Gas chromatographic study for the evaluation of the suitability of bituminous waste material as an additive for coke production

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Abstract

Waste materials derived from coking plants can be used in situ as bituminous additives in cokemaking. The effectiveness of such materials in the plastic coal range was compared with a coal-tar and four derived pitches of different applications. The volatile matter released from 400 up to 500°C by the additives (VM400–500), which was evaluated by thermogravimetric analysis, was clearly related to the extent of the modification of the Gieseler maximum fluidity of coking coal/additive blends. The decrease in the amount of volatile fraction in the CS_2 extracts of the additives and the increase in the abundance of polycyclic aromatic hydrocarbons (PAHs) of relatively high molecular mass were evaluated by capillary gas chromatography with flame ionization detection (GC–FID) analysis. From regression analysis, it can be deduced that there is a relationship between the compositional parameters deduced from GC–FID analysis and the volatile matter released in the plastic range of a coking coal (VM400–500). Both composition and VM400–500 of the additive, were found to be responsible for the enhancement in fluidity caused by the presence of the additive in the co-carbonization system. GC–FID analysis may be a good method to assess the effectiveness of a bituminous additive in the coal plastic stage and to acquire a better understanding of the components involved in this critical stage of the carbonization process. The changes induced in the plastic range by the additive modify the development of coke anisotropy and the bonding between coke matrix and inert material and, consequently, are responsible for the improvement in the coke properties. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Every year coking plants produce a significant quantity of coal-tar sludge from the tar decanter of the by-products plant and a pitch-like residue from the distillation column of benzol [1–3]. Sometimes, these wastes are disposed of in large on-site waste pits [4]. Modifications in coke-oven operational conditions, including oven-heating practice, oven charging procedure and coal preparation techniques, have minimized the generation of waste materials,

but the disposal problem still remains. Environmental protection requires increased recycling, reutilization of waste material and a further reduction in waste production. Methods for the elimination of wastes such as burial, incineration and biodecomposition burial are commonly used, but in this case they are ineffective. The utilization of such materials as additives to coal blends [1,2,4,5] or as a binder for making briquettes in coke manufacture could be an effective procedure for solving the disposal problem. This alternative use has the advantage that waste materials are utilized in situ in the coking plants. As these tar- and pitch-like waste materials undergo

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some fluctuations in composition due to operating coking conditions, a characterization methodology is necessary, firstly to evaluate the thermal behaviour and coking capacity of waste material in co-carbonizing systems with coking coals, and secondly, to compare them with the more conventional binders.

As for industrial tars and pitches, the use of gas chromatography with flame ionization detection (GC–FID) can provide relevant information not only about the composition of tar- and pitch-like waste materials such as the concentration of each individual compound in the volatile-chromatographed fraction and the distribution of the different families [6–11], but also about components which are relevant in the development of thermoplasticity in coal/additive systems. One of the limitations for using GC–FID in the characterization of industrial tars and pitches is the very low amount of material which can be analyzed due to the lower volatility of large polycyclic aromatic compounds (PACs) [10,11]. In addition, when heat treatment of such materials is performed, other limitations become apparent due to the removal of most of the lighter PACs from the carbonizing system [12,13]. In spite of such limitations, in previous studies GC–FID has proved to be a useful technique for differentiating the composition of tars produced under different coking conditions [11]; pitches derived from different parent tars and with different properties [11,14]; and the pyrolysis behaviours of pitches [12,14–16]. Moreover, the importance of low-molecular-mass compounds lies in the fact that they influence the structural parameters of the whole, i.e., C/H atomic ratio, aromaticity [14–16]. Low-molecular-mass compounds must therefore have implications for the bulk of the tar, pitch and waste material, especially thermal behaviour and plastic properties. Both are critical factors in the development of coke structure, i.e., the development of coke anisotropy and the interaction between the active and inert components in the co-carbonizing system [5,17–21]. Although it cannot be assumed that the unchromatographed fraction consists of compounds similar to those contained in the chromatographed fraction of the extract, most of the unchromatographed fraction is probably composed of compounds that differ in their degree of condensation [14–16]. Given this assumption, the volatile-chromatographed fraction of tars and pitches ana-

lyzed by GC–FID could be taken as fingerprints of the whole extractable material and therefore provide information about thermal behaviour.

