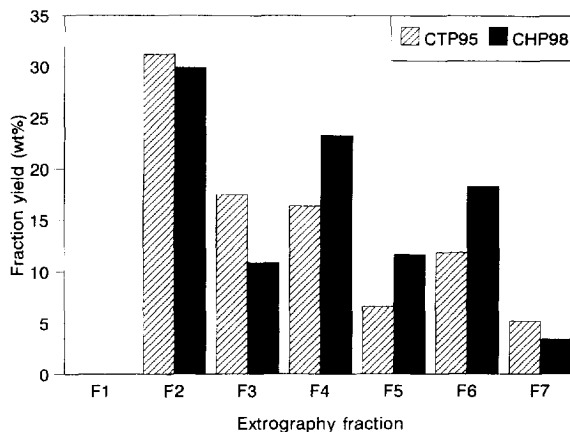


Fig. 2. Distribution of extrography fractions of the pitches.

F1 indicates that no aliphatic compounds are present in both pitches. This is in agreement with previous results of several coal-tar pitches produced from different coal-tars and production conditions [11–13]. The recovery of remaining fractions (F2–F7) was 88.8% (w/w) for CTP95 and 97.5% (w/w) for CHP98. Losses of material during fractionation by extrography are usually due to the quinoline insoluble material (QI) and highly polar compounds irreversibly adsorbed on the silica gel. CTP95 with the highest quinoline insoluble content (5.9% (w/w) QI vs. 0.1% (w/w) for CHP98) has the lowest recovery of fractions. The distribution for CTP95 is rather typical of binder pitches from coke oven tars [11–13]. The most significant difference between pitch distributions lies in the higher amount of F4, F5 and F6 for CHP98, which confirmed the greater presence of highly polar components in this pitch, according with analytical data (Table 1).

Molecular masses (M_r) of extrography fractions increase with the elution depth. All CHP98 fractions have higher M_r values than corresponding CTP95 constituents, except for F2 and F7. This is striking in particularly for F5 and F6 (Table 3). The surprisingly low M_r of F7 from CHP98, obtained by soxhlet

Table 3
Molecular mass of the extrography fractions

	F2	F3	F4	F5	F6	F7
CTP95	330	384	493	512	592	783
CHP98	315	435	542	725	967	380

extraction of extrography column residue, can be explained by the splitting of hydrogen bonds between the silica gel and highly polar components, by hot pyridine. The general higher M_r of CHP98 polar fractions reveals the higher molecular size of its components as well as their higher solubility in the extrographic eluents in agreement with the lower aromaticity and condensation degree of CHP98 [25].

The control of the efficiency of fractionations was carried out by FTIR spectroscopy of fractions. FTIR spectra of F2 confirmed the aromatic nature of this fraction with some contribution of aliphatic C–H bonds, higher in CHP98 and showing that it does not contain any compounds bearing NH or OH groups.

The presence in F3 of neutral polynuclear nitrogen compounds (PANCs) is confirmed by a band at 3420 cm^{-1} corresponding to N–H stretching vibrations. In spectra of fractions F4 and F5 from CTP95, the band at 1720 cm^{-1} can be assigned to the overlapping of the contribution of different types of carbonyl groups which can be associated with the band at 1280 cm^{-1} and then attributed to the ester group attached to a phenyl group whereas structures containing a more highly conjugated carbonyl group such as diaryl ketones or polycyclic quinones should be responsible for the band at 1650 cm^{-1} . In corresponding fractions from CHP98, the bands at 1650 and 1720 cm^{-1} occur only as a weaker shoulder on aromatic C–C band near 1600 cm^{-1} , instead a band at 3400 cm^{-1} due to phenolic O–H can be observed. This proves that different functionalities are present in F4 and F5 from CTP95 and CHP98.

FTIR spectra of F6 and F7 contain specific bands at 3400 , 1700 and 1280 cm^{-1} indicating the polar nature of these fractions. The first absorption band is stronger for fraction F7 from CHP98.

