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Journal of Chromatography A, 945 (2002) 161–172

JOURNAL OF
CHROMATOGRAPHY A

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Study of the composition of tars produced from blends of coal and polyethylene wastes using high-performance liquid chromatography[☆]

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Received 12 June 2001; received in revised form 8 November 2001; accepted 8 November 2001

Abstract

Tars produced at semi-industrial scale in a coke oven of $6 \cdot 10^3$ kg capacity were used to investigate the effect of using polyethylene waste as an additive in the carbonization process with coal. The polyethylene wastes used were low-density polyethylene from the agriculture greenhouses and high-density polyethylene from domestic sources. The high-performance liquid chromatography analysis of the soluble fractions in toluene and carbon disulfide, using two polystyrene–divinylbenzene columns and a mixture of dichloromethane–methanol as a mobile phase, provides useful information on the composition of tars and their derived pitches in terms of the substitution and molecular topology of polynuclear aromatic compounds (PACs). Differences in composition of tars produced with polyethylene waste at 1% (w/w) have been found to be negligible, while a higher amount of the waste (3%, w/w) promoted the formation of *peri*-condensed PACs at the expense of the substituted *cata*-condensed PACs. This behaviour is due to more extensive secondary reactions of tar precursors via dealkylation and aromatic condensation taking place during the carbonization process as a consequence of a more viscous co-carbonizing system. Changes in tar composition caused by this amount of polyethylene waste addition were comparable to those promoted by an increase in the carbonization temperature at semi-industrial and industrial ovens and by the coal preheating before the carbonization process. The characteristic features in tar composition were also found for the derived pitches from tars obtained with the polyethylene waste addition. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tars; Coal tar; Coal; Polyethylene; Polynuclear aromatic hydrocarbons

1. Introduction

Effective recycling processes for plastic waste

[☆]Presented at the 30th Scientific Meeting of the Spanish Group of Chromatography and Related Techniques/1st Meeting of the Spanish Society of Chromatography and Related Techniques, Valencia, 18–20 April 2001.

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have become a major challenge in the protection of the environment and natural resources. Different routes are currently employed such as mechanical, chemical and energy recovery [1–4]. The further development of plastic recycling is addressed to integration of various options to produce an environmentally and economically sustainable waste management system. Thus, alternative and complementary recycling technologies need to be explored, especially as plastic waste may be incorporated into existing processes, to avoid the various

problems arising from simple incineration of plastic waste and from the shortage of landfill sites. In this sense, much attention has been directed towards the use of plastics and other hydrocarbon wastes in combination with coal [5–13]. Integrated steel plants may also contribute to expand plastic waste recycling by two routes. The first route involves the injection of plastic waste through the tuyeres of a blast furnace as a fuel in a similar way as coal or fuel oil [11,14–16]; and the second one, the co-carbonization of plastic waste with coal for metallurgical coke manufacture, may also provide another potential solution [11,12].

In an attempt to contribute to the last alternative route, the objective of this study was to determine how tar composition was affected by the plastic waste addition and if changes in composition could be related to those caused by the variation of operational parameters in the industrial carbonization process such as the mean flue heating temperature and the charging method. Our attention addressed two types of thermoplastics from different sources. The first was low-density polyethylene (LDPE) from agriculture greenhouses for which recycling routes are limited by the deterioration degree of its properties during use and the contamination during collecting process. The second one was high-density polyethylene (HDPE) from domestic bottles, one of the most abundant thermoplastics in municipal solid waste.

It is important to point out that the main purpose of the coking industry is the production of coke to feed the blast furnace in ironmaking. However, secondary products formed during the process are also of great importance. This is the case of tar which is considered a secondary or by-product by the coking industry, but at the same time tar is a valuable raw material (feedstock) in the chemical and pitch manufacture industries [17–22]. Coal tar and the derived pitches is a very complex mixture in constitution and it is usually composed of a large number of polynuclear aromatic compounds (PACs) in a wide range of concentrations. In general, coal tar is mainly composed of aromatic hydrocarbons ranging from benzene and its alkyl derivatives to compounds containing possibly as many as 20 or more rings and small amounts of partially hydrogenated compounds. Heterocyclic compounds containing

oxygen in a five-membered ring, nitrogen in pyridinic or pyrrolic systems or sulfur in thiophene systems are also present and there is rarely more than one non-carbon atom in their ring systems. The aromatic and heterocyclic structures occur in substituted and unsubstituted forms, the main substituent groups being methyl, ethyl or hydroxyl [17,23,24]. To overcome this heterogeneity, the PACs present belong to relatively few classes of compounds in terms of functionality and types but differ in molecular size and shape and their separation into PAC classes is attempted.