Bearing this assumption in mind, the main objective of this work is to establish if there is any relationship between compositional parameters deduced by GC–FID and the effectiveness of the bituminous materials as additives for cokemaking. The assessment was carried out by means of: (i) thermogravimetric (TG)/differential TG (DTG) analysis for studying the evolution of volatile matter during pyrolysis up to 1000°C; (ii) Gieseler plastometry of coal/additive blends, a technique generally used for coal blending, for studying the modifications induced by the additive in the plastic stage of a given coal; and, (iii) GC–FID for detecting the amount and composition of the volatile-chromatographed fraction in CS_2 extracts.

2. Experimental

A series of bituminous materials to be used as additives in coal blends included three samples of tar-like waste materials from tar decanter (M) and two pitch-like residues from the distillation column of benzol in the by-products plant (RP). For the purposes of comparison, four commercial pitches with different characteristics and industrial applications (BI1: one impregnating pitch and CTP: three binder coal-tar pitches) and one commercial high-temperature coal-tar (T) were also used. The main characteristics of these potential cokemaking additives are shown in Table 1.

The thermogravimetric measurements of the additives were carried out using a Perkin-Elmer TGA7 thermobalance. Samples (100 mg) were heated to 1000°C at a rate of 3°C/min and a nitrogen flow of 95 ml/min. The equipment gave a continuous automatic recording of mass loss (TG) and rate of mass loss (DTG). The following parameters are used in this study: coke yield (CY) as the mass percent of residue after heat treatment, the percentage of the volatile matter released (VM) at different intervals of temperature and the temperature at which the maximum release of VM takes place on the basis of DTG curves (T_{max}). The TG/DTG data are presented in Table 2.

Table 1
Main characteristics of the additives

	T	M1	M2	M3	RP1	RP2	BI1	CTP1	CTP2	CTP3
C/H[a]	1.43	1.64	1.95	1.71	1.59	1.55	1.58	1.98	1.87	1.75
SP (°C)[b]	–	–	–	–	53	75	50	98	85	93
CS_2-I (%, w/w)[c]	12.4	20.0	24.9	21.9	30.0	37.9	26.9	37.0	29.5	33.9

[a] Carbon:hydrogen atomic ratio from elemental analysis.
[b] Softening point determined by the Kramer–Sarnow method.
[c] CS_2-I: Carbon disulphide insoluble content.

Table 2
Coke yield, TG and DTG data for the additives studied

	T	M1	M2	M3	RP1	RP2	BI1	CTP1	CTP2	CTP3
Coke yield (%, w/w)	13.9	23.6	29.2	32.5	30.8	35.2	38.0	44.8	41.8	42.4
Total VM (%, w/w)	86.1	76.4	70.8	67.5	69.2	64.8	62.0	55.2	58.2	57.6
T_{max} (°C)[a]	106	250	257	272	262	231	348	396	398	381
VM300 (%, w/w)[b]	87.4	70.1	71.7	65.0	61.5	59.4	42.3	18.4	20.2	16.8
VM300–400 (%, w/w)[b]	8.7	20.2	18.0	22.9	25.6	23.7	34.7	39.1	40.5	45.2
VM400–500 (%, w/w)[b]	3.2	7.8	7.5	9.7	8.9	14.0	20.1	35.4	33.3	30.5
VM500–1000 (%, w/w)[b]	0.7	1.9	2.8	2.4	4.0	2.9	2.9	7.1	6.0	7.5

[a] Temperature of maximum volatile matter released based on DTG curves.
[b] Volatile matter evolved at a specific temperature range.

The maximum fluidity of the blends of a coking coal (VM: 27%, w/w in dry basis) and the additive (90:10, w/w) was assessed by means of a Gieseler plastometer test, following ASTM D2639-74 standard procedure. In this test, 5 g of the blend with a particle size smaller than 0.425 mm was heated at a constant rate of 3°C/min and subjected to constant torque stirring. The parameters derived from this test were: (i) the maximum fluidity (MF) measured as dial divisions per minute (ddpm) and expressed as the logarithm on the base 10; (ii) the temperature at which this fluidity is attained (T_f); (iii) the softening temperature (T_s) at which the blend starts to be fluid; (iv) the resolidification temperature (T_r). An additional parameter (plastic range) can be defined as the difference between the resolidification temperature (T_r) and the softening temperature (T_s). The data for the coal/additive blends are given in Table 3.