FTIR spectroscopy only gives an indication of the major structural types of molecules present in each fraction. To improve information about the composition of the more volatile fractions (F2–F4), GC–FID and GC–MS were used.

GC–FID and GC–MS analysis of the predominant fraction F2 reveal the presence of polynuclear aromatic *cata*- and *peri*-condensed hydrocarbons of M_r of about ≤ 300 normally present in coal-tar pitches and no components bearing N atoms as detected by FTIR. As an example, Fig. 3 shows the chromatograms of F2 for both pitches. The peak numbers

refer to the selected polynuclear aromatic hydrocarbons (PAHs) and PAH classes listed in Table 4. Although chromatograms show a similar profile of the major components of F2, differences in the relative abundance of some components can be easily observed. This is the case of the relative abundance of benzofluorenes (peaks 11 and 12), benz[*a*]anthracene and chrysene (peaks 19 and 20), benzofluoranthenes (peaks 23–25) and benzopyrenes (peaks 27 and 28). Compounds bearing one S atom in the structure, i.e. phenanthro[4,5-*bcd*]thiophene (peak 7) and benzo[*b*]naphto[2,1-*d*]thiophene (peak 16) also eluted in this fraction.

The volatile fraction of the extrography fraction F3 from both pitches (Fig. 4) contains as major components: carbazole (peak 1), benzocarbazoles (peaks 6–8) and methyl derivatives (peaks referred to as 2 and 9). The peaks with retention time above 60 min corresponds to dibenzocarbazoles with M_r of 267 and PAHs with $M_r \geq 276$ daltons, which are also present in minor amounts (Table 5). Phenantro[*bcd*]pyrrole and benzo derivatives can be also identified (peaks 3 and 10–11 in Fig. 4).

Earlier work, using probe–MS, revealed the presence in F3 and F4 from coal-tar pitches of a number of PAHs with molecular masses ranging from 302 to 450 [12]. The point emerging is that the separation based on the polarity of the different PAC classes by extrography is to some extent overlapped by a separation according to increasing molecular mass of PAHs [12]. Due to relatively high molecular mass of constituents present in F4 (Table 3), a very limited portion of this fraction F4 can be analyzed by GC–FID. The GC–FID analysis of F5–F7, of much higher M_r than the preceding fractions, cannot be performed due to the minimum volatilization of these samples.

In contrast to the two above fractions (F2 and F3), the chromatograms of the F4 differ significantly depending on pitch origin. Basic PANCs such as benzoacridine and azaderivatives of $\text{C}_{20}\text{H}_{12}$ can only be identified in F4 from CTP95 by GC–FID. The low volatility of the samples make a precise identification of the possible compounds in these fractions very difficult. More informative are the experiments carried out by probe–MS by heating samples (F4) to 260°C at 7 K/min in vacuum. They have demonstrated the presence of two distinct mass spectral

