

Evolution of volatile products of coal and plastic wastes during co-pyrolysis

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Abstract

The aim of this study was to evaluate the pyrolytic characteristics of blends made up of coking coals and several plastics by determining the evolution pattern of selected evolving products during their co-pyrolysis. For this purpose, simultaneous thermogravimetric–mass spectrometric analyses (TG-MS) of the blends were performed by thermal treatment up to 1000 °C in a helium atmosphere under dynamic conditions at a heating rate of 25 °C/min. The plastics used for blending with coal at an addition rate of 5 wt% were: five thermoplastics commonly found in municipal wastes (LDPE, HDPE, PP, PS and PET) and two mixtures with different compositions. Different characteristic ion fragments from selected families of evolving products during the co-pyrolysis process such as hydrogen, aliphatic hydrocarbons with one to four carbon atoms, aromatic hydrocarbons and carbon dioxide were monitored together with their thermogravimetric parameters (temperature, mass) at different times. Hydrogen evolution profiles have similar shapes and the maximum evolution temperature was not greatly affected by the addition of plastic wastes. In contrast, the evolution patterns of aliphatic hydrocarbons (alkanes and alkenes) were characterized by a low temperature of evolution and a high relative proportion of these components. The delay in the decomposition of the plastics together with the changes in the composition of volatiles promoted interactions between the components and had negative effects on coal fluidity.

Keywords: coal, plastic wastes, co-pyrolysis, evolved gas, TG-MS

1. Introduction

Currently, the co-pyrolysis of single or mixed plastics with fossil fuels (coal and petroleum) are being investigated in order to recover chemicals, to partially replace fossil fuels in well-established industrial conversion processes of fossil fuels and to

contribute to the protection of the environment. Among the different routes based on co-pyrolysis, the co-processing of coking coals with plastics from municipal wastes for metallurgical coke production has been implemented at industrial scale [1,2]. The composition of the plastic waste added has been shown to be a critical factor in controlling the effect on the coal thermoplastic properties, coking pressure generation during coking and the structure and properties of metallurgical coke [3-5]. In accordance with the different structure and thermal behaviour of the plastics contained in municipal wastes, opposite effects have been observed: polyolefins which cause a slight decrease in fluid coal properties [6-10], improve or maintain coke strength and reactivity and increase the wall pressure generated during coking up to extremely high values. Aromatic polymers such PET and PS, however, which are the strongest modifiers of coal fluidity, cause a deterioration in coke reactivity towards CO₂, and help to balance the wall pressure [3-5].

The aim of this study is to gain additional information about the interactions between coal and plastics in order to explain the different effects on the fluidity of the coal and the generation of the wall pressure during coking. For this purpose, TG-MS was employed to obtain information on the different events which take place during co-pyrolysis and the chemical composition of the evolved gases.

2. Experimental section

An industrial coal blend, PA, was used to prepare mixtures with several plastics at an addition rate of 5 wt%. The mixed plastic waste Wa was composed of 73 wt% high-density polyethylene (HDPE), 20 wt% polypropylene (PP), 5 wt% polyethylene terephthalate (PET) and 2 wt% cellulose and the mixture Wb was a more heterogeneous waste containing the six thermoplastics: PP, 39.2 %; PET, 18.8 %; PS, 16.6 %; HDPE, 0.7 %; LDPE, 5.4 %; PVC, 1.2 % and 6.9 % of non-identified plastics. Both plastic wastes were provided by the Spanish recycling company Abornasa.

The powdered mixtures (7 g, < 0.212 mm size) were subjected to thermogravimetric-mass spectrometric analysis (TG-MS) in a simultaneous TA Instrument SDT2960 analyzer coupled to a quadrupole mass spectrometer (Balzers, Thermostar GSD-300T) by a fused silica transfer line heated at 200 °C. About 7 mg of the mixtures was heated from room temperature up to 1000 °C at a heating rate of 25 °C min⁻¹ using a helium flow rate of 100 ml/min to sweep out the volatile products. The

evolution of the temperature of the evolved gaseous products and the intensity of the selected ion fragments were monitored together with the thermogravimetric parameters (temperature, mass) at different times.

3. Results and Discussion

The DTG curves of the plastic wastes, the coal blend PA and their mixtures at an addition rate of 5 wt% of the plastics are shown in Figures 1 and 2. The temperature of maximum decomposition of plastics varies in the following order: PS < PET < PP < LDPE < HDPE (Figure 1). The position of the DTG_{max} of the two plastic mixtures, Wa and Wb, are slightly lower than what might be expected from their composition. In the case of Wa (73 wt% HDPE, 20 wt% PP and 5 wt% PET), the T_{max} value is located between PP (475 °C) and PET (449 °C) whereas Wb presents a similar value to that of PET and PS (442 °C), which make up about 35 wt% of the waste.