The GC study of the volatile fraction of the additives was performed on the carbon disulphide

Table 3
Maximum fluidity and main temperatures in the development of fluidity of a coking coal and its blends with the bituminous additives studied

	MF (ddpm)	T_s (°C)	T_f (°C)	T_r (°C)	$T_r - T_s$ (°C)
Coal	73	413	452	478	65
Coal + additive (90:10, w/w)					
T	643	393	453	484	91
M1	516	391	447	483	92
M2	650	391	451	478	87
M3	894	392	452	483	91
RP1	1225	385	449	481	96
RP2	1308	390	450	491	101
BI1	3887	380	448	484	104
CTP1	10 202	377	452	488	111
CTP2	5779	379	449	484	105
CTP3	7552	386	449	491	105

extracts. This solvent is one of the most handy solvents for extractions and is able to extract a high percentage of the whole bituminous material [22]. Extractions were carried out at room temperature in an ultrasonic bath (2 g of sample: 40 ml of CS_2) and after filtration the solvent was eliminated from the filtrate in a rotary apparatus at reduced pressure and a temperature of 30°C. Due to the big differences in solubility between PACs all samples to be analyzed were dissolved in pyridine again (50–60 mg of sample: 1 ml of solvent) and kept for a few minutes in an ultrasonic bath in order to obtain total dissolution.

The chromatographic analyses were carried out on a Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph equipped with FID and a Hewlett-Packard Vectra ES/12 computer for storing the chromatograms. Separations were carried out on a fused-silica capillary column of 25 m×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 a rate of 4°C/min. Hydrogen was used as the carrier gas at a flow-rate of 2 ml/min and a splitting ratio of 1:87 was used. The detector and injector temperature were 350 and 300°C, respectively, and the volume of sample injected was 1 μl. Chromatographic peaks were identified by comparing retention time data of available standards and data from previous studies [6–11]. Relative response factors (RRFs) were determined for each compound in the CS_2 extracts and based upon the response of fluoranthene as external standard. The absolute calibration method with a separate standard (reference compound, fluoranthene) was used because in previous studies no significant differences were found using internal and external standards [10]. According to the previously described method [10], mixtures of various commercially available PACs with known concentrations were analysed using the above mentioned chromatographic conditions. The standard compounds with a purity greater than 98% were obtained from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI, USA), Merck (Darmastadt, Germany) 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 were peak-area counts and masses of the compounds, respectively. Taking into account the RRF values given in a previous study [10,23], the determination of the main PACs of the volatile fraction of CS_2 extracts was carried out. The quantitative data are at least the average of three chromatographic determinations. The total percentage of the chromatographed material of CS_2 extracts (CME) was estimated by using fluoranthene as the separate standard compound and assuming response factors of unity for all components. For calculation, CME was defined as:

$$CME = (M_F A_{Total} / A_F M_s)100$$

where M_F was the amount of fluoranthene in the sample; 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 M_s, the amount of the sample analyzed.

CM in the whole additive (CMA) was also calculated by multiplying the CM in the extract (CME) by the extract yield using CS_2 as a solvent.

3. Results and discussion

The main characteristics of the waste materials and commercial tar and pitches are presented in Table 1. The selected materials to be used as an additive to coal blends in coke manufacture are very different not only in their C/H atomic ratio, but also in their solubility in CS_2. As might be expected, tar (T) has the lowest C/H atomic ratio and the highest solubility in CS_2 (lower insoluble fraction), whereas binder coal-tar pitches (CTPs) have lower solubility in CS_2 (higher insoluble fraction). Tar decanter sludges (M1, M2 and M3) always contained a higher insoluble fraction than industrial tar, but a lower one than commercial pitches. On the other hand, pitch-like residues (RP1 and RP2) show an insoluble fraction content equivalent to the selected CTP1 and CTP2. The C/H atomic ratio of these pitch-like residues is always lower than those for binder CTPs and close to the value for the impregnating pitch (BI1). The relative abundance of soluble and insoluble fractions of the waste materials in organic

solvents depends on coking conditions and probably plays an important role in the thermoplastic behaviour of a coking coal in a co-carbonizing system. Thus, on the one hand, the soluble fraction in organic solvents can be expected to act as a binding component. On the other hand, the insoluble fraction serves as a poorly-caking filler component. Furthermore, it is generally accepted that properties and thermal behaviour are governed not only by the amount of soluble fraction, but the composition of the soluble fraction should also be considered for an effective utilization of these materials [11,12,14,24]. For these reasons, a study of the additives including the evolution of volatile matter during heat treatment up to 1000°C (TG/DTG analysis), the modification of plastic properties of a coking coal (Gieseler plastometry) and the GC–FID analysis of the CS_2 extracts was carried out.