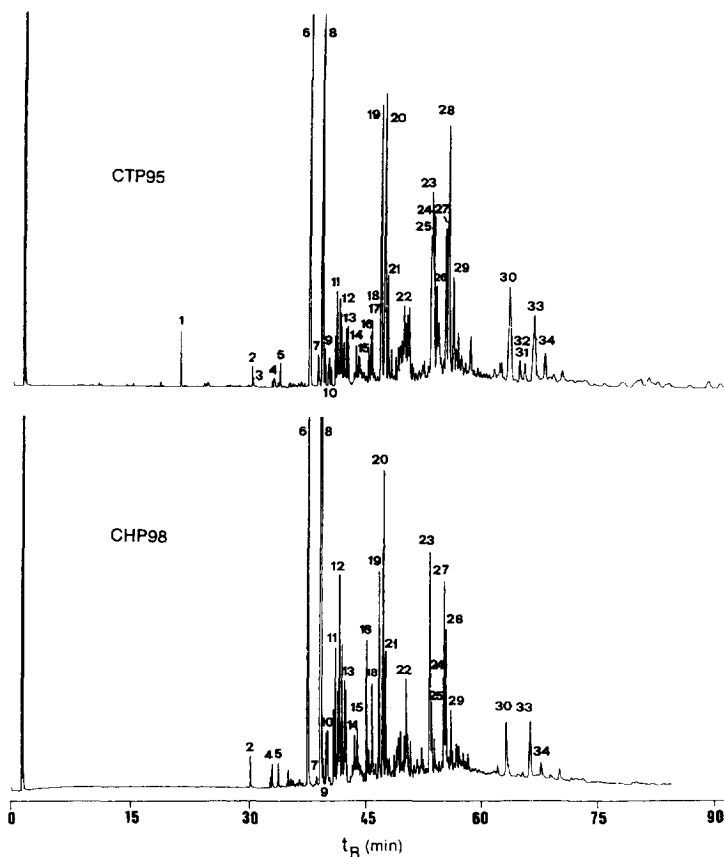


Fig. 3. GC-FID chromatograms of F2 from CTP95 and CHP98.

patterns corresponding to PANCs and PACs, not containing one N atom in the structure. Fig. 5 shows, as an example, a low-, intermediates- and high-temperature component spectra of F4 from CTP95. At low probe-temperature, the principal contributors of the spectrum (Fig. 5a) are odd-number signals at m/z 179, 229, 279 (acridine type or isomer and its benzo derivatives); m/z 203, 253, which can be associated to compounds such as azafluoranthenes/pyrene type and their benzo derivative and m/z 169 may be due to methylazaacenaphthene or cyclopentaquinoline type ($C_{12}H_{11}N$); m/z 193 (methylacridine type); m/z 217 (methyl derivatives of the parent compounds with m/z at 203). Raising the probe-temperature led to volatilization of more sample and increases in the intensity of signals corresponding to high- M_r compounds in the above series

(Fig. 5b Fig. 5c). This is the case of compounds with M_r of 253 which predominates in the spectrum in Fig. 5b. The mass spectral patterns with signals at m/z 203, 253, 303, 353 (azafluoranthene/pyrene type and benzo derivatives), m/z at 217 and 267 (methyl derivatives), m/z at 179, 229, 279, 329 (acridine type and its benzo derivatives) and m/z at 193, 243 (methyl derivatives) and m/z at 267, 277, 327, 377 (azaderivatives of $C_{21}H_{14}$, $C_{22}H_{12}$, $C_{26}H_{14}$, $C_{30}H_{18}$) can be identified. A series of unsubstituted PACs are formed in two ways from a given parent compound: (1) addition of four carbon and two hydrogen atoms to the parent compound to one end-ring in the system with the highest π -electron density (series differing in 50 mass units); and (2) addition of two carbon atoms to a three-sided bay region (series differing in 24 mass units) [26,27]. The series of compounds

Table 4
Major PAHs identified in extrography fraction F2 of the pitches

Peak no.	Compound	M_r
1	Acenaphthene	154
2	Phenanthrene	178
3	Anthracene	178
4	Methylphenanthrene, anthracene	192
5	4H-Cyclopenta[def]phenanthrene	190
6	Fluoranthene	202
7	Phenanthro[4,5- <i>bcd</i>]thiophene	208
8	Pyrene	202
9	2-phenylnaththalene	204
10	Benzonaphthofuranes or isomers ^a	218
11	Benzo[<i>a</i>]fluorene	216
12	Benzo[<i>b</i>]fluorene	216
13	C ₁₇ H ₁₂ , C ₁₇ H ₁₄	216, 218
14	C ₁₈ H ₁₄ , C ₁₈ H ₁₆ , C ₁₆ H ₁₀ S	230, 232, 234
15	C ₁₈ H ₁₄	230
16	Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene	234
17	Benzo[<i>ghi</i>]fluoranthene	226
18	Benzo[<i>b</i>]phenanthrene	226
19	Benz[<i>a</i>]anthracene	228
20	Chrysene	228
21	Triphenylene	228
22	C ₁₉ H ₁₂ , C ₁₉ H ₁₄ , C ₁₈ H ₁₀ S	240, 242, 258
23	Benzo[<i>j</i>]fluoranthene	252
24	Benzo[<i>b</i>]fluoranthene	252
25	Benzo[<i>k</i>]fluoranthene	252
26	Benzo[<i>a</i>]fluoranthene	252
27	Benzo[<i>e</i>]pyrene	252
28	Benzo[<i>a</i>]pyrene	252
29	Perylene	252
30	Indenopyrene or isomer	276
31	Dibenz[<i>a,h</i>]anthracene	278
32	Benzo[<i>b</i>]chrysene	278
33	Benzo[<i>ghi</i>]perylene	276
34	Anthanthrene	276