Lafleur and Wornat [25] reported a separation method of PACs by size-exclusion chromatography using polydivinylbenzene and dichloromethane as stationary and mobile phases, respectively. In such conditions, the elution behaviour of PACs is, however, governed by both size- and non-size-dependent effects. The non-ideal elution behaviour of PACs provides a useful method for the separation of substituted and unsubstituted *cata*-condensed and *peri*-condensed PACs [25,26]. Taking the advantage of such anomalies, a modified method has been also developed by Martin et al. [27] and applied to pitch characterization. It allowed the separation of PACs into five classes: *cata*1, heteroaromatics and compounds substituted with alkyl, aryl and heteroatomic groups; *cata*2, alkyl- and aryl-substituted PACs together to hydroaromatic and naphthenic compounds; *cata*3, unsubstituted planar PACs; and two groups of *peri*-condensed compounds. In this modified procedure, a mixture of dichloromethane and methanol as a mobile phase was employed and two columns packed with polystyrene–divinylbenzene of different nominal size as a stationary phase was used. Application of this method to the study of extrographic fractions from coal-tar pitches [28], tars [29] and pitches derived from coal and petroleum [27–30] showed to be a relatively simple and rapid method with great utility in detecting differences in composition of the soluble fractions of tars and pitches without the limitation of volatilisation which occurs when gas chromatography is used [31–33]. For this reason, high-performance liquid chromatography (HPLC) analysis using the above conditions has been selected to assess the changes in tar composition caused by the co-carbonization of coal with polyethylene waste.

2. Experimental

2.1. Tar production

For tar production, the polyethylene wastes used were granulated LDPE—less than 5 mm in size—from agriculture greenhouses and laminated HDPE—less than 1 cm in size—from bottles of domestic uses. These wastes were added to a coal blend used by the Spanish steel industry for blast-furnace coke manufacture at proportions of 1 and 3% (w/w) and, then, carbonized at the Incar semi-industrial coking plant using a coke oven of $6 \cdot 10^3$ kg capacity. The carbonization temperature measured as the mean flue heating temperature over the carbonizing period was 1240 ± 10 °C and the coking time of 18 h [12]. The coal blend was also carbonized without polyethylene waste addition and the tar B recovered taken as a reference.

To assess the influence of plastic waste addition on tar composition, seven tars produced at different carbonization conditions and oven dimensions were also used. Four of the tars were produced at the industrial scale in Aceralia coking plants using a different mean flue heating temperature. In the first

series, two tars were produced at 1190 °C for 20 h (LT-AV) and 1230 °C for 17 h (HT-AV), while the other two tars were produced at 1200 °C for 23 h (LT-GI) and 1260 °C for 16.5 h (HT-GI) in bigger coke ovens. Table 1 summarizes the carbonization conditions and the origin of each tar together with three tars produced in the same Incar coke oven. Two of them were produced using wet charges and carbonized at mean flue temperatures of 1180 and 1280 °C and coking times of 19.5 and 18.5 h for LT-IN and HT-IN, respectively. Another tar was obtained from a preheated charge of the same coal blend (preheating temperature 214 °C) and, then, carbonized at 1200 °C for 14.5 h (PT-IN). For coal preheating before carbonization, a $2 \cdot 10^3$ kg/h pilot plant using the Precarbon process, built on-line with the Incar coking plant, was used. Details of the Incar coking plant and the preheating plant are described elsewhere [34].

2.2. Tar and pitch characterization

Tars were subjected to standard characterization including elemental analysis, insoluble content in quinoline (QI) and toluene (TI) and distillation

Table 1
Origin and carbonization conditions of the tars studied

Tar	Oven dimensions (m)	Mean flue temperature (°C)	Coking time (h)
Semi-industrial tars produced with polyethylene waste addition			
B		1248	18
B1LDPE	Semi-industrial scale	1235	18
B3LDPE	6.5×2.8×0.450	1230	18
B1HDPE		1242	18
B3HDPE		1236	18
Semi-industrial tars from wet charging			
LT-IN	Semi-industrial scale	1180	19.5
HT-IN	6.5×2.8×0.450	1280	18.5
Semi-industrial tars from preheated charging			
PT-IN	Semi-industrial scale 6.5×2.8×0.450	1200	14.5
Industrial tars			
LT-AV	Industrial oven 1	1190	20
HT-AV	13.5×4.5×0.400	1230	17
LT-GI	Industrial oven 2	1200	23
HT-GI	15.9×6.5×0.420	1260	16.5

Table 2
Main characteristics of reference tar (B) and tars produced with plastic waste addition

Tar	C/H ^a	QI (%, w/w) ^b	TI (%, w/w) ^b	β-Resin (%, w/w) ^c	CS ₂ -I (%, w/w) ^b	Pitch yield (%, w/w) ^d
B	1.06	1.9	3.5	1.6	3.4	52.0
B1LDPE	1.17	1.5	3.3	1.8	4.0	51.7
B3LDPE	1.24	5.6	9.3	3.7	7.7	59.4
B1HDPE	1.20	2.2	4.6	2.4	4.3	51.3
B3HDPE	1.29	4.6	8.1	3.5	5.8	57.7

^a Carbon:hydrogen atomic ratio from elemental analysis.