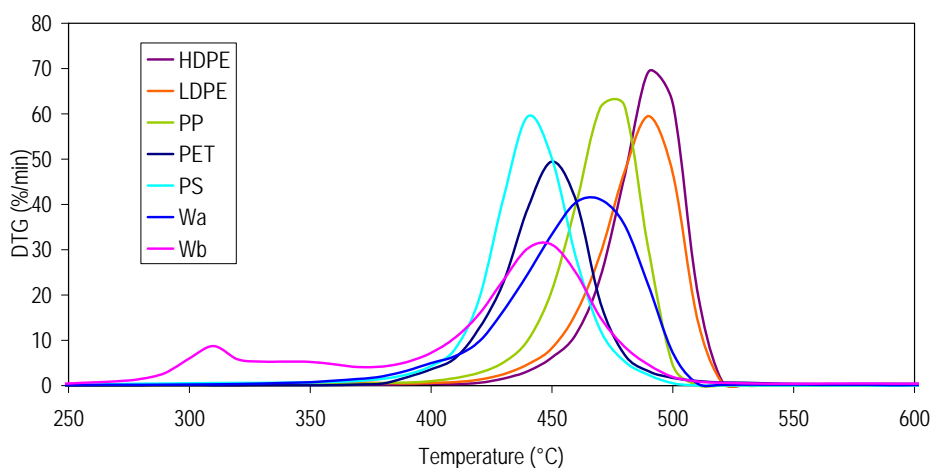


Figure 1. DTG curves of plastic wastes studied.

The DTG profile of the coal blend shows a main peak at about 505 °C, which is also shown in blends containing the three polyolefins (HDPE, LDPE and PP). Under the pyrolysis conditions applied, polyolefins have the narrowest decomposition temperature ranges with a T_{max} inside the thermal degradation of the macromolecular network of the coal, whereas the degradation of PS and PET takes place close to the early stages of coal decomposition (Figure 2). An examination of the DTG profiles of the blends shows that blends with HDPE, LDPE and PP show a single peak at a temperature slightly lower than that of the coal blend PA (495-499 vs. 505 °C). However, when PS and PET are added to coal, these blends present a bimodal evolution of volatiles, with the first peak

being attributed to plastic decomposition and the high-temperature peak to coal devolatilization. When comparing the profiles of the blend and the corresponding plastic, a shift in the evolution of volatiles from the plastic in the blend towards a higher temperature can be clearly observed. This suggests that some degree of physical and chemical interaction may occur during the co-pyrolysis of plastics with coal. PET is the exception to the general tendency (Figure 2).