The additives evaluated by TG analysis differ in their thermal behaviour (Table 2) and their capacity to modify the plastic properties of coal (Table 3). The different nature of the additives affects the total mass loss percentage, which drops from about 86% for coal-tar T to 55% for CTP1. This decrease is accompanied by a simultaneous displacement towards higher values of the temperature at which the maximum amount of volatile matter is released (Table 2).

In an attempt to establish how the volatile matter released during the pyrolysis of the additive affects the development of thermoplastic properties, specific temperature ranges were defined on the basis of the physical changes of a coking coal (see Table 3). The initial temperature ranges up to 400°C cover the pre-plastic stage of a coking coal, that is the temperature range before the softening of the coal. The next one, from 400 to 500°C, corresponds to the step where the coal becomes fluid. In this stage the coal particles agglomerate to form a plastic mass which resolidifies into coke at a temperature of around 500°C. This stage is referred to as the ''plastic stage''. Finally, the final temperature range, which extends from 500°C to the end of the pyrolysis process (1000°C), corresponds to the post-plastic stage [25]. The volatile matter evolved over different temperature ranges is also given in Table 2. It can be seen that the distribution of the volatile matter released for coal-tar (T) is mainly concentrated at a lower temperature than the other materials tested. In general, going from tar to pitch and passing through the waste materials there is a shift in the evolution of volatile matter towards higher temperatures (Table 2), which is accompanied by an increase in coke yield (decrease in total volatile matter released). All the bituminous additives tested have a common feature. For all of them, most of the volatile matter is lost at temperature below 500°C and only a small amount is lost at a higher temperature than 500°C (<7.5%, Table 2). In addition, CTPs lose around 75% of their total volatile matter in the temperature range between 300 and 500°C, whereas most of the VM in tar and waste materials is lost in the early stages of pyrolysis (temperature<300°C). A different behaviour for these materials can therefore be expected during co-carbonization with coking coal. Indeed, a different contribution to the generation of fluidity in the coal/additive system can be deduced from data in Table 3. The addition of such materials always produces an increase in the MF of the blend because they supply additional fluid components to the system and contribute to the plasticization of the inert components of the coal. No significant influence of the lighter compounds evolved below 350–400°C can be expected in the formation of the plastic mass. The components of this volatile matter fraction will probably be distilled before coal becomes a fluid mass. However, the volatile matter released by an additive in the temperature range between 400 and 500°C (VM400–500) as evaluated by TG analysis might serve as an appropriate parameter for reflecting the modification induced by the additive in the plastic range of a given coking coal. Fig. 1 displays a linear relationship between the VM400–500 of the additive and the Gieseler maximum fluidity (MF expressed as logarithm on the base 10) of mixtures of the coking coal and the additive (90:10, w/w). The higher the VM400–500 from the additive, the more effective the additive in modifying the plastic behaviour of the coking coal. This means that the waste materials studied are slightly more effective additives than industrial coal-tars, but much less effective than binder CTPs.

The addition of a bituminous additive not only modifies the maximum fluidity of the system, but also increases the plastic temperature ranges $(T_r - T_s)$ by decreasing the softening temperature (T_s). At the
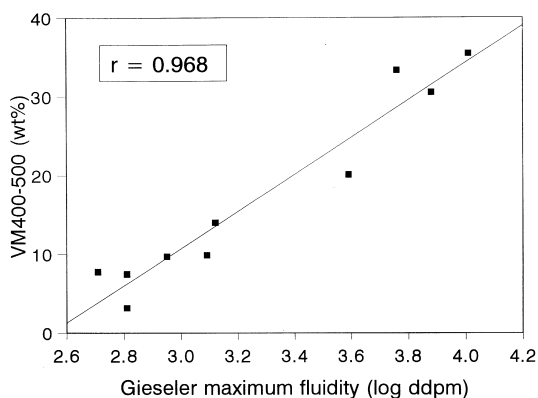
Fig. 1. Relationship between the volatile matter released from 400 to 500°C (VM400–500) by the additive and the Gieseler maximum fluidity of the coal/additive blend.

same time, a slight lowering in maximum fluidity temperature is observed, which clearly does not depend on the nature of the bituminous additives studied (Table 3).