^b QI; Quinoline insoluble; TI, toluene insoluble, CS₂-I, carbon disulfide insoluble.

^c β-Resin, difference between toluene and quinoline insoluble contents (TI-QI).

^d Yield of pitch with a similar softening point (95±2 °C) obtained by distillation process of the tar.

process to determine the pitch yield as well as the insoluble content in carbon disulfide (CS₂-I). Tables 2 and 3 show the main characteristics of the series of tars produced using plastic waste addition and those produced at different carbonization conditions and coking plants, respectively. Pitches obtained from semi-industrial tars produced by the addition of polyethylene waste were only studied. Pitches with a softening point of 95±2 °C, as determined by the Kraemer–Sarnow method, were produced by a laboratory-scale distillation process. Table 4 gives the main characteristics of the derived pitches.

Soluble fractions of the tars in toluene (TS) were obtained following the standard method ISO 6376 (2 g of sample:100 ml toluene at 90–100 °C), with the solution filtered through a filtering crucible with a pore size of 10–16 μm. Extractions with CS₂ were

carried out at room temperature in an ultrasonic bath (2 g of sample:40 ml of CS₂) and the solution was filtered through a PTFE filter with a pore size of 0.45 μm using vacuum filtration. After filtration, the solvent (toluene and CS₂) was removed from the filtrate in a rotary evaporator at reduced pressure. Both insoluble and soluble fractions were dried until constant mass.

2.3. HPLC analyses of soluble fractions

For HPLC analyses, the soluble fractions in toluene and CS₂ of the tars studied were solubilized in dichloromethane at a concentration of about 0.6 mg/ml. A 5 μl sample, previously filtered, was injected into a Hewlett-Packard HP1100 system which incorporates two PLGel columns (300 mm×

Table 3
Main characteristics of coal tars produced at different carbonization conditions in different coke ovens

Tar	C/H ^a	QI (%, w/w) ^b	TI (%, w/w) ^b	β-Resin (%, w/w) ^c	CS ₂ -I (%, w/w) ^b	Pitch yield (%, w/w) ^d
Industrial tars						
LT-AV	1.23	5.4	6.7	1.3	6.3	nd
HT-AV	1.68	4.7	9.1	4.4	8.2	nd
LT-GI	1.33	1.8	4.9	3.1	5.2	nd
HT-GI	1.55	1.1	5.3	4.2	5.1	nd
Semi-industrial tars from wet charging						
LT-IN	1.28	2.3	5.1	2.8	6.8	47.7
HT-IN	1.35	2.2	5.0	2.8	6.7	48.7
Semi-industrial tar from preheated charging						
PT-IN	1.41	7.6	11.1	3.5	12.5	56.3

^a, ^b, ^c, ^d: See corresponding footnotes in Table 2.

nd: Not determined.

Table 4
Main characteristics of coal-tar pitches from tars obtained from blends containing polyethylene wastes

Pitch	C/H ^a	QI (%, w/w) ^b	TI (%, w/w) ^b	β-Resin (%, w/w) ^c	CS ₂ -I (%, w/w) ^b	β-Resin formed (%, w/w) ^d
PB	1.74	3.9	26.7	22.8	23.1	19.7
PB1LDPE	1.73	2.8	26.3	23.5	23.3	20.0
PB3LDPE	1.82	11.5	34.4	22.9	29.3	16.7
PB1HDPE	1.86	4.9	30.8	25.9	27.4	21.2
PB3HDPE	1.78	9.0	32.1	23.1	27.9	17.0

^a, ^b, ^c: See corresponding footnotes in Table 2.

^d: Estimated amount of β-resin formed during the distillation process of the crude tar.

7.5 mm I.D.) packed with polystyrene–divinylbenzene of different nominal pore sizes (500 and 100 Å, respectively) and connected in series. The mobile phase was dichloromethane–methanol (9:1, v/v) at a flow-rate of 1 ml/min. A diode array detector operating at a wavelength of 254 nm was used. Based on previous studies [27], the 254 nm wavelength was shown to be appropriate for the different classes of PACs present in tars and pitches. The HPLC method applied allows a separation of *cata*- and *peri*-condensed PACs occurring in tars and derived pitches. The so-called “characteristic graph” or “skeleton graph”, where the centers of the rings of a given PAC are joined by a line, is used to classify these two classes of PACs [35]. *Cata*-condensed structures have a tree (open graph) as the characteristic graph and they include non-branched and branched systems. If the characteristic graph includes a cycle (close graph) the PAC is classified as *peri*-condensed structure. The latter can be further divided into alternant systems containing only six-membered rings and non-alternant systems containing at least one five-membered ring in the structure [36]. Fig. 1 displays some examples of the characteristic graph of selected PACs

