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Chromatographic evaluation of some selected polycyclic aromatic hydrocarbons of coal tars produced under different coking conditions and pitches derived from them

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Abstract

The volatile fractions of carbon disulfide extracts in tars and pitches have been studied by gas chromatography (GC), using the stationary phase OV-1701. Major polycyclic aromatic hydrocarbons (PAHs) in the fractions were selected as a basis for assessment of differences in the compositions of tars associated with their production. Several coal tars produced by wet charging carbonization in industrial- and semi-industrial-scale ovens with different mean flue heating temperatures were analyzed. The effects of preheating coal at about 200°C prior to the coking process were also studied. From chromatographic data, ratios of different individual compounds or classes of compounds were calculated. They revealed that an increase in the carbonization temperature and coal preheating produced similar effects on tar and pitch composition, leading to a reduction in methyl-substituted PAHs, non-alternant PAH systems and highly reactive compounds such as acenaphthylene. A higher proportion of *peri*-condensed PAHs and PAHs with a higher degree of condensation were also observed. GC analysis provides an adequate method for estimating the degree of pyrolysis of tars in coke ovens and their thermal stability in pitch production.

1. Introduction

Coal tar, a by-product of the coking process, is an important raw material in the manufacture of pitch for industrial products such as electrodes and carbon fibres [1]. The more volatile and soluble fractions separated from coal tars and pitches are complex mixtures of organic compounds including substituted and unsubstituted aromatics, partially hydrogenated aromatics and polar compounds containing oxygen, nitrogen or sulfur atoms [2–4]. The distribution of such compounds in tars is to a large extent dependent on the temperature at which the production is carried out (mean flue temperature), the rank of

the coal and the charging method used. It is difficult to control tar quality since the operating procedure of the oven has to be designed to produce metallurgical cokes of optimum quality.

Useful information on the composition of coal tars and pitches has been obtained using a range of chromatographic and spectroscopic techniques [5–7]. Capillary gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) are two powerful techniques for studying the composition of the volatile fraction of these materials [8–12]. The identity of numerous polycyclic aromatic hydrocarbons (PAHs) in coal tar and pitch has been reported, but there is less information concerning the compositional changes induced by different operational conditions in the coking process and the influence of

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these on those properties of pitch that affect its behaviour in technical processes. It is generally accepted that the properties, reactivity and behaviour of tars and pitches are governed by their composition, which constitutes the key to effective utilization of these materials [13]. More detailed knowledge of their chemical composition is required, therefore, in particular to make it possible to predict their influence on the properties of the final products.

In the study described in this paper, a chromatographic evaluation of the main polyaromatic hydrocarbons (PAHs) present in the volatile fraction of the carbon disulfide extracts of eight coal tars and pitches derived from them was carried out. Four of the coal tars were obtained from the same industrial coal blend by conventional wet charging on an industrial and a semi-industrial scale so that the effects of the carbonization temperature of heating could be assessed, giving an indication of the coking rate (series M). In addition, a fifth tar produced from a preheated charge of the same blend was included so that the effects of preheating at about 220°C prior to carbonization in coke ovens could be studied. Finally, an additional series of tars was also examined (series C) with the aim of increasing understanding of the compositional changes induced by coal preheating. These tars were produced from a high-volatile bituminous coal at fixed temperatures using wet (W) and preheated (P) charges.

2. Experimental

Eight coal tars were produced at different carbonization temperatures (taken as the mean flue heating temperature) and using different charging methods (*wet and preheated*) in the industrial ovens of the Spanish Company, EN-SIDESA, (MT-AV and MT-GI) and an INCAR semi-industrial coke oven. Pitches with the same Kramer–Sarnow softening point (92°C) were obtained by laboratory-scale distillation. The INCAR experimental coking test plant, the Precarbon pilot plant (2 t/h) [14], and the main characteristics of these coal tars and the pitches

derived from them, have been described in detail elsewhere [15,16].

The GC study of the volatile fraction of coal tars was performed on carbon disulfide (Merck, Darmstadt, Germany) extracts, due to the high extractive ability of this solvent (83–93 wt.% and 66–80 wt.% of the whole coal tar and pitch, respectively). Extractions were carried out at room temperature in an ultrasonic bath (1 g of sample:20 ml of CS₂). After filtration, the solvent was removed from the filtrate in a rotary apparatus at reduced pressure and 30°C. The origin and the yield of CS₂ extracts from the coal tars and pitches are given in Table 1. In view of the great differences in solubility between PAHs, all samples to be analyzed were again dissolved in CS₂ (150 mg of sample:1 ml of solvent) and kept a few minutes in an ultrasonic bath in order to obtain total dissolution.

The chromatographic analyses were performed on a Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) and a Hewlett-Packard Vectra ES/12 computer to store the chromatograms. Separations were carried out on a fused-silica capillary column 25 m in length and with 0.22 mm I.D. (Quadrex, New Haven, CT, USA) coated with OV-1701 stationary phase (McReynolds polarity = 789). The temperature was programmed from 50 to 300°C at 4°C/min with hydrogen as the carrier gas at a flow-rate of 2 ml/min and a splitting ratio of 1:87. The detector and injector temperatures were 350 and 300°C, respectively, and the volume of sample injected was 1 µl.

