Gas chromatographic study of the volatile products from co-pyrolysis of coal and polyethylene wastes ☆

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Abstract

The aim of this study was to determine the volatile products distribution of co-processing of coal with two plastic wastes, low-density polyethylene from agriculture greenhouses and high-density polyethylene from domestic uses, in order to explain the observed decrease in coal fluidity caused by polyethylene waste addition. Polymeric materials, although they are not volatile themselves, may be analysed by gas chromatography through the use of pyrolysis experiments. In this way, a series of pyrolysis tests were performed at 400 and 500°C in a Gray-King oven with each of the two plastic wastes, one high-volatile bituminous coal and blends made up of coal and plastic waste (9:1, w/w, ratio). The pyrolysis temperatures, 400 and 500°C, were selected on the basis of the beginning and the end of the coal plastic stage. The organic products evolved from the oven were collected, dissolved in pyridine and analysed by capillary gas chromatography using a flame ionization detector. The analysis of the primary tars indicated that the amount of n-alkanes is always higher than that of n-alkenes and the formation of the alkenes is favoured by increasing the pyrolysis temperature. However, this effect may be influenced by the size of the hydrocarbon. Thus, the fraction $C_{17}-C_{31}$ showed a higher increase of n-alkenes/n-alkanes ratio than other fractions. On the other hand, the difference between the experimental and estimated values from tars produced from single components was positive for n-alkanes and n-alkenes, indicating that co-pyrolysis of the two materials enhanced the chemical reactivity during pyrolysis and produced a higher conversion than that from individual components. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nowadays, plastic waste has become an increased problem in many industrialized countries. Environ-mental protection requires increased recycling and reutilization instead of being landfilled or inciner-ated. High costs of pollution control for incinerators and the decreasing acceptance of this method in waste management demands for alternative treatment of plastic wastes where they are considered as an additional resource of energy and chemical raw materials [1–4]. Currently, alternative plastic waste recycling by methods others than combustion, me-chanical and classical chemical process is of great interest, especially if plastic waste can be incorpo-

rated into existing industrial processes [5–8]. In this sense, integrated steel plants may contribute to expand plastic recycling by the blast-furnace route where plastic waste is injected into the blast-furnace as a fuel. After considering theoretical studies on combustibility and environmental impact of plastic waste into blast furnaces, this recycling route has reached industrial application [6–8]. Another alternative approach to upgrade plastic waste could be achieved through the utilization of plastic waste as a minor component of coal blend for metallurgical coke production to be used in the blast furnace. Recently, the exploration of this new alternative route has become of great interest to have several recycling options available for the plastic wastes collected from different post-consumer sources [8–11]. Recent industrial trials at Kimutsu coke ovens by incorporating a poly(vinyl chloride)-free mixture of plastic waste as minor component in coal blend makes this new approach to be quite promising for the near future [8].

In addition to the above-described industrial processes, another way to recycle plastic waste has been focused to an efficient conversion of plastic waste with coal or oil shales into hydrocarbon fuels or other valuable products such as lubricants [12–17]. It has been suggested that the addition of plastic waste may enhance coal conversion due to the hydrogen-rich character of the polymers [12,13].

During the carbonization process carried out in an inert atmosphere, the polymeric structure of plastics is broken down, producing smaller intermediate species, which can further react and produce smaller hydrocarbon molecules, liquids and gases [18–21]. The formation of such hydrocarbons could modify the thermal behaviour of coal, especially in the critical stage of the metallurgical coke formation at high temperature. This stage of the carbonization process occurs in the temperature interval between 400 and 500°C, when the coal exists in the form of a plastic phase that finally resolidifies to give a semicoke, which is then transformed to coke [22–24]. The molecular species that evolved in the temperature range between 400 and 500°C are responsible for maintaining a fluid system and play a fundamental role in the development of coke properties [25–30]. When coal starts to soft, molecular fragmentation produces the release of small mole-