The entire group of *cata*-condensed PACs eluted between 12 and 19.8 ml and it can be further divided into three groups—*cata*1, *cata*2 and *cata*3—with the following intervals of elution volume (V_r) and assignments. The *cata*1 group with V_r in the region between 12 and 17.9 ml is mainly composed of heteroaromatics and compounds substituted with alkyl, aryl and heteroatomic (OH, NH, Ar–O–Ar, etc.) groups. The *cata*2 (V_r =17.9–19.1 ml) mainly contains alkyl- and aryl-substituted PACs together to hydroaromatic and naphthenic compounds, while the

*cata*3 (V_r =19.1–19.8 ml), mainly consists of unsubstituted planar polynuclear aromatic hydrocarbons (PAHs). An elution volume greater than 19.8 ml was assigned to *peri*-condensed compounds. Furthermore, a division of this chromatographic region into two groups—*peri*1 (V_r =19.8–20.8 ml) and *peri*2 (V_r >20.8 ml)—with the elution volume increasing can provide an idea of the degree of condensation and molecular mass of this PAC class. Fig. 2 summarizes the assignments for the different PAC classes and the elution volume intervals, which were established on the basis of a previous work using 80 standard PACs with molecular masses ranging from 78 to 533 amu and with different functionalities, commonly present in tars and pitches [27]. Taking into account that no significant differences were found from the response factors of one fraction to another, the integration area under the five major elution regions of the chromato-

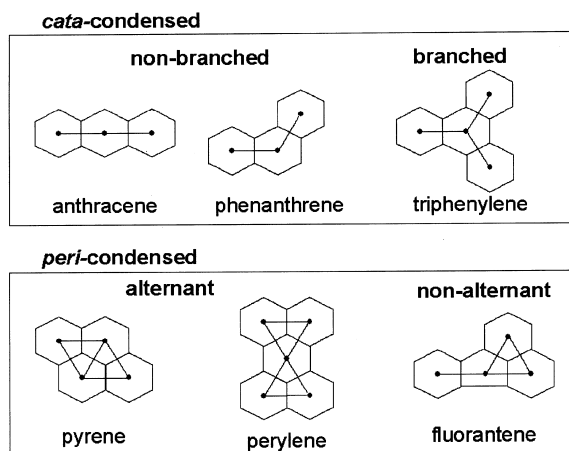


Fig. 1. Schematic representation of the characteristic graphs of some selected PACs.

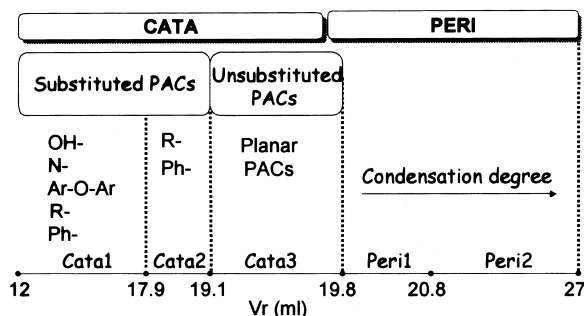


Fig. 2. Elution volume for different classes of PACs.

grams was considered for a quantitative analysis, assuming response factors of unity for all the fractions. A detailed description of the optimization of this method has been previously reported [27].

3. Results and discussion

3.1. Effect of polyethylene wastes addition on tar composition

The main characteristics of the tars produced using both polyethylenes (LDPE and HDPE) as additives in the carbonization process with a coal blend, determined by standard methods, are summarized in Table 2. It can be seen that the content of material insoluble in organic solvents (quinoline, toluene and CS_2) of the two tars produced at 1% (w/w) LDPE and HDPE addition is very similar to that produced from the coal blend without plastic waste addition (tar B). However, blends containing plastic waste at 3% (w/w) produced an increase in the insoluble material of the tars that is accompanied by an increase in the yield of pitch obtained by a laboratory-distillation process. The C/H atomic ratio increased with increasing polyethylene addition, suggesting a higher condensation degree of the aromatic units in tars.

Although quinoline is one of the most powerful organic solvents used in tar and pitch characterization for industrial applications, the quinoline extracts were not selected for HPLC analysis because of the difficulty in total removal of the solvent and the partially solubilization in dichloromethane of this fraction. This is not the case of toluene and CS_2 ,

which are more handy solvents and they are also able to extract a high percentage of the whole tar (>90%). By these reasons, toluene and CS_2 soluble fractions (TS and CS_2 -S) were selected for the study on the distribution of the different classes of PACs by HPLC. Other reasons support the selection of the two solvents. On the one hand, toluene together with quinoline are the most extended solvents used in tar and pitch standardized characterization; and, on the other hand, CS_2 is an adequate non-aromatic and non-containing hydrogen solvent to be used in tar and pitch characterization, having similar extraction power to toluene and dichloromethane.