Compounds were identified by comparison of retention time data with those for available PAH standards and data from previous studies [10–12], and confirmed by GC–MS. Relative response factors (RRFs) were determined for each compound in coal-tar CS₂ extracts on the basis of the response of fluoranthene (Fluka, Buchs, Switzerland), which served as an external standard. The absolute calibration method with a separate standard (reference compound fluoranthene) was used because in previous results obtained with internal and external standards no significant differences had been found [12].

Mixtures of different commercially available

PAH compounds with known concentrations were analyzed according to the method described previously [12] using the above-mentioned chromatographic conditions. The standard compounds, all of >98% purity, were obtained from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA), Merck and Janssen (Beerse, Belgium). The RRF for a compound i in relation to the reference compound, fluoranthene (F), was defined as $RRF_i = A_F M_i / M_F A_i$, where A and M are peak-area counts and weights of the compounds, respectively.

Taking into account the RRF values given in a previous study [12], the main PAHs of the volatile fractions of CS₂ extracts of coal tars and pitches were determined. The total percentage of chromatographed material in the CS₂ extracts (C.M.) was estimated by using fluoranthene as the separate standard compound and assuming response factors of unity for all components (Table 2). For calculation, C.M. was defined as

$C.M. = (C_F A_{Total} / A_F C_s) \cdot 100$, where C_F is the amount of fluoranthene injected per μl , A_F the peak-area counts of the fluoranthene peak, A_{Total} the total peak-area counts of the GC analysis of the sample and C_s the concentration of the sample analyzed.

The quantitative data presented in Tables 3 and 4 are the average of at least three chromatographic determinations. The average of the relative standard deviation (R.S.D.) for each compound in the volatile fractions of CS₂ extracts is also given. These values were calculated from the average of the R.S.D. corresponding to each tar or pitch.

3. Results and discussion

The origins of the tars and pitches and their extraction yields (solubilities) in CS₂ are shown in Table 1. The extraction yield in CS₂ is very

Table 1
Origins and extraction yields of coal tars and coal-tar pitches

Coal tar	Origin	Tar CS ₂ extract (wt. %)	Pitch yield (wt. %)	Resultant pitch	Pitch CS ₂ extract (wt. %)
MT-AV	Industrial oven No. 1 Wet coal blend charge 1230°C ^a	94.0	52.5	MP-AV	80.2
MT-GI	Industrial oven No. 2 Wet coal blend charge 1280°C ^a	92.7	48.5	MP-GI	74.2
MT-IL	Semi-industrial oven Wet coal blend charge 1180°C ^a	93.2	48.3	MP-IL	73.3
MT-IH	Semi-industrial oven Wet coal blend charge 1280°C ^a	93.3	48.7	MP-IH	74.2
MT-IP	Semi-industrial oven Coal blend charge preheated at 215°C 1200°C ^a	87.5	56.3	MP-IP	71.5
CT-W	Semi-industrial oven Wet coal charge 1250°C ^a	86.6	60.0	CP-W	70.9
CT-P1	Semi-industrial oven Coal charge preheated at 220°C 1210°C ^a	82.9	63.6	CP-P1	66.5
CT-P2	Semi-industrial oven Coal charge preheated at 220°C 1230°C ^a	85.9	60.6	CP-P2	72.2

^a Mean flue heating temperature.

similar for all tars obtained from a wet coal blend charge (series M: 93 wt.%), whereas that for tar produced from the preheated coal charge (MT-IP) is lower. This finding was also observed in tars produced from the preheated charge of a high-volatile bituminous coal (series C). Of the pitches, MP-AV shows the highest yield in CS₂, whereas CP-P1 shows the lowest extraction yield.

Table 2 shows the total percentage of the chromatographed material present in the CS₂ extracts of coal tars and pitches (C.M.), estimated by using response factors of unity for all compounds, the total peak area of the GC analysis and fluoranthene as the external standard. As can be seen, the amount of chromatographed material decreases with increasing carbonization temperature (taken as the mean flue heating temperature). Although both tars, MT-GI and MT-IH, were obtained from the same blend and at the same carbonization temperature, MT-GI shows a lower content of chromatographed material due to the influence of the size of the industrial oven on the temperature and residence time of the gas evolving in the process. Preheating of the charge produced a tar with a higher content of chromatographed material when a high-volatile bituminous coal was used. The tar which was obtained at the lowest carbonization temperature (CT-P1) and had the lowest yield in CS₂, contained, surprisingly, more chromatographed material. Lower extraction yield and more chromatographed material are also observed for the corresponding pitch (CP-P1). On the other hand, no significant differences can be observed for the pitches from semi-industrial tars. As expected, data corre-

sponding to derived pitches are always lower than those for parent tars; however, no relation between the extraction yield in CS₂ and the amount of chromatographed material could be found.

GC analysis reveals that chromatographic profiles for all the CS₂ extracts from tars and their derived pitches are qualitatively similar. In line with previous results [8,9], the tar fractions examined are composed mainly of polynuclear aromatic *cata*- and *peri*-condensed hydrocarbons with from two to six rings, acenaphthene and fluorene and their benzoderivatives, a small number of partially hydrogenated PAHs and benzoderivatives of quinoline, carbazole, thiophene and furan, and alkyl and phenyl derivatives of the above compounds. Fig. 1 shows an example of gas chromatograms of the CS₂ extracts of coal tars CT-W and CT-P2 and the corresponding pitches, CP-W and CP-P2. The peak numbers refer to the selected PAHs listed in Tables 3 and 4. The results reveal that no light aromatic hydrocarbons, from naphthalene to fluorene (peaks Nos. 1–7), are present in pitch extracts, except in the extract from pitch CP-W, in which some of the compounds thermally reactive in pyrolysis treatment, such as acenaphthylene and acephenanthrylene (peaks No. 6 and 16, respectively) [1,11,17], are present in very small amounts near to the experimental error.