cules, which are donor hydrogen-rich species, already present in the coal macromolecular network. They act to stabilize free radicals from thermal decomposition and to convert them into 'solvating' molecules. As the carbonization temperature increases, an increase in the production of radical fragments takes place together with an increase in the fluidity. If these radicals are highly reactives and they are not stabilized by hydrogen transfer reactions, they may recombine with other molecules and, then, a viscous (low fluid) system is formed. As a result the structure of the resulting carbon material is more disordered. However, when the free radicals are moderately reactive and stabilized by hydrogen transfer reactions, low-molecular-mass molecules keep the system at an optimum fluidity level. Consequently, growth and orientation of the aromatic molecules take place and a more ordered anisotropic carbon material is obtained. The formation and the effective stabilization of free radicals by hydrogen transfer are influenced by chemical composition of the raw materials. The incorporation of additives to the system modifies the available transferable hydrogen in the co-carbonization system. A high chemical activity of additives for enhancing fluidity can be related to the presence of molecules, which exhibit high hydrogen donor ability, such as hydroaromatic rings. So far our attention has been focused on how specific plastic waste influences the fluid stage of a given coal and the relevance of volatile products derived from the plastic waste in this critical stage of the process. The plastic wastes selected for this study are two polyethylenes from specific uses, low-density polyethylene (LDPE) from agriculture greenhouses and high-density polyethylene (HDPE) from bottles range from milk bottles to highly pigmented liquid detergent bottles. The latter constitutes more than 30% (w/w) of the overall post-consumer flow in municipal waste [4].

The use of gas chromatography with flame ionization detection (GC–FID) can provide relevant information not only about the composition of primary tars evolved in the pyrolysis process such as the concentration of each individual compound and the distribution of the different families, but also about components which can be relevant in the development of coal plasticity in the presence of plastic waste. GC–FID has also been successfully applied in

the study of coking additives such as tar, pitch and waste materials derived from by-products of coking plants [30].

2. Experimental

2.1. Materials

The plastic wastes used in this study were agglomerated LDPE from agriculture greenhouses and laminated HDPE from bottles of domestic uses, and they were provided by Repsol Química. For the preparation of blends, a bituminous coal SF with 31.5% (w/w) dry basis (db) volatile matter and a Gieseler maximum fluidity of 9754 ddpm was selected. The binary blends (SF10LDPE and SF10HDPE) were prepared on the basis of coal SF with 10% (w/w) of each plastic waste by a mechanical method.

2.2. Coal plasticity

To evaluate the apparent fluidity of the coking coal SF and its blends with 10% (w/w) of plastic waste, a constant-torque Gieseler plastometer was used, which is described in the standard procedure ASTM D2639-74. Briefly, a compacted 5 g of coal and blends 90:10 (w/w) with a particle size <0.425 mm were heated over a temperature range from 300 to 550°C at a constant rate of 3°C/min and subjected to a constantly applied torque on a stirrer placed in a crucible into which the coal/blend was charged. The rates of movement of the stirrer were recorded in relation to increase in temperature and expressed as dial divisions per minute (ddpm). The parameters derived from this test are: (i) softening temperature, the temperature at which the blend starts to be fluid and the stirrer rotation reaches 1 ddpm; (ii) the temperature of maximum fluidity, the temperature at which stirrer rotation rate reaches a maximum value; (iii) resolidification temperature, the temperature at which the fluid mass resolidifies and the last stirrer rotation is observed; (iv) plastic range, which is defined as the difference between the resolidification and softening temperatures; and (v) maximum fluidity, the measured maximum stirrer rotation rate reported as ddpm.

2.3. Thermogravimetric analysis

The blends and single components (coal and plastic waste) were subjected to thermogravimetric analysis (TG) in a Perkin-Elmer TGA7 thermobalance. A sample of about 20 mg of sample was heated at a rate of 3°C/min from room temperature to 1000°C. A nitrogen flow of 95 ml/min was used to sweep out the volatile products. The equipment gave a continuous automatic recording of mass loss and the derivative of the mass loss (DTG). The following parameters are used in this study: the temperatures at which the mass loss was 2 and 98% (T_{ini} and T_{fin}, respectively); the temperature interval of volatile matter released (ΔT); the temperature at which the maximum release of volatile matter take place on the basis of DTG curve (T_{max}) and the percentage of the volatile matter released (VM) at different temperature intervals.