Figs. 3 and 4 show, as an example, the HPLC profiles of the TS and CS_2 -S fractions, respectively, corresponding to the tar produced from the single coal blend (B) and those obtained using LDPE and HDPE as additives in the coal blend at a proportion of 3% (w/w). No qualitative differences can be distinguished between the profiles of the tar soluble fractions. In all cases, the HPLC profiles comprise a major peak centred at an elution volume of about 19.4 ml in the region which is assigned to unsubstituted planar *cata*-condensed compounds (*cata3*). To assess quantitative differences, the proportion of the different classes of aromatic compounds in the tar TS and CS_2 -S fractions are given in Table 5. As far as these fractions are concerned, differences in composition of fractions in both solvents corresponding

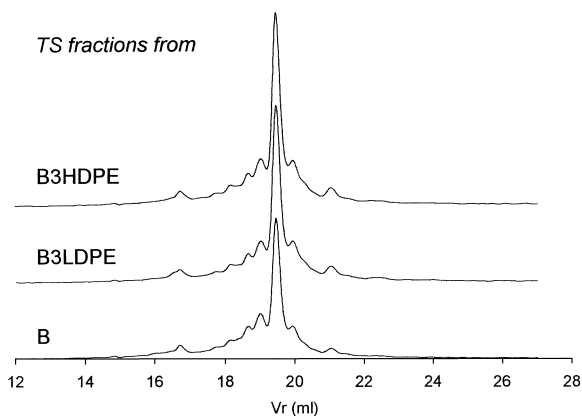


Fig. 3. HPLC chromatograms of the toluene soluble (TS) fractions of tars produced from the coal blend (B), the coal blend with low-density polyethylene waste at 3% (w/w) (B3LDPE) and the coal blend with high-density polyethylene waste at 3% (w/w) (B3HDPE).

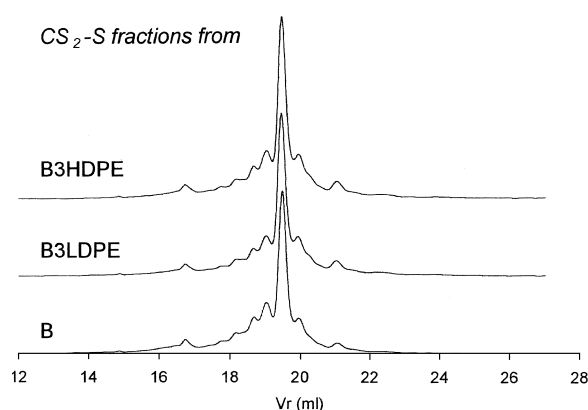


Fig. 4. HPLC chromatograms of the carbon disulfide soluble (CS_2 -S) fractions of tars produced from the coal blend (B), the coal blend with low-density polyethylene waste at 3% (w/w) (B3LDPE) and the coal blend with high-density polyethylene waste at 3% (w/w) (B3HDPE).

to a given tar are not significant and they are in the limit of experimental error. As the data clearly show that TS and CS_2 -S fractions are comparable in composition, the same considerations can be drawn for the effects of plastic waste additions. Both fractions are rich in total *cata*-condensed PACs (72–80% of the fraction) and, in particular, in unsubstituted *cata*-condensed PACs (34–38%). On the contrary, heteroaromatics and PACs with alkyl, aryl and heteroaromatic groups as substituents falling in the region of *cata1* are in a much lower proportion (13–16%). The contribution of total *peri*-condensed compounds accounts for 20–28% depending on the

tar origin and PACs eluting in the region of *cata2* are of a similar order (21–28%).

When comparing to the soluble fraction of tar produced from the single coal blend (tar B), no clear effect can be observed in the distribution of PACs classes in the soluble fractions of tars produced with an addition of polyethylene waste at 1% (w/w) (B1LDPE and B1HDPE). However, by increasing the levels of addition of LDPE and HDPE up to 3% (w/w) (B3LDPE and B3HDPE), the compositional changes are more evident. They are characterized by a decrease in the proportion of the *cata*-condensed PACs having alkyl- and aryl-groups as substituents and hydroaromatic compounds (*cata2*) as well as by an increase in the *peri*-condensed PACs with higher condensation degree (*peri2*). Although in a less extent, a slight decrease in the heteroaromatic compounds and PACs with different functional groups (*cata1*) can be also observed.

As a coking coal or a blend of coking coals is heated up to 1000 °C in an inert atmosphere it undergoes a series of depolymerization and decomposition reactions via free radicals resulting in the evolution of gas and condensable vapours and leaving behind a solid residue of high carbon content (coke). The chemical reactions are accompanied with the ability of coking coals to soften at a temperature between 350 and 400 °C, become plastic upon heating, swell, coalesce to form a coherent mass and then resolidify at a temperature of about 500 °C into a green coke or semicoke [37]. Among other factors, the degree of plasticity or fluidity and swelling

Table 5

Proportion of different classes of PACs in the TS and CS_2 -S fractions of tars produced from coal blends containing polyethylene waste