Before considering the quantitative differences it is important to point out that the thermal reactivity of coal-tar and coal-tar-pitch components is the factor controlling coal-tar-pitch behaviour in the pyrolysis processes. Although it is difficult to establish a reactivity scale among the

Table 2
Percentage of the chromatographed material (C.M.) in the CS₂ extracts of tars and pitches

Coal tar	MT-AV	MT-GI	MT-IL	MT-IH	MT-IP	CT-W	CT-P1	CT-P2
C.M. (%)	68.9	64.6	74.9	68.7	72.0	60.9	84.7	68.4
Pitch	MP-AV	MP-GI	MP-IL	MP-IH	MP-IP	CP-W	CP-P1	CP-P2
C.M. (%)	42.1	45.9	52.1	52.2	53.7	48.2	61.9	45.1

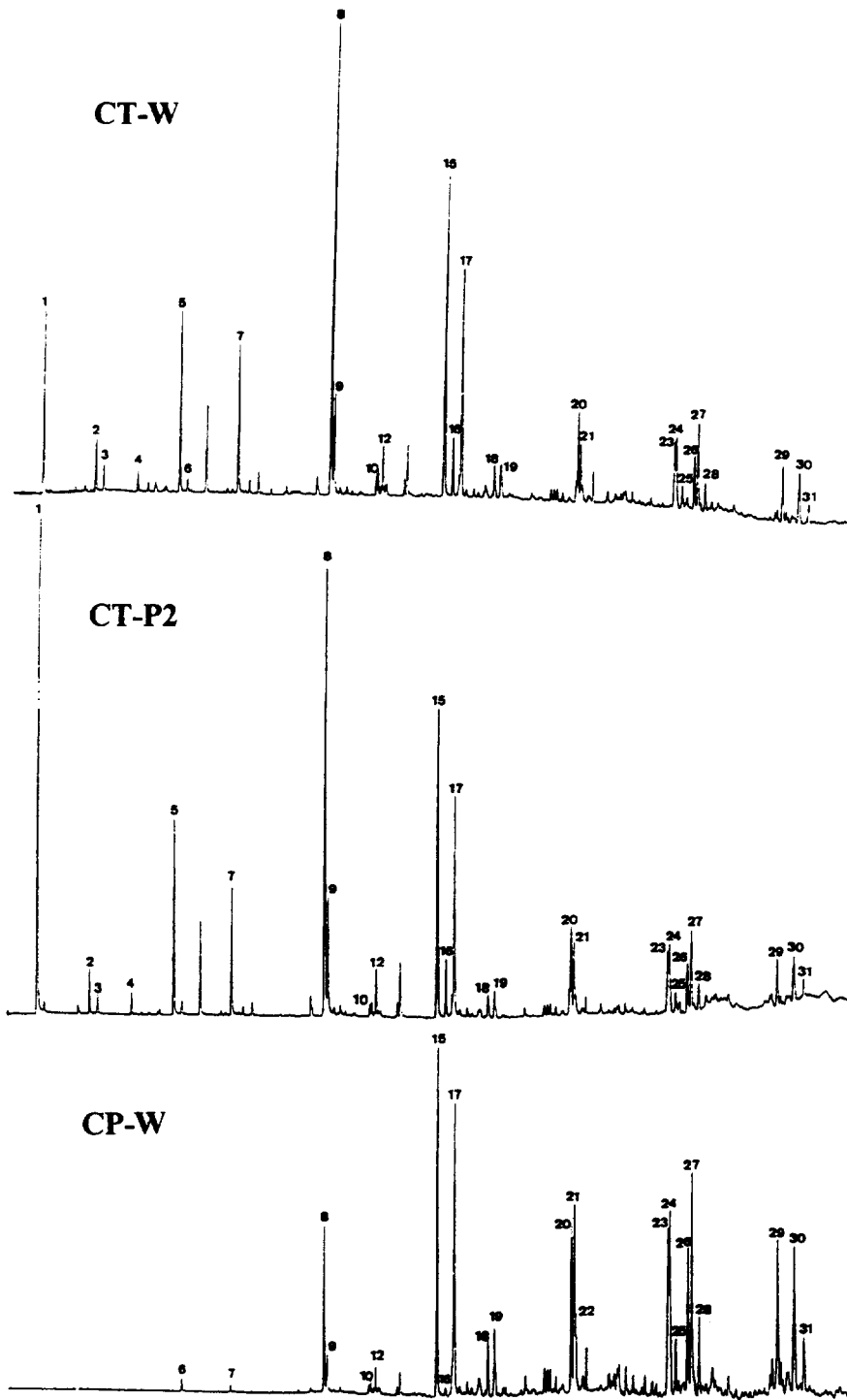


Fig. 1. (continued on p. 186)