The next task to investigate is how the plastic stage is affected by the chemical composition of the additives. On the one hand, it is generally accepted that the properties and chemical reactivity of tars and pitches are governed by their composition [11–14,21] and, on the other hand, it is well known that the "fluid products" which plasticize the inert components of the coal to form a plastic (fluid) coal mass during carbonization are soluble in organic solvents [26–29]. It is obvious therefore that the composition of the soluble fraction in CS_2 of the additive must play an important role in its thermal behaviour and, consequently, in the changes induced in thermoplasticity of the blend with a coking coal. The influence that composition of the additive might have on the thermoplasticity of the blends suggests the need for a deeper study on composition by GC–FID.

Fig. 2 shows, as an example, the chromatograms of the CS_2 extracts of two waste materials studied here. The top chromatogram corresponds to a tar-decanter sludge (M1) and the bottom one to a pitch-like residue from the distillation column of benzol (RP1). The volatile fraction of all additives studied, ranging from indene (peak 1, b.p. 182°C, M_r=116) to anthanthrene (peak 82, M_r=276), is made up of the same compounds, but the concentrations of
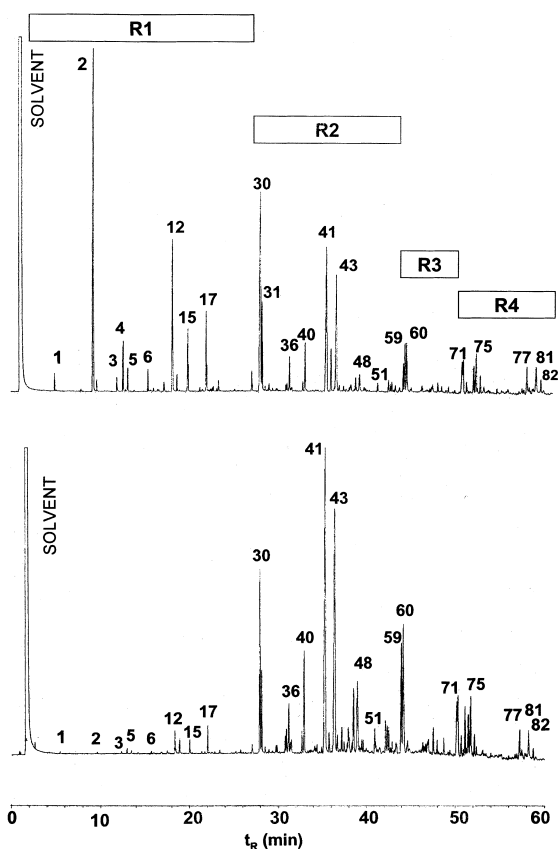

Fig. 2. Capillary gas chromatograms of the volatile fraction of a tar-decanter sludge (top) and a pitch-like residue (bottom) on OV-1701 stationary phase. For peak identification see Table 4. R1, R2, R3 and R4 correspond to the chromatographic regions defined.

certain PACs differ from one additive to another. In addition, the presence or absence of some of the lighter aromatic compounds in the indene (peak 1)–phenanthrene (peak 30) range also differs in the series of additives going from tar to pitch. Despite the large number of PACs present in the volatile fraction of the CS_2 extracts from the additives, they can all be classified into a few classes of compounds [30] which are described in Table 4. Quantitative comparisons of the distribution of the different families in the additives can be made from data given in Table 5. The polycyclic aromatic hydrocarbons (PAHs) including the cata- and peri-condensed ones (the latter being alternant and non-alternant) are in all cases the most dominant class of

Table 4
Different classes of polycyclic aromatic compounds present in the chromatographed fraction of the additives (numbers in parentheses correspond to the peak numbers in Fig. 2)