Tar	Cata1	Cata2	Cata3	Peri1	Peri2	Σ Cata	Σ Peri
Toluene soluble (TS) fraction							
B	15.6	28.1	35.9	12.7	7.7	79.6	20.4
B1LDPE	16.1	27.7	34.5	13.1	8.6	78.3	21.7
B3LDPE	13.1	21.3	38.1	14.7	12.8	72.5	27.5
B1HDPE	14.7	27.0	36.6	13.3	8.4	78.3	21.7
B3HDPE	13.9	21.3	37.2	14.2	13.4	72.4	27.6
CS_2 soluble (CS_2 -S) fraction							
B	16.3	27.8	35.8	12.4	7.7	79.9	20.1
B1LDPE	16.5	28.3	34.1	12.9	8.2	78.9	21.1
B3LDPE	13.2	21.5	37.3	14.9	13.1	72.0	28.0
B1HDPE	14.6	27.6	37.1	13.0	7.7	79.3	20.7
B3HDPE	13.3	22.6	36.9	14.7	12.5	72.8	27.2

during the carbonization process of a given coal or blend of standard particle size is the dominant property upon which the formation of coke and tar depends. It is therefore during the fluid stage of coal, generally taking place between 400 and 500 °C, that the most of the tar recovered in the process is produced [37]. The use of polyethylene waste as an additive to a coking coal modifies the fluidity development, producing a decrease in the maximum fluidity reached in the co-carbonization system [13]. This may be due to the nature and the amount of volatile matter released by the plastic waste at this stage of the process, which may be caused a competitiveness between the free-radicals derived from the plastic waste and the coal by the hydrogen present in the co-carbonization system [10,13]. In addition, the moment at which the maximum volatile matter released takes place is another important factor to be considered [10]. Thus, the plastic layer of coal when polyethylene is present in the co-carbonization system is more viscous (low fluidity) and it is expected that the residence time of the gas and condensable vapours increases due to the difficulty to escape from the zone occupied by the coke-coal mass in the oven. As a result, the primary volatile matter gives rise to a larger extent of secondary dealkylation and aromatic condensation reactions that produce: (i) a reduction in the amount of heterocyclic compounds and PACs substituted with different types of substituents (alkyl-, aryl- and N, O and S functionalities) (cata1 and cata2 classes); (ii) the formation of *peri*-condensed PACs which are soluble in toluene and CS₂; and, (iii) the formation of high-molecular-mass (HMW) compounds which are insolubles in quinoline (QI) and those which are soluble in quinoline, but insoluble in toluene (β -resins). These effects are clearly observed in Fig. 5, which represents the difference between the relative amount of a given PAC class or solvent fraction of a tar produced with polyethylene addition and the tar B taken as a reference. The greater differences account for the tars produced when both polyethylene wastes, LDPE and HDPE, are added to a proportion of 3% (w/w).

To assess these effects caused by the addition of polyethylene waste on tar composition, tars produced from industrial coal blends without any waste addition under different carbonization conditions, which

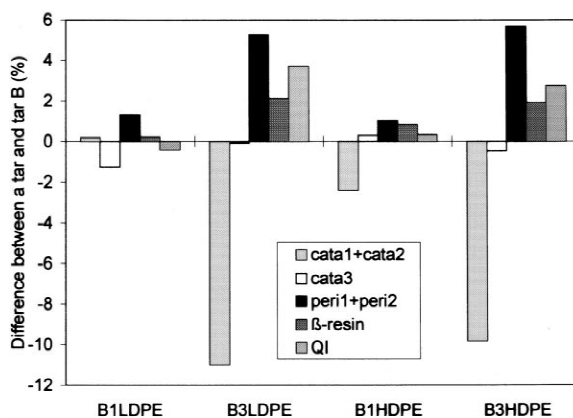


Fig. 5. Variation of the composition of tars produced from the coal blend containing polyethylene waste, showing the differences in the distribution of PAC classes in the toluene soluble fraction and the amount of the insoluble fractions respect to tar B.

are applied in the process at industrial scale (carbonization temperature and coking time), were also studied by HPLC. For comparison purposes, a tar produced from a preheated charge and then carbonized at semi-industrial scale is also included.

3.2. Effect of the carbonization temperature on tar composition

Table 3 shows the main characteristics of tars produced at industrial and semi-industrial scales. Industrial tars, LT-AV and HT-AV, were produced in the same coking plant, but using different carbonization temperature and time. The coal blends used for tar production were similar in terms of volatile matter content, fluid properties and maceral composition to that used for blending with polyethylene waste. This means that differences in tar composition should be more related to the carbonization conditions applied in the process than a consequence of the composition of the coal blend used. The increasing mean flue temperature and the reduction of the coking time leads to a slight decrease in QI, an increase in TI, β -resin and CS₂ contents and an increase in C/H atomic ratio. In general, tars LT-GI and HT-GI seem to follow the same trend. Semi-industrial tars produced from wet charges and at different carbonization temperatures and times (LT-IN and HT-IN), however, have similar contents of

insoluble material in organic solvents and they only differ in the C/H atomic ratio.