2.4. Pyrolysis experiments

Pyrolysis tests were carried out in a Gray-King apparatus according to the standard procedure ISO502. For each pyrolysis test, a sample of 10 g (<1 mm in size) was placed in a quartz reactor (250 mm length and 20 mm internal diameter), which was heated in a horizontal electrically heated oven at 5°C/min to final temperatures of 400 and 500°C in the atmosphere of evolved gases and without soaking time. Volatile products after leaving the reactor were collected; firstly, in a trap cooled by an ice–salt bath (primary tar) and in a gas bag (gas). Primary tars were separated from the water decomposition by decantation and were dissolved in pyridine (20 mg sample:1 ml solvent) for chromatographic analysis. Pyridine was selected as solvent to ensure a complete dissolution of the sample. In the case of pyrolysis of single plastic waste, oil and wax were collected in the on-line trap and they are also referred as primary tars. The solid residue was removed from the oven after cooling at room temperature.

2.5. Capillary GC–FID analysis

The chromatographic analyses of primary tars produced in the Gray-King oven were carried out on a Hewlett-Packard 5890 Series II gas chromatograph

Table 1

Gieseler maximum fluidity and main temperatures in the development of fluidity of a coking coal and its blends with the plastic waste studied

	SF	SF10LDPE	SF10HDPE
Softening temperature (°C)	394	378	389
Maximum fluidity temperature (°C)	446	444	443
Resolidification temperature (°C)	482	481	484
Plastic range (°C)	88	103	95
Maximum fluidity (ddpm)	9754	4325	4489

equipped with a flame ionization detector. Separations were carried out on a fused-silica capillary column of 25 m×0.25 mm I.D. coated with OV-1701 stationary phase (McReynolds polarity=789). The temperature was programmed from 50 to 290°C at a rate of 4°C/min. Hydrogen was used as the carrier gas at a flow-rate of 1.7 ml/min and a splitting ratio of 1:42 was used. The detector and injector temperatures were 350 and 300°C, respectively, and the volume of sample injected was 1 μl. Chromatographic peaks were identified by comparing retention data of available standards and confirmed by gas chromatography coupled to mass spectrometry (GC–MS).

For quantification, two *n*-alkanes C_{16} and C_{26}, eluting at the beginning and the end of the chromatogram, were selected as external standards. Compounds that elute before C_{20} were quantified using the *n*-alkane C_{16}, meanwhile C_{26} was used for the evaluation of those compounds with a greater retention time than C_{20}. The total percentage of the chromatographed material (CM) was estimated by means of the sum of the peak areas of the two chromatogram regions $<C_{20}$ and $>C_{20}$.

3. Results and discussion

The two polyethylene wastes, LDPE and HDPE, differ in their capacity to modify the plastic properties of coal (Table 1) and the coal thermal behaviour evaluated by TG analysis (Table 2). Data from Table 1 reveals that the addition of polyethylene waste reduces the maximum fluidity of the system and the extent of the reduction is of the order of 55%. In addition, these plastic waste produces a decrease in the softening temperature, no significant changes in the maximum fluidity and resolidification temperatures and, consequently, a wider plastic range.

As regards thermal behaviour, the first point to note is that, although both plastic wastes release the

Table 2

TG and DTG data of the plastic wastes, coking coal SF and their blends

	LDPE	HDPE	SF	SF10LDPE	SF10HDPE
T_{ini} (°C)[a]	372	387	295	306	308
T_{fin} (°C)[b]	463	466	901	786	778
ΔT (°C)[c]	91	79	606	480	470
T_{max} (°C)[d]	448	449	422	453	460
VM400[e]	4.9	3.2	20.1	12.0	10.2
VM400–450 (%, w/w)[e]	68.1	64.8	35.5	38.5	29.9
VM450–500 (%, w/w)[e]	26.1	32.0	15.2	31.2	42.1
VM500 (%, w/w)[e]	0.9	0.0	29.2	18.3	17.8

[a] Temperature at which the mass loss is 2% (w/w).

[b] Temperature at which the mass loss is 98% (w/w).

[c] $\Delta T = T_{fin} - T_{ini}$.

[d] Temperature of the maximum volatile matter released based on DTG curves.