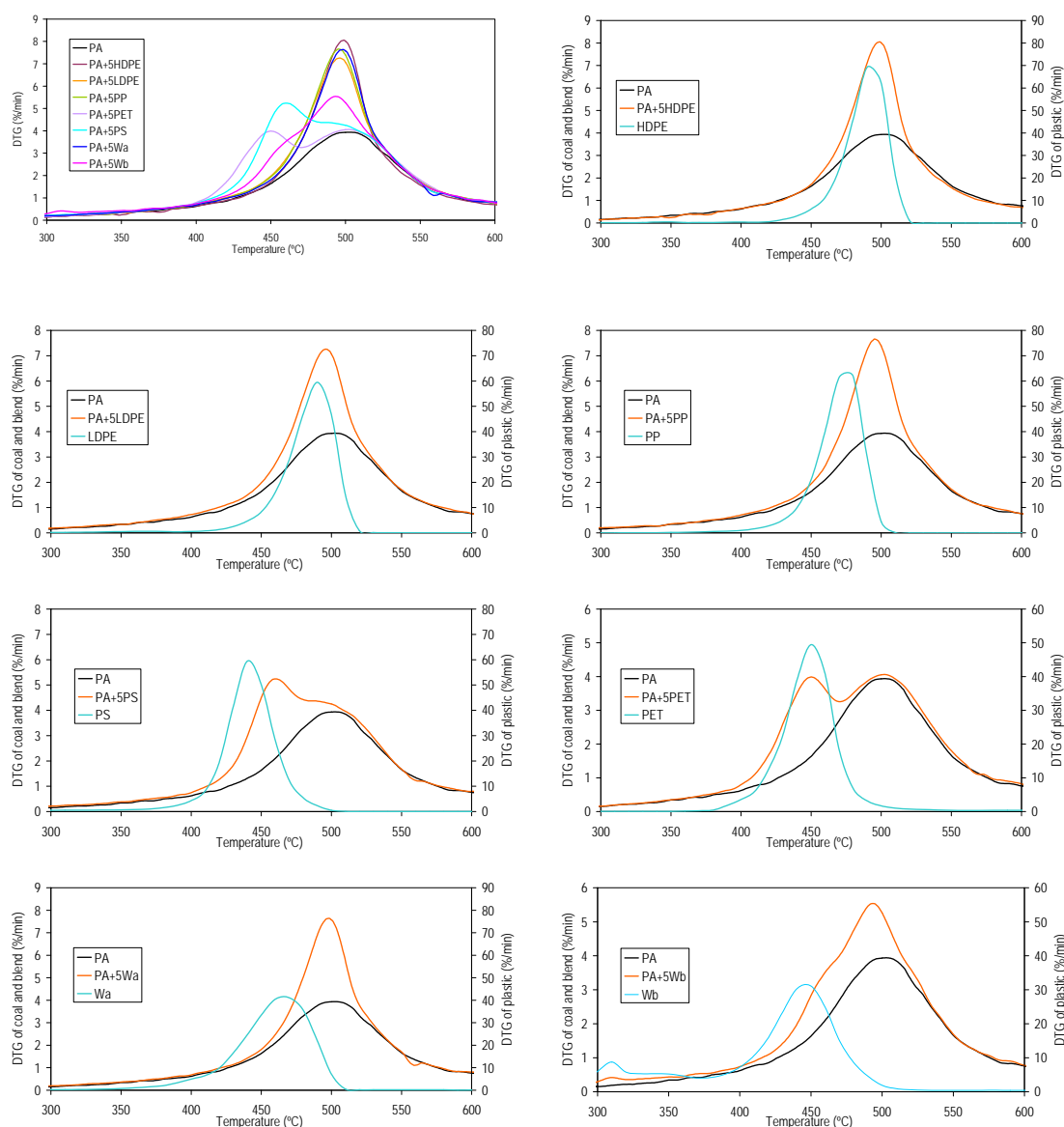


Figure 2. DTG profiles of the coal blend PA, the plastics and their mixtures at an addition rate of 5 wt%.

When plastic decomposition via radical chain reactions occurs close to the decomposition of the macromolecular network of the coal, there is greater opportunity for the small size species from coal decomposition which are responsible for the

development and maintenance of fluidity to volatilize and then to be stabilized by hydrogen transfer or cross-linking reactions. As a consequence of this, the fluidity decreases drastically. PS and PET are good examples of strong modifiers of coal thermal behaviour [7-11]. Then decrease the fluidity of the coal and give rise to more disordered carbon structures in the semicokes [7,8]. However, if the degradation products of the plastics are produced close to the range of maximum evolution of volatiles from the coal, when the maximum amount of gas and tar is produced and solidification sets in, the decomposition products from plastic will be trapped in the co-pyrolysis system and, then, incorporated into the semicoke [5,7,8]. This behaviour is exhibited by the polyolefins which overlap over a wide interval as the coal volatiles evolve.

The interactions between the coal and plastics are also influenced by the chemical composition of the volatiles. By means of TG-MS analysis, it is possible to obtain information about the more volatile species evolved during co-pyrolysis. The ion fragment signals presented in Table 1 represent different families of compounds which were monitored during the co-pyrolysis.

Table 1. Ion fragments monitored by TG-MS analysis.

m/z	Assignment
2	H_2^+
15	CH_3^+
29, 43, 57	Alkane series: C_2H_5^+ , C_3H_7^+ , C_4H_9^+ ... $\text{C}_n\text{H}_{2n+1}^+$
27, 41, 55	Alkene series: C_2H_3^+ , C_3H_5^+ , C_4H_7^+ ... $\text{C}_n\text{H}_{2n-1}^+$
77, 78, 91	Aromatic series: C_6H_5^+ , C_6H_6^+ , C_7H_7^+
44	CO_2^+

Above 450 °C, the most abundant hydrocarbon during the pyrolysis of the coal blend and its mixtures with plastics was methane which was accompanied by the release of other aliphatic and aromatic hydrocarbons. Paraffinic and olefinic fragments always evolve in the temperature range of 495 to 550 °C, the temperature increasing as the number of carbon atoms increases. In most of the blends containing plastics the maximum temperature of hydrocarbons occurs at a lower temperature than the coal blend PA. Hydrogen was detected in more intensity in the last stages of thermal decomposition of the blends and coming mainly from the condensation of the aromatic

structures at a high temperature (782-790 °C).