The CS₂-S fractions of these series of tars were subjected to HPLC analysis and similar profiles to those presented in Fig. 4 were obtained. The quantitative data are shown in Table 6. The increase in *peri*-condensed PACs, in particular PACs having higher degree of condensation and molecular mass (*peri*2), is a common feature when comparing tars produced in the same industrial and semi-industrial coke oven, but increasing the carbonization temperature at which the tar was produced. Such a view agrees with previous studies on the evaluation of PACs of the volatile fraction of CS₂ extracts of tars ranging from indene to coronene by capillary gas chromatography with flame ionization detection, GC–FID [31]. It suggests that the total soluble fraction of tars produced at a higher carbonization temperature have the same feature than the chromatographed and volatilized fraction which was analysed by GC–FID.

In addition, an increase in the carbonization temperature also produces a decrease in the amount of *cata*2 and *cata*3, the latter being more evident for the tar HT-AV.

The compositional changes induced by an increase in the carbonization temperature may be regarded as a consequence of secondary pyrolysis reactions of tar precursors in the free-space of the oven (area of the oven not occupied by the charge) and the residence time in the coal-coke mass leading to: (i) a higher amount of high-molecular-mass compounds in the β -resin fraction by aromatic condensation reactions,

with the exception of semi-industrial tars (Table 3); and (ii) a higher amount of *peri*-condensed PACs at expenses of the PACs with or without alkyl- and aryl-groups as substituents (Table 6). It is important to point out that semi-industrial tars do not have a higher content of the β -resin fraction, probably due to the smaller dimensions of the oven used.

3.3. Effects of coal preheating on tar composition

Considerable differences in conventional parameters are apparent between tar produced from the preheated charge (PT-IN) and those produced by wet charging, LT-IN and HT-IN (Table 3). It has been demonstrated that the higher QI content in tars produced by preheated charges is a consequence of the major contribution of the greater carryover of coal generated during and immediately after charging the preheated coal blend in the coke oven together with a minor contribution of the aromatic condensation reactions taking place during the carbonization process [29,38,39]. Preheating of the charge produced a tar with a higher C/H atomic ratio and a higher pitch yield by distillation process than those produced from wet charges.

As regards the distribution of PACs in the soluble fraction in CS₂, the use of coal preheating produced significant differences, which are apparently greater than expected from the mean flue temperature at which this tar was produced (1200 °C). Comparing to tars LT-IN and HT-IN, the coal preheating process before carbonization may enhance dealkylation reactions giving rise to a decrease in the substituted

Table 6
Proportion of different classes of PACs in the CS₂-S fractions of tars produced at different carbonization conditions and coke ovens

Tar	Cata1	Cata2	Cata3	Peri1	Peri2	Σ Cata	Σ Peri
Industrial tars							
LT-AV	13.2	25.0	40.2	12.4	9.2	78.4	21.6
HT-AV	14.3	23.6	35.6	14.8	11.8	73.4	26.6
LT-GI	14.1	25.8	37.8	13.7	8.7	77.6	22.4
HT-GI	15.2	23.2	36.3	14.9	10.4	74.7	25.3
Semi-industrial tars from wet charging							
LT-IN	17.4	20.7	38.5	14.2	9.2	76.6	23.4
HT-IN	17.3	19.4	37.6	14.3	11.4	74.3	25.7
Semi-industrial tars from preheated charging							
PT-IN	12.0	17.7	43.5	16.4	10.3	73.3	26.7

PACs (cata1 and cata2) which is accompanied by an increase in planar unsubstituted PACs (cata3) and does not have a large effect upon the *peri*-condensed PACs (Table 6).

Taking into account that the preheated coal charge is more compact, it progresses more uniform and its plastic layer is less fluid, the residence time of primary volatile matter would be greater than for the wet charging. In such conditions, as in the case of the incorporation of polyethylene waste, cracking gives rise to more of the unsubstituted PACs and less substituted PACs in the tar recovered. However, it could be said that in the case of coal preheating, the secondary reactions taking place are more likely to occur with formation of unsubstituted *cata*-condensed PACs, whereas PACs with different molecular topology (*peri*-condensed) are more likely to be formed when plastic waste is present in the co-carbonizing system.

3.4. Relevance of polyethylene wastes addition to pitch composition

Table 4 shows the main characteristic of pitches obtained by a laboratory-distillation process. Pitches were produced with a similar softening point (95 ± 2 °C) in order to avoid differences in composition caused by a more or less severity in the obtaining process. As for the parent tars, the QI, TI and CS₂-I contents of the pitches derived from tars B3LDPE and B3HDPE are quite different to that of pitch B. The higher amount of QI material in pitches does not correspond to new QI formed during the distillation process of the parent tar, because experimental and estimated values are very closed. However, the increase in TI is due to an increase in β -resin during the distillation process at a final temperature of about 340 °C. The formation of such compounds depends on the nature and proportion of thermal reactive compounds in the tar which are suitable to form oligo-aryl systems [23]. Differences between experimental and estimated values suggest a lower ability of the pitches PB3LDPE and PB3HDPE to form β -resin.