[e] Volatile matter evolved at a specific temperature range and normalized to 100% (w/w).

major amount of volatile matter at a similar temperature near 450°C (T_{max}), HDPE starts the volatile matter generation at a higher temperature and the volatile matter released takes place in a shorter temperature range than LDPE (Table 2). Comparing with the coal itself, polyethylene waste releases the major amount of volatile products at a much higher T_{max} and in a shorter temperature interval (Table 2). T_{max} is close to the temperature at which the maximum fluidity of the carbonization system is achieved (Table 1). As a result of the thermal behaviour of plastic waste, a modification of the amount and the moment of the volatile matter generation of the blends containing 10% (w/w) of plastic waste can be observed. A common feature of the plastic waste addition is a shift in the volatile matter evolution to a stage of the pyrolysis after the maximum fluidity of the system and prior to resolidification (450–500°C). The evolution of volatile products in gaseous form (VM) by an additive to coal is considered a critical stage in the mechanism of carbonization and this phenomenon is associated to the effects on thermoplastic properties of coal. That is, the effectiveness of an additive to modify the co-carbonization system can be related to the quantity and composition of VM released by the additive as well as the stage at which the VM is released (*before*, *during and after the coal plastic stage*) [28–30]. If the release of volatile matter is produced too early, before the coal starts to soften, it leaves the reaction system without contributing to fluidity. This is not the case of the two polyalkenes studied, because the amount of the VM released by the plastic

wastes within the earlier stage of the carbonization process (pre-plastic stage) is very small. However, most of the volatile products from these plastics are released within the range of coal fluidity, but they are not progressively released during the entire plastic range. As mentioned above, plastic waste addition increases the amount of volatile matter released in the temperature range between 450 and 500°C (VM450–500). At least in part, the non-progressive volatile matter released by the plastic waste could explain the modification induced in coal fluidity. However, taking into account that plastic waste is extremely able to reduce coal thermoplastic properties, other factors need to be considered.

It is well known that variations in coal fluidity are controlled by both the physical and chemical phenomena of the reacting system. The chemical phenomenon in this stage is quite complicated due to those reactions taking place simultaneously within the system, i.e., cracking, isomerization, cross-linking and polycondensation reactions [22,25]. Thus, the type of compounds evolved by the additive in the critical temperature range between 400 and 500°C must play an important role in the modification of thermal behaviour of the co-carbonization system and, consequently, in the changes induced in thermoplastic properties of coal.

In an attempt to elucidate how plastic waste affects the development of coal thermoplastic properties, a deeper investigation of the composition of primary tars produced from the single coal SF, the plastic wastes (LDPE and HDPE) and their blends at 400 and 500°C was carried out. The two pyrolysis

Table 3
Yields of products obtained in the pyrolysis experiments in a Gray-King oven

	LDPE	HDPE	SF	SF10LDPE	SF10HDPE
Pyrolysis temperature 400°C:					
Solid (%, w/w, db)[a]	92.2	93.1	92.9	94.5 (92.8)[b]	92.4 (92.9)[b]
Gas (%, w/w, db)[a]	0.5	1.9	3.0	2.7 (2.7)[b]	2.8 (2.9)[b]
Tar (%, w/w, db)[a,c]	7.3	5.0	4.1	2.8 (4.4)[b]	4.8 (4.2)[b]
Pyrolysis temperature 500°C:					
Solid (%, w/w, db)[a]	5.1	9.7	81.7	73.6 (74.0)[b]	72.8 (74.5)[b]
Gas (%, w/w, db)[a]	12.8	8.1	6.5	6.4 (7.1)[b]	6.1 (6.7)[b]
Tar (%, w/w, db)[a,c]	82.1	82.2	11.8	20.0 (18.8)[b]	21.1 (18.8)[b]

[a] db, expressed in a dry basis.

[b] Values in parenthesis refer to the product yield estimated by considering individual components of the blend.

[c] For pyrolysis experiments of LDPE and HDPE, tar means oil or wax.

temperatures were selected on the basis of the beginning and the end of the plastic state of a coking coal (Table 1). The mass balance obtained in the Gray-King pyrolysis experiments carried out at 400 and 500°C is presented in Table 3 together with the estimated yields by considering those from the pyrolysis experiments of individual components of the blend. The results of these experiments employing a slow heating rate show that the major part of the product was solid due to the low decomposition degree at 400°C, while at a higher temperature (500°C) the decomposition of raw materials was more complete and the main products were a solid and some gas and condensable liquid (tar).

