Role of selected coal- and petroleum-based additives in low- and high-temperature co-pyrolysis with coal blends

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Abstract

The co-pyrolysis of a coal blend with coal- and petroleum-based additives was investigated under slow-heating rate conditions and final temperatures of 600 and 900 ºC. A series of four additives was selected on the basis of their proportion of aliphatic hydrocarbons in the composition of the additive and/or in the primary tar obtained from the pyrolysis. They included a low-rank coal (HVC), a deposit from coke oven gas pipelines (TUB), high-density polyethylene (HDPE) from domestic containers and a lubricating oil of petrochemical origin (LUB). Each additive was added to a coal blend used in the production of blast-furnace coke at addition rates of 2 and 5 wt%. The main objective of this study is to determine how these additives affect the pyrolytic and rheological behaviour of the coal blend, the composition of tars and the microstructure of the semicokes and cokes obtained at lab-scale. All the additives were observed to decrease the semicoke and coke yields at the expense of tar and gas formation. Both HVC and TUB exhibited similar trends in the yields of the major pyrolysis products (semicoke/coke, tar and gas), enhancing the formation of gas species, whereas LUB and HDPE promoted the molecular species that make up the tar. Although other factors also need to be considered, the amount of heavier hydrocarbons in the primary tars obtained from every coal+additive mixture is related to the reduction of coal fluidity caused by the additive. All the additives produced cokes with a more disordered carbon microstructure, as was detected by Raman spectroscopy.

Keywords: coal, wastes, co-pyrolysis, fluidity, tars, semicoke, coke

1. Introduction

The use of carbon sources as inert and reactive additives to coal blends is a subject that is continually arising in cokemaking, in relation with the improvement of the

coking properties of blends, to safeguarding of good-quality coal, the recycling of wastes and the reduction of costs of raw materials.

Chemical and physical properties of cokes are known to be closely related to their structure, which clearly depends on the fluidity of the parent coal [1-3]. For this reason, fluidity developed between 350 and 500 ºC is one of the coal properties that is used to predict the blending potential of additives used in cokemaking. The degree of interactions between components determines the influence of a specific additive not only on the thermoplastic properties of coal, but also on the composition of the carbonization by-products (tar and gas) and on the structure of high-temperature coke.

Among the wide spectrum of coal- and petroleum-derived additives for cokemaking [4-9], three wastes were selected to evaluate the modifications in thermoplastic behaviour of a coal, the distribution of the primary products from co-carbonization, the composition of the primary tar and the coke structure. Two of the wastes were generated in an integrated steel plant: a deposit from coke oven gas pipelines and a lubricating oil of petrochemical origin used in the steel rolling mills. The other waste used was a high-density polyethylene (HDPE) from domestic containers. For comparison purposes, a non-coking coal of high volatile matter content was also used. These four additives were selected on the basis of the presence of aliphatic hydrocarbons in their composition (lub oil and deposit from COG pipeline) and/or in the primary tar obtained from their pyrolysis (non-coking coal and HDPE).

2. Experimental section

Raw materials and wastes

Coal blend A was prepared and supplied by ArcelorMittal in Spain. The main characteristics of coal blend A are as follows: ash, 8.9 wt% db, volatile matter, 22.5 wt% db, S, 0.57 wt% db, Gieseler maximum fluidity, 312 ddpm.

The additives used included a low-rank coal (HVC) used for pulverized coal injection in blast furnaces, a deposit from the coke oven gas pipelines (TUB), high-density polyethylene (HDPE) from domestic containers and a lubricating oil of petrochemical origin (LUB). Each additive was added to coal blend A at addition rates of 2 and 5 wt% and, then, subjected to Gieseler plastometry and co-pyrolyzed in a lab-scale horizontal oven.

Gieseler fluidity development

The Gieseler fluidity was determined in an R.B. Automazione PL2000 plastometer, following the ASTM D2639 procedure. The specific parameters use to measure the fluidity development of the coal blend and its mixtures are: (i) the softening temperature at which the coal starts to be fluid; (ii) the temperature of maximum fluidity reached during the thermal heating; (iii) the resolidification temperature at which the fluid mass resolidifies into a semicoke; and (iv) maximum fluidity, expressed as dial divisions per minute (ddpm).

Co-pyrolysis and products characterization

Co-pyrolysis experiments were performed on mixtures of coal blend A and the selected additives in a Gray-King type furnace. A sample of about 8 g with a particle size of < 0.212 mm was pyrolyzed from ambient temperature to a final temperature of 600 or 900 ºC at a heating rate of 5 ºC/min in an atmosphere of evolving gases, with a soaking time of 15 min. The condensable products (primary tar) obtained during the pyrolysis experiment were collected by means of an ice-cooled trap. Primary tars were separated from the decomposed water by decantation before subsequent analysis. The semicoke/coke and primary tar yields were calculated relative to the starting material on a dry basis and the non-condensable gas fraction was calculated by difference.