Cata-condensed PAHs	Naphthalene (2); phenanthrene (30); anthracene (31); benz[a]anthracene (59); chrysene (60); triphenylene (61); dibenz[ah]anthracene (78); benzo[b]chrysene (79); picene (80)
Alternant peri-condensed PAHs	Pyrene (43); benzo[e]pyrene (74); benzo[a]pyrene (75); perylene (76); benzo[ghi]perylene (81); anthanthrene (82)
Non-alternant peri-condensed PAHs	Fluoranthene (41); benzo[ghi]fluoranthene (56); benzo[j]fluoranthene (71); benzo[b]fluoranthene (72); benzo[k]fluoranthene (73); indenopyrene (77)
Alkyl and phenyl derivatives	2-Methylnaphthalene (4); 1-methylnaphthalene (5); biphenyl (6); 2-ethylnaphthalene (7); dimethylnaphthalenes (8-11); methylbiphenyl (14); methylacenaphthenes (18–20); methyldibenzofuranes (21,22); methylfluorenes (24, 25); dimethyldibenzofuranes (26, 27); methylphenanthrenes (34, 35, 37, 38); 2-phenylnaphthalene (39); methylbenzonaphthofuran (49); methylpyrene (50); dimethylfluoranthenes (52, 53); methylbenzo[a]anthracenes (62–64)
PAHs with a –CH$_2$– group	Acenaphthene (13); 4H-cyclopenta[def]phenanthrene (36); fluorene (17); benzo[a]fluorene (47); benzo[b]fluorene (48); 11H-benzo[ac]aceanthrylene (65); 4H-cyclopenta[def]chrysene (66) 4H-cyclopenta[def]triphenylene (67)
Hydrogenated PAHs	9,10-Dihydroanthracene (23); 1,2,3,4-tetrahydroanthracene (28); tetrahydrochrysene (55)
PAHs with olefinic group	Indene (1); acenaphthylene (12); acephenanthrylene (42)
Oxygen compounds	Dibenzofuran (15); benzonaphthofuranes (44, 45); benzo[kl]xanthene (46)
Pyrrole derivatives	Carbazole (40); 4H-benzo[def]carbazole (51); 11H-benzo[a]carbazole (68); 7H-benzo[c]carbazole (69); 5H-benzo[b]carbazole (70)
Pyridine derivatives	Quinoline (3); azaacenaphthylene (16); benzoquinolines (32, 33); dibenzoquinolines (57)
Thiophene derivatives	Dibenzo[bd]thiophene (29); benzo[b]naphtho[2,1-d]thiophene (54); benzo[b]naphtho[2,3-d]thiophene (58)

compounds, with one exception (impregnation pitch – BI1 – which has a high concentration of alkyl-substituted PAHs, mainly methylnaphthalenes). The distribution of such PAHs varies from tar and tar-decanter sludge, which are made up of a higher proportion of cata-condensed PAHs, to residual pitch and commercial pitches, which have a more homogeneous distribution consisting of the three classes of

Table 5
Distribution of the different classes of PACs in the chromatographed fraction of the additives

	T	M1	M2	M3	RP1	RP2	BI1	CTP1	CTP2	CTP3
Cata-condensed PAHs	37.7	32.9	35.6	35.4	20.7	26.7	15.1	20.4	20.5	22.2
Alternant peri-condensed PAHs	14.5	13.2	16.3	17.1	23.5	21.0	19.3	31.1	28.7	24.4
Non-alternant peri-condensed PAHs	16.5	16.6	18.1	19.0	27.5	23.2	19.0	27.4	26.2	26.2
Alkyl and phenyl derivatives	6.6	8.0	5.5	4.8	5.5	7.4	26.4	4.4	5.2	6.3
PAHs with a –CH$_2$– group	7.1	10.1	7.0	6.4	9.4	8.9	9.4	8.3	10.5	9.3
Hydrogenated PAHs	0.3	0.3	0.3	0.3	1.0	0.7	0.6	0.9	0.9	1.0
PAHs with olefinic group	7.9	7.6	7.7	7.8	1.0	1.7	0.1	0.2	0.2	0.2
Oxygen derivatives	3.4	3.7	3.0	2.9	2.4	2.7	2.8	1.3	1.5	1.0
Pyrrole derivatives	2.9	4.1	3.3	3.2	6.2	4.6	2.9	4.1	4.3	5.2
Pyridine derivatives	1.5	1.6	1.3	1.3	0.8	1.0	3.3	0.4	0.7	0.4
Thiophene derivatives	1.6	1.9	1.9	1.8	2.0	2.1	1.1	1.5	1.3	3.8

PAHs. The same thing can be said of compounds with an olefinic group in a five-membered ring. A higher amount of this class of compounds is present in the chromatographed fraction of tar and tar-decanter sludges (approx. 7%). No clear trend attributable to the concentration of a specific class of compounds could be established in the development of the fluidity of the coal/additive blends.