At 400°C, estimated and experimental yield values are identical, except for the blend containing 10% (w/w) of LDPE (SF10LDPE). In this case, comparing with the predicted yields LDPE produces a slight increase in coke yield and a decrease in tar yield. For the two blends, the thermal treatment at 500°C seems to promote the release of volatile products as primary tars, indicating that synergism may exist between coal and plastic waste. However, the small differences between estimated and experimental tar yields suggest that synergetic effects should occur in a low degree.

Fig. 1 shows, as an example, the chromatograms of tars produced from pyrolysis of coal SF, HDPE plastic waste and the blend made up of 90% (w/w) coal SF and 10% (w/w) HDPE at 500°C. Although considerable differences are apparent from the GC–FID profiles, a common feature of all tars is the majority of the series of n-alkanes. However, tars produced from the pyrolysis of plastic wastes and blends at 400 and 500°C are characterized by a series of double and triplet peaks, corresponding to the n-alkane, n-alkene and diene having the same number of carbons. The elution order is n-alkane, followed by n-alkene and diene. The relative abundance of each hydrocarbon type is sensitive to pyrolysis temperature and the plastic waste.

In line with the identification of primary tar components, four different families of compounds were established. The first includes n-alkanes, the second and the third include n-alkenes and dienes, respectively, and, finally, the fourth corresponds to substituted alkanes, aromatic and polar compounds. The presence of such hydrocarbons in pyrolysis of
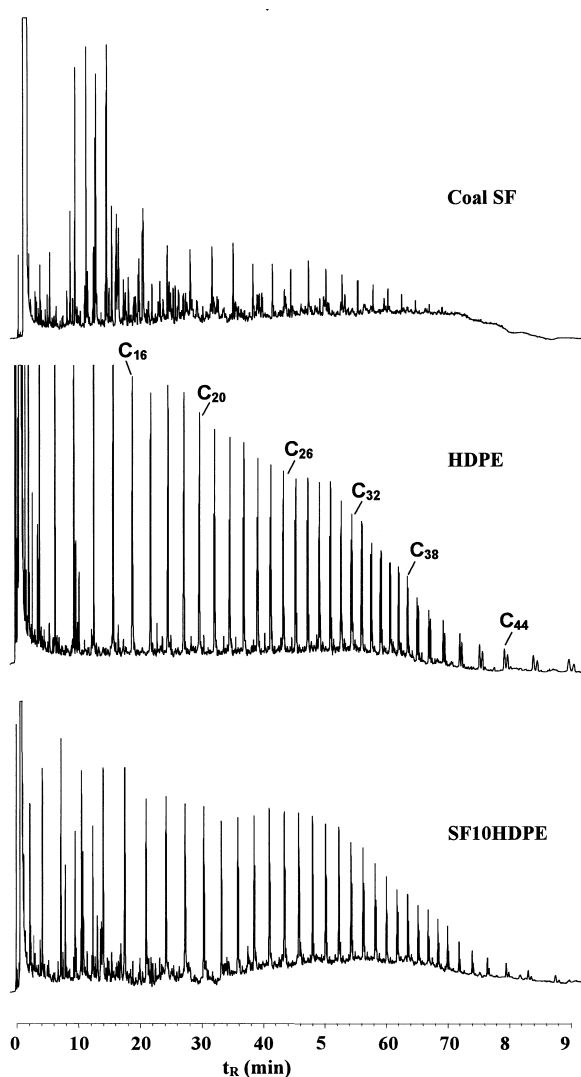

Fig. 1. Capillary gas chromatograms of primary tars produced from pyrolysis of coal SF, plastic waste HDPE and their blend (SF10HDPE) at 500°C.

polyethylenes and coals is in agreement with previous results from other authors [16,17,31–33]. The distribution of these families in the primary tars is given in Table 4 together with the distribution of hydrocarbons classified by carbon number. The percentages of chromatographed material in the tar (CM) and the estimated values for tars from the blends are also presented in Table 4.