with M_r differing by 50 mass units indicate the linear or angular addition of an aromatic ring to the lower M_r nuclei (*ortho*-ring addition), while the series differing by 24 mass units can be interpreted as ring closure to form a more highly condensed ring system (*peri*-ring addition). The reaction pathway of the parent PANCs with m/z 179 and its benzo derivatives is presented in Fig. 6 to illustrate the two above reaction types. In the higher temperatures (Fig. 5c Fig. 5d) signals at m/z with even-numbers can be distinguished. They are probably due to PACs with M_r of 432, 400, 424, and 450. The two latter compounds can be derived from an *peri*- and *ortho*-

ring addition from m/z 400, respectively. The odd-mass peaks at m/z 149 and 151 with a relatively high intensity are not readily recognisable as members of the above series. As shown in Fig. 7, the spectra of the F4 from CHP98 reveals a completely different type of spectra with regards to the population of main mass signals. The mass signal of volatilized components were in the range of 113 to 500 daltons with low abundance of signals above m/z 300. In contrast to the above F4 of CTP95, it appears to contain the largest amount of the lighter PANCs in the series with m/z at 203, 253 and alkyl derivatives at 217 (or azafluorene), 231 and a series of even-mass signals tentatively assigned to high- M_r PACs (i.e. low abundance of m/z 400 -C₃₂H₁₆- and 500 -C₄₀H₂₀-). In addition, a series of even mass signals can be distinguished from the low-temperature spectra (Fig. 7a). The signals at m/z 189 and 230 could be due to alkylsubstituted tetrahydroquinoline and benzanthrone, respectively, or isomers. Carbonyl derivatives with M_r of 230 has been previously identified by GC-MS and GC-FID as components of coal-tars [19,28]. From GC-MS analysis of this F4, the presence of isomeric carbonyl compounds of M_r of 230 in CHP98 was confirmed. The MS spectra showed the characteristic fragments at M-28, M-29, (M-28/2) and (M-29/2). The latter fragmentation peaks being of greater intensity than M/2. Taking into account the high oxygen content of this pitch, the series at m/z 304, 328 and 354 could also be assigned to carbonyl compounds connected with its benzo derivatives formed by *peri*- and *ortho*-ring additions. The series at m/z 218, 268, 318, 368 can be due to benzonaphthofurans and their benzo derivatives. However, hydroxypyrene (M_r 218) or isomers and their benzo derivatives cannot be excluded. Further support for the presence of hydroxy aromatic components comes from the intensity of the broad band at 3400 cm⁻¹ in the FTIR spectrum of this fraction. However, the presence of such compound types needs more accurate identification. An additional series of even-numbers at m/z 364, 438, 466 and odd-numbers at m/z 401, 415, 455 are also present in the spectra of F4 of CHP98. The structural nature of the even-numbers should be associated with PAHs containing one or more heteroatoms in the system. Consequently, not only the amount of F4 of CHP98 is higher than the corresponding one of