Table 6 shows the total percentage of the chromatographed material in the extract (CME) and in the whole additive (CMA). It must be pointed out that these parameters do not represent real values. They are only an estimation of the concentration of the chromatographed fraction because the relative response factor for each compound is not taken into account. According to values in Table 6, it can be deduced that the CME for tar decanter sludges and pitch-like residue (RP1) are quite similar to that corresponding to the commercial tar, whereas pitch values are always the lowest. A low value of CME accounts for the impregnation pitch (BI1) in spite of the high amount of soluble components present. This may be related to the industrial production process applied to this type of pitch, which is different to the progressive distillation process of a coal-tar. Taking into account the extraction yield in CS_2 and the concentration of CME, it might be concluded that tar and waste materials as a whole are the richest in volatile compounds as evaluated by GC (higher values of CMA). In general, it can be said that an inverse relation exists between the CMA, the volatile matter released between 400 and 500°C and the Gieseler maximum fluidity of coal/additive blend. Fig. 3 shows the relation between the logarithm of the Gieseler maximum fluidity of coal/additive blends and the amount of chromatographed material in the additive (CMA). The scattering in Fig. 3 can be ascribed to the fact that additives are made from different feedstocks, by different processes and under different conditions and, also, to the fact that not all
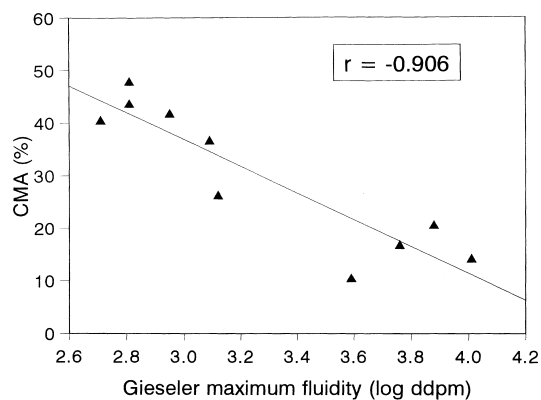

Fig. 3. Relation between the chromatographed material in the additive (CMA) and the Gieseler maximum fluidity of the coal/additive blend.

of the CMA is involved in the development of the fluidity of the blend.

In an attempt to obtain more precise information on the influence of the composition of the additives on their pyrolysis behaviour and the class of compounds that produce enhancement in fluidity development, four chromatographic regions were defined (see Fig. 2). The first region (R1) includes PACs with a lower molecular mass (M_r) and boiling point (b.p.) than phenanthrene (peak 30, $M_r = 178$ and b.p. $= 338$°C). The second region (R2) is composed of PACs from phenanthrene to benz[*a*]anthracene (peak 59, $M_r = 228$ and b.p. $= 437$°C) and the third region (R3) includes the range from benzo[*a*]anthracene to benzo[*j*]fluoranthene (peak 71, $M_r = 252$, b.p. $= 480$°C). Finally, the fourth region (R4) is composed of the heavier PACs from benzo-[*j*]fluoranthene to the end of the chromatogram. Table 7 gives the chromatographic data for the volatile fraction of each additive, according to the different regions defined. The correlations between these parameters and those derived from TG analysis and Gieseler plastometry are described. The relation

Table 6
Percentage of the chromatographed material in the CS_2 extract (CME) and in the whole additive (CMA)

	T	M1	M2	M3	RP1	RP2	BI1	CTP1	CTP2	CTP3
CME (%)	54.8	50.7	58.2	53.5	52.4	42.3	14.3	22.5	23.9	31.2
CMA (%)	47.9	40.5	43.7	41.8	36.7	26.3	10.5	14.2	16.8	20.6