In all cases, the total amount of n-alkanes in the primary tars is always higher than that of n-alkenes,

Table 4
Distribution of the different hydrocarbon families in the primary tars

	LDPE	HDPE	SF	SF10LDPE	SF10HDPE
Pyrolysis temperature 400°C					
Σn-alkanes	19.7	23.3	10.7	12.8 (12.2)[a]	12.8 (12.2)[a]
$C_{10}-C_{16}$	3.0	4.0	3.9	3.1	2.6
$C_{17}-C_{31}$	14.0	11.7	6.7	8.8	8.1
$C_{32}-C_{46}$	2.7	7.6	0.1	0.9	2.1
Σn-alkenes	13.5	18.0	0.0	1.1 (2.2)[a]	2.7 (2.2)[a]
$C_{10}-C_{16}$	1.3	0.6	0.0	0.0	0.0
$C_{17}-C_{31}$	10.4	11.9	0.0	1.0	2.2
$C_{32}-C_{46}$	1.7	5.5	0.0	0.1	0.5
Σdienes	1.4	2.7	0.0	0.0	0.0
Others[b]	15.2	10.6	16.2	13.7	12.2
CM[c]	49.8	54.6	26.9	27.6 (30.7)[c]	27.7 (30.1)[a]
Pyrolysis temperature 500°C					
Σn-alkanes	13.9	20.4	8.0	14.0 (10.5)[a]	17.3 (13.4)[a]
$C_{10}-C_{16}$	5.3	9.5	3.8	4.4	5.9
$C_{17}-C_{31}$	5.7	7.7	4.2	7.5	9.2
$C_{32}-C_{46}$	2.9	3.2	<0.1	2.1	2.2
Σn-alkenes	10.4	11.9	0.0	5.0 (4.5)[a]	6.5 (5.2)[a]
$C_{10}-C_{16}$	0.0	0.0	0.0	0.0	0.0
$C_{17}-C_{31}$	7.8	8.9	0.0	3.9	5.3
$C_{32}-C_{46}$	2.6	3.0	0.0	1.0	1.2
Σdienes	1.3	1.9	0.0	0.6	0.5
Others[b]	3.8	3.5	19.5	7.9	8.0
CM[c]	29.4	37.7	27.5	27.5 (28.2)[a]	32.3 (31.9)[a]

[a] Values in parentheses refer to the estimated values by considering individual components of the blend.
[b] Other compounds (aromatic, polar) present in the chromatographed and volatile fraction and different to the three families described.
[c] Chromatographed material of the tars.

the latter compounds being totally absent in tars from the coal SF. In general, the higher contribution to these families of hydrocarbons is of those containing 17–31 carbon atoms in the structure. When individual compounds are considered, the relative abundance of each *n*-alkane in primary tars from blends at the two temperatures tested is always higher than the corresponding *n*-alkene with the same carbon atoms. Figs. 2 and 3 clearly show the relative abundance of *n*-alkanes and *n*-alkenes in primary tars from single components and blends at 400 and 500°C, respectively. The series of *n*-alkanes in the tars from the blends and coal SF present a relative maximum at C_{15}, which is not observed in tars from the pyrolysis of the plastic wastes at 500°C. The latter presents a relative abundance of each *n*-alkane containing 17–31 carbon atoms lower than that of *n*-alkene with the same C-number. In such con-

ditions, the stabilization of the free radicals from the plastic waste by dehydrogenation should be promoted, indicating a clear dependence of the size of the hydrocarbon.

For tars from blends at 500°C, the differences between experimental and predicted amounts of *n*-alkanes and *n*-alkenes are always positive; suggesting that co-pyrolysis of the two materials enhanced chemical reactivity and produced a higher conversion.