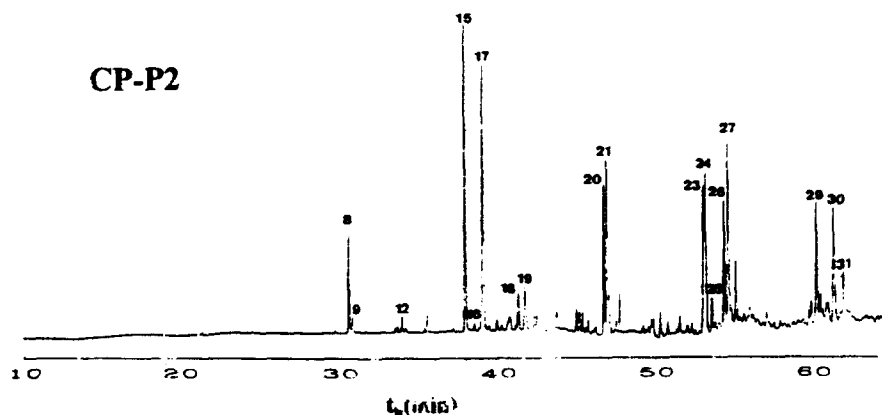
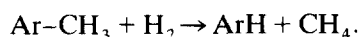


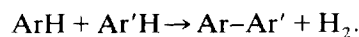
Fig. 1. Capillary gas chromatograms of the volatile fractions of CS₂ extracts of coal tars and their derived pitches on OV-1701 stationary phase. See Tables 3 and 4 for peak identification.

different constituents of these materials due to the number of reaction possibilities that exists for the pyrolysis of hydrocarbons and the interaction between components, some general trends can be observed [17]. On the basis of the percentage of carbon yield, experimental results from the pyrolysis of pure aromatic compounds at 400–500°C have shown that: (i) the alkyl-substituted PAHs are more reactive than the unsubstituted PAHs, the effect being more pronounced the greater the number and the length of the alkyl groups [17–19]; (ii) among the unsubstituted PAHs the most thermally reactive compounds to form polynuclear aromatics by chemical condensation are those having an anthracene configuration; and (iii) the highest reactivity is exhibited by aromatic-containing five-membered ring systems [17–19]. In the case of the latter group, the pyrolysis of acenaphthylene has generated great interest since acenaphthylene is an aromatic compound which produces extremely graphitizable carbon [17]. Further, this aromatic compound can be partially converted into the corresponding acenaphthene by hydrogen transfer during tar distillation at >360°C [1,17].

Although the overall process of pyrolysis is extremely complex, major reactions involved in the pyrolysis of aromatic hydrocarbons can be considered. Complex cracking reactions take place in the pyrolysis of the methyl aromatic hydrocarbons, which undergo a hydrodemethylation reaction of the type



This reaction is one of the most characteristic ones in the change from medium-temperature to high-temperature pyrolysis. Thus it is possible to define ratios of such compounds as an indication of the degree of cracking of a tar. At the same time, the aromatic hydrocarbons begin to condense with elimination of hydrogen to give higher-molecular-mass compounds:



Tables 3 and 4 show the results of quantification of the volatile fractions of CS₂ extracts of coal tars and pitches derived from them. The reproducibilities of the determinations, represented by the average R.S.D.s, are also included.

Although identical qualitative trends of PAHs among tar or pitch extracts can be observed, the relative concentrations of individual PAHs vary from tar to tar and from pitch to pitch, depending on the origin and on the conditions used for tar production. Thus, it can be seen that the proportions in tars of non-alternant PAHs (aromatic systems with at least one five-membered ring [4]) such as 4H-cyclopenta[def]phenanthrene, fluoranthene and its benzofluoranthene derivatives, acephenanthrylene and indenopyrene (peaks 12, 15, 23, 24, 25, 16 and 29) and alternant PAHs (aromatic systems with only six-membered rings) such as pyrene, benzo[a]anthracene, chrysene, triphenylene, ben-

Table 3
Relative yield in selected PAHs in the volatile fraction of CS₂ extracts of the tars studied