Table 7
Percentages of PACs eluting in different chromatographic regions

	T	M1	M2	M3	RP1	RP2	BI1	CTP1	CTP2	CTP3
R1 (%)[a]	34.2	29.5	29.0	27.8	2.1	13.5	34.7	4.7	2.5	0.1
R2 (%)[b]	42.7	46.1	45.5	44.9	62.6	50.6	20.8	28.5	37.2	33.7
R3 (%)[c]	7.8	9.1	8.1	8.8	17.9	10.7	13.9	18.6	19.4	25.3
R4 (%)[d]	15.3	15.3	17.4	18.5	17.3	25.2	30.6	48.3	40.9	40.9

[a] R1: PACs with lower molecular mass (M_r) and boiling point (b.p.) than phenanthrene (peak 30, Fig. 2).
[b] R2: PACs from phenanthrene to benz[*a*]anthracene (not included).
[c] R3: PACs from benz[*a*]anthracene (peak 59, Fig. 2) to benzo[*j*]fluoranthene (not included).
[d] R4: PACs from benzo[*j*]fluoranthene (peak 71, Fig. 2) to the end of the chromatogram.

between the volatile matter released at a temperature below 300°C (VM300) and the lightest PACs eluting in the chromatographic regions R1 and R2 can be expressed by a multi-regression equation in the form:

$$VM300 = -33.62 + 1.38R1 + 1.46R2$$
$$r = 0.981 \tag{1}$$

Eq. (1) may indicate that the volatile compounds with the lowest and intermediate M_r (regions R1 and R2, respectively) are mainly removed from the co-carbonization system by a progressive distillation process before the coal particles soften and become fluid-like. The components of the chromatographed fraction eluting in region R3 affect the volatile matter released from 300 up to 400°C (VM300–400) ($r = 0.891$) and from 400 up to 500°C (VM400–500) ($r = 0.822$). Finally, the percentage of the heavier PACs in the chromatographed fraction of the CS_2 extract (region R4) has a big influence on the amount of the volatile matter evolved in the temperature range between 400 and 500°C (VM400–500) and on the maximum fluidity developed by the coal/additive blend. A high correlation coefficient was obtained when these parameters (R4, VM400–500 and MF) were considered in the form of Eqs. (2) and (3):

$$VM400{-}500 = -8.38 + 0.95R4 \quad r = 0.988 \tag{2}$$

$$\log MF = 2.24 + 0.04R4 \quad r = 0.974 \tag{3}$$

Turning to the other chromatographic regions R1, R2 and R3, no correlation was found between the Gieseler MF of the blend and R1 and R2 ($r < 0.65$).

A better correlation was obtained when R3 was considered ($r = 0.852$).

Using multi-regression analysis, a correlation was obtained when the two chromatographic regions R3 and R4 were considered together.

$$VM400{-}500 = -9.30 + 0.25R3 + 0.85R4$$
$$r = 0.991 \tag{4}$$

$$\log MF = 2.168 + 0.019R3 + 0.031R4$$
$$r = 0.985 \tag{5}$$

The following deductions can be made from an examination of the results. A high fluidity of the blend can be obtained from additives with a high proportion of PAHs evaluated in regions R3 and R4. However, the components of region R4 which have a higher M_r and boiling point appear to be responsible for the higher amount of volatile matter in the plastic stage of coal and, consequently, for the enhancement of the fluidity of the co-carbonization system. This is clearly indicated by the higher contribution of the term R4 to the VM400–500 and Gieseler MF values (Eqs. (4) and (5)).

According to topology of the PAHs, alternant and non-alternant peri-condensed PAHs are more concentrated than cata-condensed PAHs in this end region of the chromatographic analysis. The ability of large PAHs to confer thermoplastic properties to coal appears to be related either to their hydrogen shuttling [17–19] or radical stabilization propensity [31]. According to the latter mechanism, large peri-condensed PAHs present in the CS_2 extracts should possess the ability to increase radical stability due to a greater delocalization, which allows a greater time

for hydrogen shuttling to occur, resulting in a slowing down of the rates of crosslinking and a greater alignment of aromatic entities to form anisotropic cokes.

4. Conclusions

A capillary GC analysis of the volatile fraction of the CS_2 extract from bituminous additives provides a useful method for estimating the ability of the additives to modify the plastic stage of a coking coal in the co-carbonization system. The effectiveness of an additive in terms of an enhancement in fluidity of the co-carbonization system can be explained by the volatile matter released in the temperature range between 400 and 500°C as well as by the amount of chromatographed material solubilized in CS_2 and, in particular, by the chromatographed sub-fraction made up of heavier PAHs.

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