On the other hand, the CM of plastics decreases with increasing pyrolysis temperature, while it does not exhibit a major variation for tars from coal SF and its blends, except for tar from SF10HDPE at 500°C. This means that primary tars from plastic waste contain a much higher proportion of heavier hydrocarbons that are not volatilized in the GC analysis.
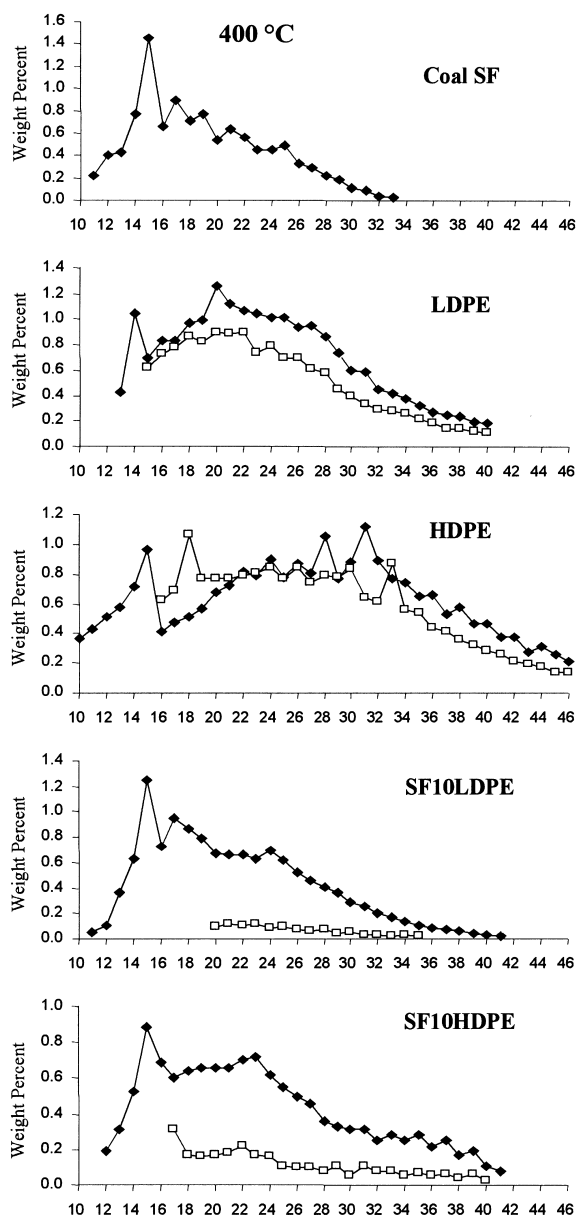
Fig. 2. The *n*-alkanes and *n*-alkenes distribution of primary tars from coal SF, plastic wastes, LDPE and HDPE, and their blends containing 10% (w/w) of plastic waste at 400°C. (♦) *n*-Alkanes; (□) *n*-alkenes.
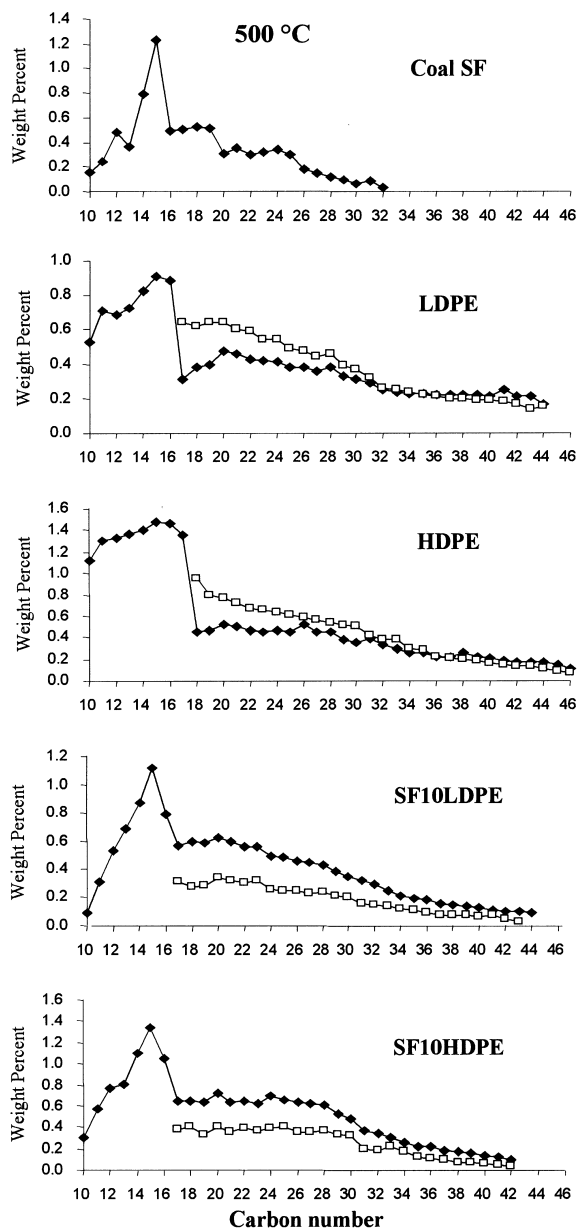

Fig. 3. The *n*-alkanes and *n*-alkenes distribution of primary tars from coal SF, plastic wastes, LDPE and HDPE, and their blends containing 10% (w/w) of plastic waste at 500°C. (♦) *n*-Alkanes; (□) *n*-alkenes.