Peak No.	Compound	MT-AV	MT-GI	MT-IL	MT-IH	MT-IP	CT-W	CT-P1	CT-P2	R.S.D. (%)
1	Naphthalene	8.87	8.28	7.96	7.86	5.31	3.23	5.54	8.95	3.55
2	2-Methylnaphthalene	1.79	0.75	1.34	0.88	0.63	1.03	0.63	0.78	3.73
3	1-Methylnaphthalene	0.83	0.35	0.60	0.43	0.31	0.51	0.28	0.34	4.37
4	Diphenyl	0.38	0.11	0.39	0.01	0.30	0.41	0.35	0.39	3.59
5	Acenaphthylene	1.20	0.92	3.34	1.39	1.66	3.85	3.64	3.90	1.25
6	Acenaphthene	0.23	—	0.36	0.18	0.46	0.36	0.23	0.29	4.02
7	Fluorene	3.02	2.23	3.41	1.87	2.50	3.43	2.36	2.66	1.43
8	Phenanthrene	10.82	14.92	13.20	12.82	14.34	13.45	11.77	12.41	1.65
9	Anthracene	2.88	2.25	1.84	3.64	2.27	2.55	2.24	2.64	1.78
10	Methylphenanthrene, -anthracene	0.62	0.47	0.54	0.55	0.33	0.51	0.26	0.25	2.26
11	Methylphenanthrene, -anthracene	0.83	0.65	0.74	0.77	0.44	0.69	0.36	0.33	2.64
12	4H-cyclopenta[def]phenanthrene	1.23	1.68	1.41	1.54	1.23	1.28	1.01	1.04	2.17
13	Methylphenanthrene, -anthracene	0.37	0.24	0.29	0.29	0.19	0.31	0.15	—	1.50
14	Methylphenanthrene, -anthracene	0.32	0.24	0.25	0.28	0.16	0.31	0.13	—	3.07
15	Fluoranthene	8.71	13.49	9.93	12.30	11.77	10.69	9.17	10.38	1.64
16	Acphenanthrylene	0.29	0.33	1.46	1.51	0.97	1.74	1.52	1.67	3.02
17	Pyrene	5.62	9.94	6.06	7.53	7.78	7.43	6.20	7.15	1.53
18	Benzol[a]fluorene	1.63	1.46	1.49	2.01	1.12	1.47	0.84	0.99	2.37
19	Benzol[b]fluorene	2.41	2.16	2.00	2.78	1.45	1.89	1.11	1.38	2.28
20	Benzol[a]anthracene	3.34	4.14	4.09	5.18	4.10	3.42	3.23	3.66	2.46
21	Chrysene	2.95	3.07	2.57	4.85	3.70	2.02	2.48	2.72	3.96
22	Triphenylene	1.01	1.56	0.78	1.09	1.10	0.48	0.62	0.77	2.83
23	Benzol[j]fluoranthene	2.45	3.61	2.64	3.90	3.49	3.13	2.68	3.12	3.34
24	Benzol[k]fluoranthene	2.81	3.76	3.20	4.03	3.47	3.33	2.78	3.32	3.31
25	Benzol[l]fluoranthene	0.81	0.97	0.94	1.12	0.92	1.14	1.15	1.06	3.45
26	Benzol[m]pyrene	1.76	2.87	1.55	2.59	2.50	2.19	2.01	2.32	2.56
27	Benzol[n]pyrene	2.80	4.13	2.40	3.88	3.69	3.32	3.21	3.68	1.89
28	Perylene	0.85	1.31	0.92	1.23	1.32	1.23	0.95	1.13	3.77
29	Indenopyrene or isomer	2.10	3.00	1.67	2.56	2.91	2.73	2.06	2.44	3.84
30	Benzol[ghi]perylene	1.55	2.42	1.55	2.12	2.49	2.67	1.97	2.56	2.17
31	Anthanthrene	0.59	0.68	0.55	0.69	0.88	1.18	0.76	1.15	5.00

Table 4
Relative yield in selected PAHs in the volatile fraction of CS₂ extracts of the pitches studied

Peak No.	Compound	MP-AV	MP-GI	MP-IL	MP-IH	MP-IP	CP-W	CP-P1	CP-P2	R.S.D. (%)
6	Acenaphthene	—	—	—	—	—	0.23	—	—	4.17
8	Phenanthrene	1.64	0.70	0.49	1.10	2.12	3.51	3.58	2.41	5.59
9	Anthracene	0.33	0.21	0.17	0.18	0.43	0.84	0.64	0.40	4.91
10	Methylphenanthrene, -anthracene	0.17	—	—	—	—	0.19	0.15	—	3.52
11	Methylphenanthrene, -anthracene	0.26	—	—	—	—	0.27	—	—	4.18
12	4H-cyclopenta[def]phenanthrene	0.39	0.23	—	0.26	0.40	0.52	0.45	0.34	2.94
15	Fluoranthene	7.06	6.33	4.54	6.37	8.70	9.01	10.03	9.22	3.25
16	Accephenanthrylene	—	—	—	—	—	0.21	0.21	0.19	3.16
17	Pyrene	6.94	6.70	4.66	6.26	8.21	9.08	9.40	8.96	3.33
18	Benzo[a]fluorene	2.20	1.60	1.36	1.58	1.29	1.66	1.39	1.62	2.74
19	Benzo[b]fluorene	3.44	2.19	1.56	2.28	1.87	2.67	1.79	1.87	2.09
20	Benzo[a]anthracene	6.01	5.59	5.55	6.00	5.71	5.15	5.39	5.37	2.08
21	Chrysene	6.24	6.25	5.73	6.29	6.22	5.35	5.83	6.02	1.94
22	Triphenylene	2.18	1.91	1.51	1.92	2.14	2.14	1.58	1.34	2.49
23	Benzo[j]fluoranthene	6.93	8.41	8.22	8.35	7.79	6.49	6.77	7.48	2.26
24	Benzo[b]fluoranthene	6.86	7.86	7.58	7.65	6.87	6.57	6.78	6.77	2.60
25	Benzo[k]fluoranthene	1.64	1.71	2.15	1.94	1.53	1.83	1.48	1.44	3.73
26	Benzo[e]pyrene	4.70	6.30	7.66	5.84	6.06	4.81	5.13	5.84	2.40
27	Benzo[a]pyrene	7.13	8.98	9.05	9.38	8.90	7.50	7.77	8.42	1.44
28	Perylene	2.23	2.86	3.31	2.54	2.75	2.59	2.37	2.69	4.20
29	Indenopyrene or isomer	5.24	7.23	7.23	6.83	7.41	6.23	6.21	6.24	2.18
30	Benzo[ghi]perylene	4.77	6.92	5.80	6.00	6.63	6.81	6.18	6.70	2.47
31	Anthanthrene	1.56	2.56	2.16	2.66	2.39	2.19	2.35	2.58	3.92

zopyrene isomers, perylene, benzo[ghi]perylene and anthanthrene (peaks 17, 20, 21, 22, 26, 27, 28, 30 and 31) increase with increasing carbonization temperature.