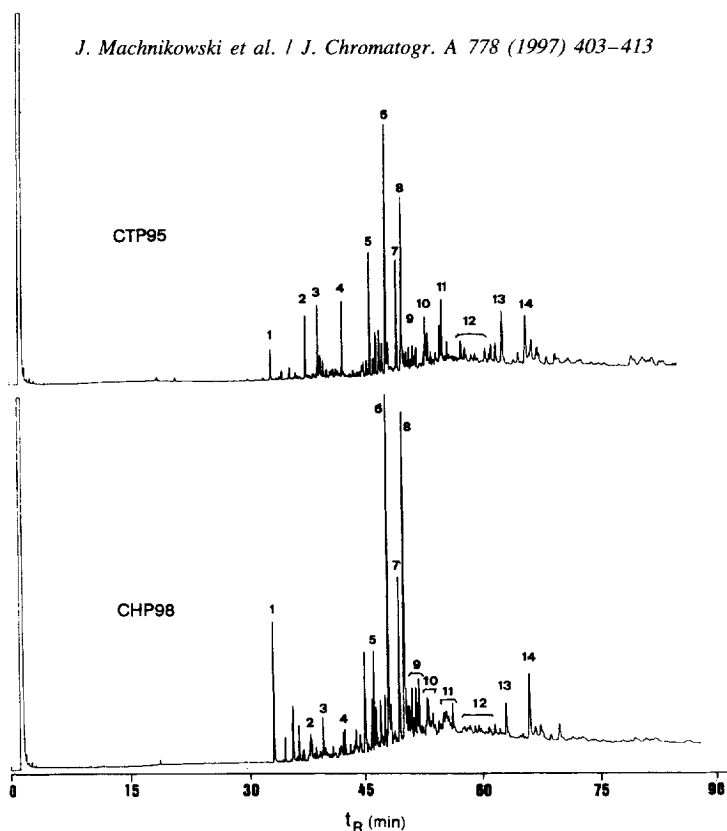


Fig. 4. GC-FID chromatograms of F3 from CTP95 and CHP98.

CTP95 (Fig. 2) but also it is mainly constituted by different kinds of compounds. Similar findings would be expected for fractions F5 and F6. The differences in composition are reflected in the forma-

tion of mesophase spheres as it will be discussed later.

3.3. Chemical composition and its influence on mesophase development

Differences in the reactivity of the diverse families of PAHs are well established as well as their different capacity to generate on pyrolysis graphitizable carbons [29,30]. As an example, *cata*-condensed PAHs are more reactive than *peri*-condensed PAHs, and alternant PAHs generate better graphitizable carbons than the non-alternant PAHs. Therefore, studies on the ratios of different classes of PAHs has been carried out to establish differences between composition of several coal-tar pitches [24,31] and the relationship with the parent tars [31], relevant to their thermal behaviour. Although no great influence of the lighter PAHs can be expected in the early stage of pitch carbonization due to their removal from the carbonizing system [32], the composition of pitch fractions and their volatile fractions has been

Table 5

Major components identified in extrography fraction F3 of the pitches

Peak no.	Compound	M_r
1	Carbazole	167
2	Methylcarbazoles	181
3	Methylcarbazoles	181
4	Phenanthro[<i>bcd</i>]pyrrole	191
5	Benzoacridine	229
6	Benzo[<i>a</i>]carbazole	217
7	Benzo[<i>c</i>]carbazole	217
8	Benzo[<i>b</i>]carbazole	217
9	Methylbenzocarbazoles	231
10	Benzophenanthro[<i>bcd</i>]pyrrole	241
11	Benzophenanthro[<i>bcd</i>]pyrrole	241
12	Dibenzocarbazoles	267
13	Indenopyrene	276
14	Benzo[<i>ghi</i>]perylene	276