Turning to the major constituents of primary tars (*n*-alkanes and *n*-alkenes), the ratios between these two types of compounds were calculated (Table 5). From these data, a different formation rate of *n*-alkanes and *n*-alkenes can be deduced for the two plastics. HDPE at 400°C promotes dehydrogenation reactions for the stabilization of free radicals, giving

Table 5
Ratios of the total *n*-alkanes and *n*-alkenes and their fractions by C-number in the primary tars

	LDPE	HDPE	SF	SF10LDPE	SF10HDPE
Pyrolysis temperature 400°C:					
n-Alkenes/	0.69	0.77	0	0.09	0.21
n-alkanes ratio				$(0.18)^{a}$	$(0.18)^{a}$
$C_{10}-C_{16}$ ratio	0.47	0.15	0	0.0	0.00
$C_{17}-C_{31}$ ratio	0.74	1.02	0	0.11	0.27
$C_{32}-C_{46}$ ratio	0.63	0.72	0	0.11	0.24
Pyrolysis temperature 500°C:					
n-Alkenes/	0.75	0.58	0	0.36	0.38
n-alkanes ratio				$(0.21)^{a}$	$(0.39)^{a}$
$C_{10}-C_{16}$ ratio	0.00	0.00	0	0.00	0.00
$C_{17}-C_{31}$ ratio	1.37	1.16	0	0.52	0.58
$C_{32}-C_{46}$ ratio	0.90	0.94	0	0.48	0.55

rise to a higher concentration of *n*-alkenes. By contrast, the stabilization of free radicals derived from LDPE favours the formation of *n*-alkanes. At 500°C, the opposite trend can be observed. In general, there is a trend to increase the *n*-alkene/*n*-alkane ratio for heavier hydrocarbons with 17–31 carbon atoms with increasing temperature. On the other hand, the increase in *n*-alkene/*n*-alkane ratio at 500°C compared to 400°C (Table 5) suggests that dehydrogenation of *n*-alkanes induced by coal-derived acceptor sites can also take place.

The above results lead to the conclusion that the presence of polyalkenes as an additive for carbonization has an influence on transferable hydrogen and free radicals reactions, resulting in an alteration in the carbonization behaviour of coal. Hydrogen donor ability of coking additives has been recognized as an important factor in the enhancement or inhibition of coal fluidity [25,28–30,34]. Coals are considered to be good hydrogen donors and acceptors [25]. Thus, the process of the modification of thermoplastic properties could be probably associated with hydrogen transfer reactions involving movement of hydrogen from the coal, which is available in the co-carbonization system, to stabilize free radicals derived from the polyalkenes and then increasing the amount of *n*-alkanes in primary tars. As the pyrolysis reaction progresses, free radicals derived from the polyalkenes, which continue to be formed, will become stabilized to give *n*-alkenes by β-scission. Dehydrogenation of *n*-alkanes may be induced by

coal-derived acceptor sites. In such conditions, free radicals derived from coal will become stabilized by polymerization and the fluidity of the system will then progressively decrease. The overall balance of stabilization reactions should determine the extent of the reduction in coal thermoplastic properties. This concept is in agreement with the well-established theory that only additives with hydrogen-donating ability can be effective for an increasing of coal thermoplastic properties.

4. Conclusions

Plastic waste addition to coal produces a decrease in the fluidity of the co-carbonization system, the extent of the reduction being influenced by the thermal behaviour of the plastic waste itself and the composition of primary tars. Gas chromatographic analysis of primary tars obtained at 400 and 500°C provides a useful method for elucidating the ability of plastic waste to modify the plastic stage of a coking coal. The modifications induced may be related to competitiveness between the free-radicals derived from the plastic waste and the coal by the hydrogen present in the co-carbonization system. During the plastic stage of the system, coal acts as a hydrogen radical source for the stabilization of the alkyl free radicals from the polyalkenes and, then, increasing the probability of a 'premature' polymerization of coal-derived radicals.

Acknowledgements

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