The HPLC profiles of the CS₂-S fractions of the pitches PB, PB3LDPE and PB3HDPE (Fig. 6) clearly show the similarity among them and the different profile to those corresponding to the parent

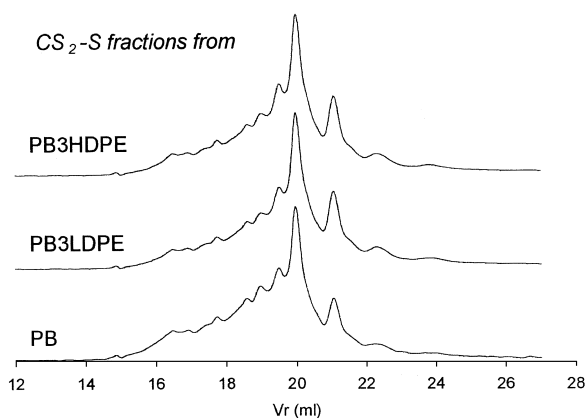


Fig. 6. HPLC chromatograms of the carbon disulfide soluble (CS₂-S) fractions of pitches obtained from tars produced from the coal blend (PB), the coal blend with low-density polyethylene waste at 3% (w/w) (PB3LDPE) and the coal blend with high-density polyethylene waste at 3% (w/w) (PB3HDPE).

tar (Fig. 4). It can be deduced a higher relative intensity in the elution volume interval corresponding to *peri*-condensed PACs ($V_r > 19.8$ ml). The data in Table 7 confirm that the total *peri*-condensed PACs are predominantly constituents in all the soluble fractions (46–55%).

As regards the effect of polyethylene waste addition, the distribution of PACs of pitch PB1LDPE is unaffected, while PB1HDPE shows small differences in the relative proportion of substituted *cata*-condensed and *peri*-condensed PACs. As for the parent tars, the higher amount of *peri*-condensed PACs at expenses of the substituted *cata*-condensed PACs is more prominent for pitches PB3LDPE and PB3HDPE. This is clearly observed in the variations of the different PACs classes, the β -resin and QI contents with respect to the reference pitch PB (Fig. 7).

4. Conclusions

The HPLC analysis applied offers an useful technique to determine different PACs classes such as substituted and unsubstituted *cata*-condensed and *peri*-condensed PACs as well as to establish the compositional changes in the tar and pitch fractions which can be solubilized in an organic solvent with

Table 7

Proportion of different classes of PACs in the CS₂-S fractions of pitches from tars obtained from blends containing polyethylene wastes

Pitch	Cata1	Cata2	Cata3	Peri1	Peri2	ΣCata	ΣPeri
PB	20.2	21.7	11.4	28.5	18.2	53.3	46.7
PB1LDPE	19.9	21.8	11.4	28.5	18.4	53.1	46.9
PB3LDPE	14.4	17.8	12.7	30.7	24.4	45.9	55.1
PB1HDPE	18.6	19.9	10.8	30.7	20.0	49.3	50.7
PB3HDPE	15.3	17.8	12.3	31.0	23.6	45.4	54.6

high extraction ability. No appreciable changes in the distribution of PACs in the soluble fractions of tars produced from blends containing 1% (w/w) of polyethylene could be observed. The coal can tolerate this amount of polyethylene without appreciable modification in tar composition. However, it does not occur when a higher amount of polyethylene is added. The reduction of the fluidity of the co-carbonization system produced a heavier tar, by increasing the amount of the *peri*-condensed PACs and by reducing the amount of substituted *cata*-condensed PACs. The effect could be comparable to that produced by an increase in the carbonization temperature with decreasing coking time and by using the preheating of coal around 215 °C before carbonization. The differences in composition found for the soluble fractions of tars using HPLC are also present in the soluble fractions of the derived pitches.

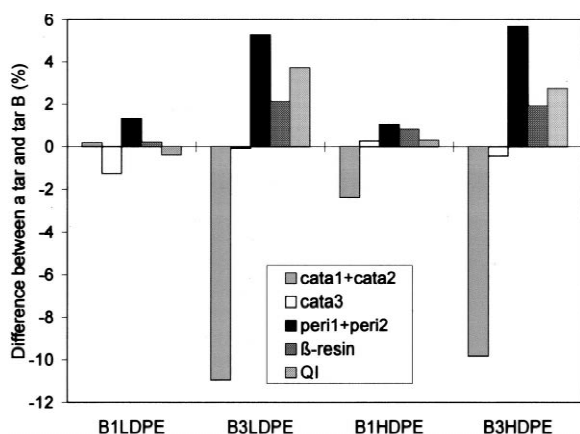


Fig. 7. Variation of the composition of pitches produced from the coal blend containing polyethylene waste, showing the differences in the distribution of PACs classes in the toluene soluble fraction and the amount of the insoluble fractions respect to pitch PB.

Acknowledgements

The authors are grateful for the financial support of CICYT (Project AMB97-0712) and ECSC (Project 7220-PR041). The support of Repsol Química S.A. who provided the plastic wastes and Aceralia who provided the coal blend and industrial tars is also acknowledged.

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