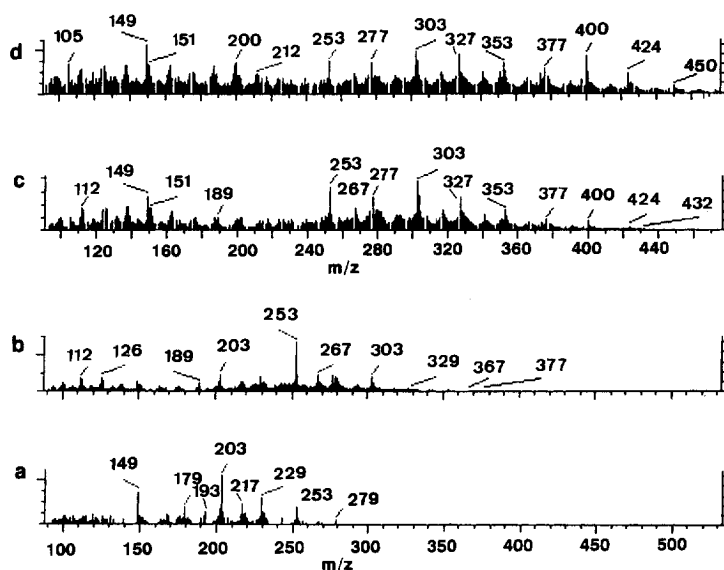


Fig. 5. Probe-MS spectra of F4 of CTP95 with increasing probe temperature: (a) low temperature, 57°C; (b and c) intermediate temperatures, 167 and 225°C; and (d) high temperature, 260°C.

related to the bulk properties and also to their behaviour during the thermal treatment [31]. This is because the information provided by the ratios, between different classes of chromatographable PAHs, can be taken as a feature of a pitch. Table 6 shows selected ratios of the major PAHs, individually or classified into different families, eluted in F2 and F3. In relation to the selected ratios for the assessment of the variation of condensation degree and the relative sizes of aromatic systems in these pitches, the pitch origin has a marked effect. All the ratios decrease for CHP98 indicating a higher proportion of relatively lighter aromatic systems (Table

6). Similar results were observed from the ratio of representative PANCs in F3. An insight into the presence of PAHs with lower M_r and smaller size of aromatic units could be also obtained by the ratios of the major alternant components with 3-, 4-, 5- and 6-aromatic rings to the total alternant PAHs. Clearly, CHP98 has a higher abundance of lighter PAHs with 3- and 4-aromatic rings than CTP95 in F2. On the other hand, the ratio of the total proportion of non-alternants (including all compounds which contain at least one five-membered ring with or without methylene groups) and alternants (containing only six-membered rings) and the ratio of some isomers of these PAHs classes were also calculated (Table 6). In general, alternant PAHs are the most abundant in both pitches (ratio < 1). CHP98 contains a higher proportion of alternant PAHs with relatively lower and higher M_r (202 and 276).

Pitch origin also influences the relative distribution of *cata*- and *peri*-condensed PAHs. Taking the representative compounds of *cata*- and *peri*-condensed PAHs with four rings (ratios showed in Table 6) an opposite trend can be observed. F2 of CHP98 has a higher relative abundance of benzofluorenes vs. fluoranthene, which is in agreement with the higher content of fluorene-type hydrogen evaluated by ^1H -

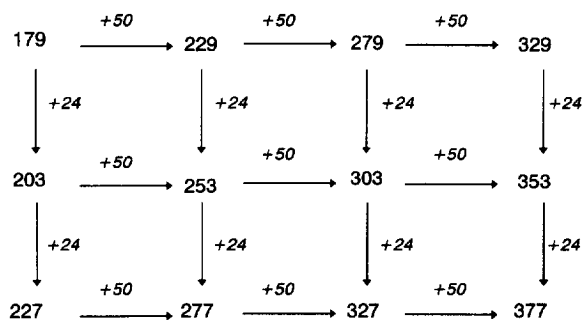


Fig. 6. Reaction pathway of PANCs in F4 of CTP95.