In contrast, lighter PAHs such as diphenyl, acenaphthylene and fluorene (peaks 4, 5 and 7) and methylnaphthalenes (peaks 2 and 3) decrease with increasing carbonization temperature. This is also observed in the decrease in the total amount of low-boiling PAHs (naphthalene to fluorene), which represents 16–17% in MT-AV and MT-IL and about 12% in high-temperature tars, MT-GI and MT-IH. The same trend is observed when phenanthrene and anthracene are included.

The differences in tars produced using the same carbonization temperature (1280°C) but ovens of different dimensions (MT-GI, industrial oven and MT-IH, semi-industrial oven) are also worth mentioning. MT-GI contains higher amounts of individual *peri*-condensed PAHs (alternants and non-alternants) and lower amount of the more reactive compounds (peaks 2, 3, 5, 6, 10, 11 and 16). This can be explained by the higher residence time of the volatile aromatic hydrocarbons in the heated area of the larger (taller) coke oven, which favours dealkylation, recombination and condensation, resulting in high-molecular-mass aromatic compounds being able to escape as condensable tar from the coal.

The effect of carbonization temperature on the distribution of the heavier PAHs also becomes evident in a direct comparison of tars CT-P1 and CT-P2, which have been produced by preheating the coal charge at different carbonization temperatures (1210 and 1230°C). The findings for high carbonization temperatures indicate that major effects in the compositional nature of tars are greatly dependent on the secondary pyrolysis reactions as outlined above.

In general, the influence on tar composition of coal preheating prior to the carbonization process on tar composition is quite similar to that found for the effect of increasing carbonization temperature. This applies, for instance, to the proportions of the individual compounds mentioned above. Comparing MT-IL and MT-IP, which were obtained at a low temperature (1180

and 1200°C, respectively) and using wet (MT-IL) and preheated (MT-IP) charging, MT-IP contains a higher proportion of those relatively stable PAHs found to be sensitive to the carbonization temperature, and a lower proportion of thermally reactive compounds (peaks no. 2, 3, 5, 10, 12, 13, 14 and 16). The same trends are evident when CT-P1 and CT-P2, of which the charge had been preheated at 220°C, are compared with the CT-W produced using wet charging at a higher temperature.

The overall trends found for tars produced by the preheated charging can be explained by the duration of the residence of volatile compounds in the oven, as this both causes and affects secondary pyrolysis reactions. The preheated coal charge is more compact (higher bulk density) and the plastic layer is more viscous and more uniform [20] during the coking process. These factors might be expected to make it more difficult for the primary tars to escape. As a result the secondary pyrolysis reactions of dealkylation and condensation would take place, thus accounting for the higher aromaticity of the CS₂ extracts of these tars [21].

Chromatographic analysis not only assists in the determination of individual compounds in tar in relation to their degree of pyrolysis in coke ovens, but also allows the relations between the coking conditions and the different families of compounds to be established. Table 5 shows ratios of the proportions of some of the PAHs most sensitive to the degree of pyrolysis and thermal reactivity of tars, individually or classified into different PAH families. The carbonization temperature has a marked effect on the unsubstituted–substituted PAH ratios, especially in industrial coke ovens (Table 5). A reduction in the amount of substituted compounds, which are among the most thermally reactive, is also observed clearly for tars produced from a preheated charge, particularly in the phenanthrene– Σ methylphenanthrenes ratio.

It is generally accepted that tar is not totally inert during the heat treatment in pitch production due to the presence of certain types of compounds of high reactivity in hydrogen transfer reactions at temperatures above 360°C.

Table 5
Ratios of different PAHs identified in the volatile fractions of tars

Ratio	MT-AV	MT-GI	MT-IL	MT-IH	MT-IP	CT-W	CT-P1	CT-P2
<i>Substituted degree ratios</i>								
Naphthalene: Σ methylanthralenes	3.38	7.28	4.10	5.95	5.65	2.10	6.09	7.99
Phenanthrene: Σ methylphenanthrene	5.06	9.32	7.25	8.67	13.92	7.39	13.08	21.40
<i>Reactivity degree ratios</i>								
Acenaphthylene:acenaphthene	5.22	-	9.28	7.72	3.61	10.69	15.83	13.45
Acphenanthrylene:acenaphthene	0.24	0.36	0.44	1.09	0.58	0.45	0.42	0.43
(4H-cyclopenta[def]phenanthrene + acephenanthrylene):fluoranthene	0.17	0.15	0.29	0.25	0.19	0.28	0.28	0.26
Acenaphthylene:fluoranthene	0.14	0.07	0.34	0.11	0.14	0.36	0.40	0.37
Acphenanthrylene:benzo[b]fluoranthene	0.10	0.09	0.45	0.37	0.28	0.52	0.55	0.50
<i>Condensation degree and size aromatic system ratios</i>								
Benzo[a]fluorene:fluorene	0.54	0.65	0.44	1.07	0.45	0.43	0.36	0.37
Benzo[b]fluorene:fluorene	0.80	0.97	0.59	1.49	0.58	0.55	0.47	0.52
Fluoranthene:fluorene	2.88	6.05	2.91	6.58	4.71	3.12	3.89	3.90
4H-cyclopenta[def]phenanthrene:fluorene	0.41	0.75	0.41	0.82	0.49	0.37	0.43	0.39
Σ Benzopyrenes:pyrene	0.81	0.70	0.65	0.86	0.80	0.74	0.84	0.84
Indenopyrene:benzo[b]fluoranthene	0.75	0.80	0.52	0.63	0.84	0.82	0.74	0.74
Benzo[ghi]perylene:perylene	1.82	1.85	1.68	1.72	1.89	2.17	2.07	2.26
<i>Non-alternant PAHs:alternant PAHs</i>								
Σ Benzofluorenes:(benzo[a]anthracene + chrysene + triphenylene)	0.55	0.41	0.47	0.43	0.29	0.57	0.31	0.32
Fluoranthene:pyrene	1.56	1.36	1.64	1.63	1.51	1.44	1.48	1.45
Σ Benzofluoranthenes: Σ benzopyrenes	1.33	1.19	1.78	1.40	1.27	1.38	1.27	1.25
Σ Benzofluoranthenes:(Σ benzopyrenes + perylene)	1.12	1.00	1.39	1.17	1.05	1.13	1.07	1.05
Indenopyrene:(benzo[ghi]perylene + anthanthrene)	0.98	0.97	0.80	0.99	0.86	0.71	0.75	0.66
Total non-alternant PAH:total alternant PAH	0.62	0.60	0.73	0.66	0.64	0.80	0.69	0.65
<i>Cata-condensed;peri-condensed ratios</i>								
Σ Benzofluorenes:fluoranthene	0.46	0.27	0.35	0.39	0.22	0.31	0.21	0.23
(Benzo[a]anthracene + chrysene + triphenylene):pyrene	1.30	0.88	1.23	1.47	1.14	0.80	1.02	1.00
Total cata-:total peri-condensed	0.79	0.61	0.76	0.72	0.65	0.60	0.63	0.60