When the compositions of the light pyrolysis products from the coal blend and its mixtures with plastics are compared, some relevant features of the co-pyrolysis of the blends made up of coal and plastics, (which were derived from the normalized areas of the corresponding peaks to that of hydrogen), are shown to be related to: (i) a higher proportion of hydrogen; (ii) a higher amount of aliphatic compounds from C2 to C4 in the form of both alkanes and alkenes; (iii) a higher relative proportion of alkenes versus alkanes, with the exception of the PA5PS blend (Figure 3).

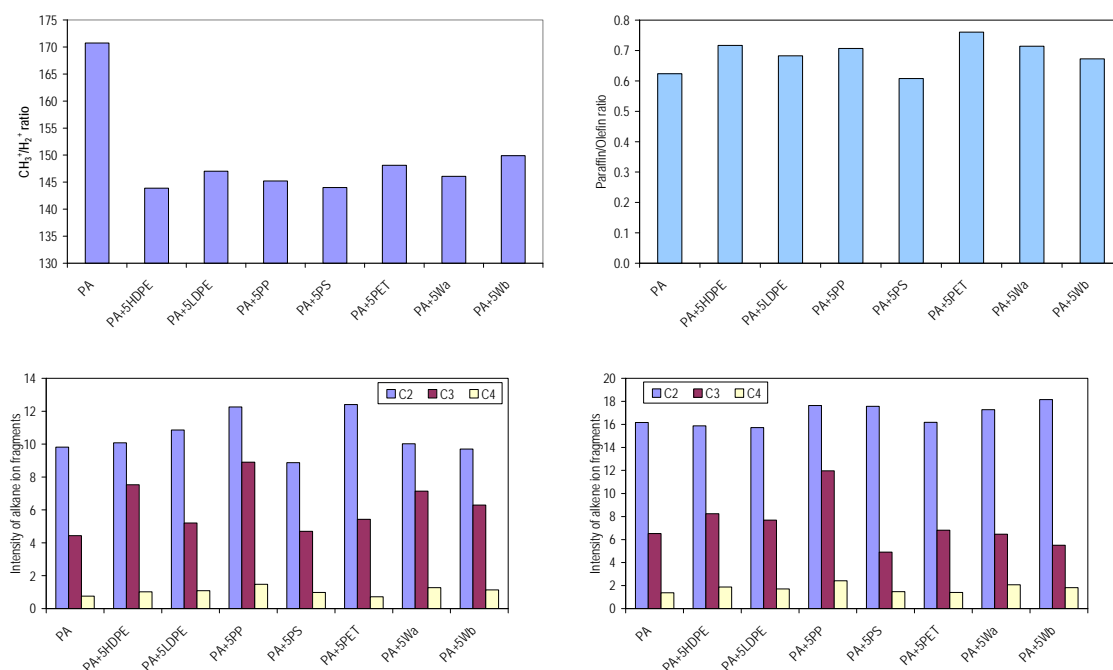


Figure 3. Variation of hydrocarbons evolved during the pyrolysis of the coal blend PA and its mixtures with the different plastic wastes.

As a consequence of the polymer structure, blends made up of PS and PET behave in a different way to polyolefins and they increase the amount of aromatic hydrocarbons. As expected, the addition of oxygen-containing polymers such as PET increases the CO₂ content in the gas, which is released at low temperatures of approximately 465 and 635 °C. Although it is difficult to attribute the origin of the two peaks of CO₂, the low-temperature peak could be linked to functional groups in the PET polymeric chain, whereas the second peak may be assigned to a cross-linking reaction during the formation of tar and coke.

4. Conclusions

A delay in the evolution of volatile species from the plastics was observed when they are blended with coal. Depending on the thermal stability of the plastics, the shift of the evolution of volatiles from the plastic towards higher temperatures and the increase in overlapping between the components may explain the degree of reduction in fluidity caused by plastics. In general, the relative proportion and the temperature of emission of light gases such as hydrogen, methane, aliphatic hydrocarbons with up to four carbon atoms (including paraffin and olefin pairs), aromatic hydrocarbons and carbon dioxide was consistent with the functional groups of the plastic added to the coal. The thermal events during co-pyrolysis and the chemical families of compounds in the gas are in agreement with the modification of the coal fluidity, the degree of ordering of the carbon structure of the semicokes and the evolution of gas pressure during the coking process.

Acknowledgements

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