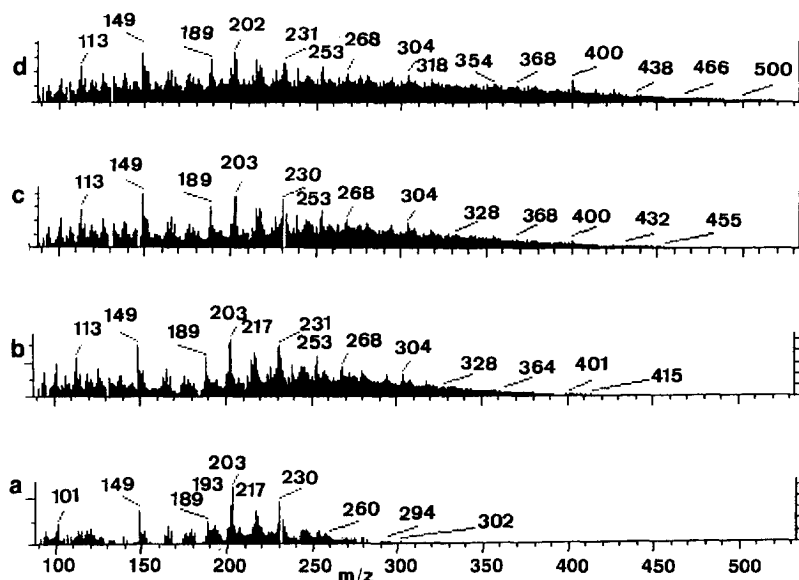


Fig. 7. Probe-MS spectra of F4 of CHP98 with increasing probe temperature: (a) low temperature, 69°C; (b and c) intermediate temperatures, 169 and 211°C; and (d) high temperature, 260°C.

NMR [25], and a higher proportion of *peri*-condensed PAHs of low M_r .

Coal hydrogenation pitch (CHP98) is characterized by a lower residue yield and a higher mesophase

formation rate as compared to CTP95 (Table 2). These characteristics are in agreement with the composition data revealed by GC-FID and GC-MS of the extrography fractions. The lower residue yield

Table 6

Ratios of different PAHs identified in the extrography fractions F2 and F3 of pitches

Ratio	CTP95	CHP98
<i>Condensation degree and size aromatic system ratios</i>		
Σ Benzopyrenes:pyrene	1.37	0.94
Σ Benzofluoranthenes:fluoranthene	1.78	1.06
Benzo[ghi]perylene:perylene	1.43	1.17
$[3\text{-aromatic rings}/\Sigma(3\text{- to }6\text{-aromatic rings})] \cdot 100^a$	0.72	0.98
4-aromatic rings/ $\Sigma(3\text{- to }6\text{-aromatic rings})^a$	0.49	0.64
5-aromatic rings/ $\Sigma(3\text{- to }6\text{-aromatic rings})^a$	0.38	0.20
6-aromatic rings/ $\Sigma(3\text{- to }6\text{-aromatic rings})^a$	0.13	0.14
Σ Benzocarbazoles:carbazole	15.29	9.82
<i>Non-alternant PAHs:alternant PAHs</i>		
Fluoranthene:pyrene	0.83	0.48
Σ Benzofluoranthenes: Σ benzopyrenes	1.08	1.83
Σ Benzofluoranthenes:(Σ benzopyrenes + perylene)	0.88	1.15
Indenopyrene:(benzo[ghi]perylene + anthanthrene)	0.91	0.73
Total non-alternant PAH:total alternant PAH	0.61	0.56
<i>cata-Condensed:peri-condensed ratios</i>		
Σ Benzofluorenes:fluoranthene	0.35	0.53
(Benz[a]anthracene + chrysene + triphenylene):pyrene	1.61	0.69

^a The ratios were calculated taking into account the major alternant PAHs.

of CHP98 is a consequence of its higher content in volatile components. The higher mesophase formation rate and sphere size of this pitch is due to the higher volatile release during carbonization and the higher chemical and thermal reactivity of its functionalized components (F4 and F5). Both effects contribute to a faster increase of molecular mass of the system during the carbonization.

4. Conclusions

GC and GC–MS of the extrography fractions provide detailed information on pitch composition in relation to the size, structure and functionality of pitch components, which is relevant to the initiation, growth and development of mesophase and, consequently, to the properties and applications of the different kinds of derived carbon materials.

Acknowledgments

The authors thank the State Committee for Scientific Research (Poland), the Spanish Culture and Education Minister and the Consejo Superior de Investigaciones Científicas -CSIC- (Spain) for the financial support of the Joint Research Project and to Dr. P. Bernad from The University of Oviedo (Spain) for GC–MS and probe-MS experiments.

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