Table 6
Ratios of different PAHs identified in the volatile fractions of pitches

Ratio	MP-AV	MP-GI	MP-IL	MP-IH	MP-IP	CP-W	CP-P1	CP-P2
<i>Condensation degree and size aromatic system ratios</i>								
Benzo[e]pyrene:pyrene	0.68	0.94	1.64	0.93	0.74	0.53	0.55	0.65
Benzo[a]pyrene:pyrene	1.03	1.34	1.94	1.50	1.08	0.83	0.83	0.94
ΣBenzopyrenes:pyrene	1.71	2.28	3.59	2.43	1.82	1.36	1.37	1.59
Benzo[j]fluoranthene:fluoranthene	0.98	1.33	1.81	1.31	0.95	0.72	0.68	0.81
Benzo[b]fluoranthene:fluoranthene	0.97	1.24	1.67	1.20	0.89	0.73	0.68	0.73
Benzo[k]fluoranthene:fluoranthene	0.23	0.27	0.47	0.30	0.18	0.20	0.15	0.16
ΣBenzofluoranthenes:fluoranthene	2.19	2.84	3.95	2.82	2.02	1.65	1.50	1.70
Anthanthrene:benzo[a]pyrene	0.22	0.29	0.24	0.28	0.27	0.29	0.30	0.31
Indenopyrene:Benzo[b]fluoranthene	0.76	0.92	0.95	0.89	1.08	0.95	0.92	0.92
Benzo[ghi]perylene:benzo[e]pyrene	1.01	1.10	0.76	1.03	1.09	1.42	1.21	1.15
Benzo[ghi]perylene:perylene	2.14	2.42	1.75	2.36	2.41	2.63	2.61	2.26
<i>Non-alternant PAHs:alternant PAHs</i>								
ΣBenzofluorenes:(benzo[a]anthracene + chrysene + triphenylene)	0.39	0.27	0.23	0.27	0.22	0.34	0.25	0.27
Fluoranthene:pyrene	1.02	0.94	0.97	1.02	1.06	0.99	1.07	1.03
ΣBenzofluoranthenes:Σbenzopyrenes	1.30	1.18	1.07	1.18	1.08	1.21	1.16	1.10
ΣBenzofluoranthenes:(Σbenzopyrenes + perylene)	1.10	0.99	0.90	1.01	0.91	1.01	0.98	0.93
Indenopyrene:(benzo[ghi]perylene + anthanthrene)	0.83	0.76	0.91	0.79	0.82	0.69	0.73	0.67
Total non-alternant PAH:total alternant PAH	0.77	0.73	0.71	0.73	0.70	0.70	0.70	0.69
<i>Cata-condensed:peri-condensed ratios</i>								
ΣBenzofluorenes:fluoranthene	0.80	0.60	0.64	0.61	0.36	0.48	0.32	0.38
(Benzo[a]anthracene + chrysene + triphenylene):pyrene	2.08	2.05	2.74	2.27	1.71	1.39	1.36	1.42
Total cata:total peri-condensed	0.41	0.28	0.26	0.30	0.29	0.39	0.31	0.28

Specifically, these compounds include acenaphthylene, acephenanthrylene and acenaphthene. Tars produced at a high carbonization temperature and those produced via charge preheating show the lowest acenaphthylene–acenaphthene and acephenanthrylene–benzo[*b*]fluoranthene ratios, suggesting that these tars have higher thermal stability (Table 5). This is also reflected in the decrease in (4H-cyclopenta[*def*]phenanthrene + acephenanthrylene)–fluorene and acenaphthylene–fluoranthene ratios. The degree of pyrolysis decreases in the same order and a relatively higher amount of acenaphthene formed in coke ovens suggests a prolonged residence time of the tar at an elevated temperature.

Possible relations between a given benzo-derivative of a PAH and its parent compound were also examined, in order to assess the variation of the degree of condensation of these tars and the relative sizes of aromatic systems. No clear relation with carbonization temperature and preheating could be found except with respect to the lighter PAHs and benzo[*ghi*]perylene–perylene (Table 5). All of them increase with increasing carbonization temperature, showing a higher proportion of relatively heavier aromatic systems. Preheated charging does not affect any ratios significantly except fluoranthene–fluorene, Σ benzopyrenes–pyrene and benzo[*ghi*]perylene–perylene.

Finally, Table 5 also shows the ratios of the total proportions of non-alternant (including all compounds which contain at least one five-membered ring, with or without methylene groups) and alternant PAHs and some representative compounds of these classes which contain four and five condensed rings. The alternant PAHs are more abundant in tars produced from a wet charge at a higher temperature or from a preheated charge at a lower carbonization temperature. Although the total non-substituted *cata*-condensed hydrocarbons are always the dominant type in the volatile fraction of tars, the relative distribution of *cata*- and *peri*-condensed compounds, depending on the number of rings in the aromatic system, may be influenced by the coking conditions. Thus, the ratios of

(benzo[*a*]anthracene + chrysene + perylene)–pyrene and Σ benzofluorenes–fluoranthene could be indicative of the relative abundance of *cata*- and *peri*-condensed hydrocarbons with four rings. It can be concluded, with some exceptions in the case of MT-IH, that the *peri*-condensed hydrocarbons which have four rings are more abundant in tars produced at a higher temperature and using a preheated charge. The same trend is observed for the ratio of the total amount of *cata*- and *peri*-condensed PAHs (from phenanthrene to anthanthrene). The decrease in the Σ benzofluorenes–fluoranthene ratio, together with an increase in the benzo[*ghi*]perylene–perylene ratio, clearly indicates a higher degree of condensation of aromatic systems for tars produced via a higher carbonization temperature and preheated charging.

The next task here is to investigate the levels of the selected PAHs that do not evaporate when the tar is heated to about 400°C for pitch production. It is important to point out that all pitches were produced with the same softening point (92°C). As can be seen from Table 4, no general trend can be observed between pitch origin and the amount of individual PAHs in the phenanthrene–triphenylene range in the volatile fraction of CS₂ extracts of pitches from industrial and semi-industrial tars. The total amount of this lighter sub-fraction increases in pitches from tars produced by preheating of coal blend M (37.09% for MP-IP). However, the increase in carbonization temperature has two opposite effects depending on coke dimensions: a decrease for the pair MP-AV and MP-GI (36.86 versus 31.71%) and an increase for MP-IL and MP-IH (25.57 versus 32.24%). When PAHs of greater size are compared, there is an increase in the proportion of PAHs such as benzo[*j*]fluoranthene, benzo[*b*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene and anthanthrene (peaks 23, 24, 27, 30 and 31) for pitches coming from tars produced at a relatively higher carbonization temperature. No clear trend attributable to charge preheating could be established in the proportion of individual PAHs in pitches.

Useful information was obtained from the study of possible relations among different types

of PAHs (non-alternant, alternant, *cata*- and *peri*-condensed PAHs) in the volatile fractions of pitches (Table 6). Simple comparison of the ratios of the degrees of condensation shows, without any exception, an increase in the higher condensed PAHs for pitches obtained from industrial tars. However, pitches MP-IL and MP-IH show the reverse trend when the compounds considered have a low degree of condensation (benzopyrene–pyrene and benzofluoranthene–fluoranthene ratios). This is consistent with the higher proportion of the lighter fraction found for MP-IH (32.24% versus 25.57% for MP-IL). Similar behaviour is observed for MP-IP, prepared via preheating of the coal blend M. However, the observations for CP-P1 and CP-P2 follow the same pattern. Similar trends are evident when non-alternant and alternant compounds are considered. Pitches (MP-AV and MP-GI) obtained from industrial tars show an increase in alternant PAHs as the carbonization temperature increases. However, this effect is only apparent for heavier PAHs when pitches from semi-industrial tars (MP-IL and MP-IH) are compared.

Finally, the total *cata*-:total *peri*-condensed PAHs ratio shows that the proportion of *peri*-condensed compounds is much higher than in the corresponding tar fraction. This type of PAH increases with increasing carbonization temperature and when preheated charging is used to produce the parent tar. The same conclusion can be drawn when compounds with a low degree of condensation are compared. This is the case of benzofluorenes–fluoranthene and *cata*-condensed four-ring aromatic systems–pyrene ratios.

The relevance of the differences in pitch composition in relation to their thermal behaviour will be the subject of a further study.

4. Conclusions

Capillary gas chromatography analysis of the volatile fraction of tars and their derived pitches provides a method for estimating the influence of coking conditions on tar and pitch quality. The

relative proportions of the major components, which can be considered individually or in groups, are closely related to the coking conditions under which the tar is produced. In both industrial and semi-industrial coke ovens, an increase in the mean flue temperature leads to a reduction in the proportion of compounds of high thermal reactivity (methyl-substituted PAHs and those promoting hydrogen transfer reactions) and of non-alternant and *cata*-condensed PAHs. Coal preheating has a similar effect to that found when the carbonization temperature is increased. Similarly, pitches obtained from these tars contain more highly condensed aromatic systems.

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