Characterization of the pyrolysis products

The primary tars were characterized by Fourier Transform infrared spectroscopy (FTIR) in transmission mode and by gas chromatography using a flame ionization detector and a mass spectrometer (GC-FID-MS).

FTIR spectra were recorded on a Nicolet IR8700 spectrometer equipped with a DTGS detector. The sample was deposited as a thin film between NaCl windows and subjected to 64 scans at a resolution of 4 cm^{-1}. For the semiquantitative analysis, the ratio between the integrated areas of the characteristic absorption bands corresponding to aliphatic hydrogen (2990-2750 cm^{-1}) and aromatic hydrogen (3100-2990 cm^{-1}) was calculated.

Gas chromatographic analyses of the primary tars were carried out on an Agilent Technologies Model 6890N Series II gas chromatograph coupled to a mass selective detector 5973 N. The experimental conditions used were described elsewhere [9].

The Raman spectra of the cokes obtained at 900 ºC were performed on a LabRam

HR UV spectroscope from Jobin Yvon Horiba equipped with a CCD camera and an argon laser excitation source (λ = 514.5 nm). The power source used was 24.3 mW. An Olympus M Plan optical microscope with a 100x objective lens was used to focus the laser beam. Each first-order Raman spectrum for the coke was deconvoluted to obtain four main components at 1595 -G band-, 1520, 1345 -D band- and around 1200 cm^{-1} [10]. The D/G ratio was used as a measure of the degree of structural order in the carbon matrix of the cokes.

3. Results and Discussion

Effect of the additives on the development of fluidity

Table 1 shows the main thermoplastic parameters of coal blend A and its mixtures with the additives at an addition rate of 2 and 5 wt%. The additives differ in their capacity to modify the plastic properties of coal. Except for the lubricating oil (LUB) that enhances the fluidity and extends the plastic temperature range, the other additives produce a decrease in the caking capacity of the coal blend. TUB is the strongest inhibitor of coal fluidity, whereas the behaviour of HDPE is very similar to that of the non-coking coal HVC. An additive which modifies the fluidity of the coal, but keeps it within the range of optimum values established for cokemaking has a good chance to produce a coke with an acceptable strength [11,12]. This is not the case for the deposits from the COG pipelines (TUB), due to the fact that the fluidity is lower than 200 ddpm and the temperature fluid interval is too narrow.

Table 1. Thermoplastic parameters of coal blend A and its mixtures with the selected additives.

Blend	Fmax (ddpm)	Ts (ºC)	Tf (ºC)	Tr (ºC)	Tr-Ts (ºC)	Fmax variation (%)
A	312	414	452	488	75	-
A2HVC	248	414	453	486	72	-20
A5HVC	222	411	452	484	73	-28
A2TUB	137	416	452	485	69	-56
A5TUB	30	426	456	483	57	-90
A5HDPE	197	409	454	487	78	-37
A5LUB	684	402	450	489	87	+119

The data also indicate that additives reduce Fmax more than can be accounted for a simple dilution of the components. In order to understand the interchemical reactions between the coal and additives, co-pyrolysis of the mixtures was also performed.

Co-pyrolysis of the coal blend and its mixtures with the additives

Table 2 shows the distribution of the pyrolysis products obtained at 600 and 900 ºC. The major pyrolysis product at 600 ºC is semicoke, its yield varying from 83.8 wt% for coal blend A to nearly 79 wt% for the mixtures containing HDPE and LUB. The lower semicoke yield is a consequence of the distillation of the hydrocarbons which make up the lubricating oil (LUB) and the transformation of HDPE into hydrocarbons which enhances the tar fraction yield. The other two additives, the low-rank coal and TUB, have different effects on the distribution of the co-pyrolysis products, which increases the yield of the non-condensable products (gas fraction). The effect on the distribution of the co-pyrolysis products at 600 ºC is confirmed at the higher temperature of 900 ºC. In the temperature interval between 600 and 900 ºC, no more tar is formed and the transformation of semicoke to coke involves the release of small molecules which pass to the gas fraction.

Table 2. Distribution of pyrolysis products at 600 and 900 ºC.

Temperature (ºC)	600			900		
	Semicoke (wt%)	Tar (wt%)	Gas (wt%)	Coke (wt%)	Tar (wt%)	Gas (wt%)
A	83.8	8.9	7.4	77.3	8.9	13.8
A2HVC	81.4	8.2	10.4	77.8	8.0	14.2
A5HVC	81.0	8.4	10.6	76.9	8.6	14.5
A2TUB	82.6	8.5	8.9	78.1	7.2	14.6
A5TUB	81.7	8.5	9.8	77.7	7.4	14.9
A5HDPE	79.2	11.9	8.9	75.0	11.2	13.7
A5LUB	79.1	13.6	7.3	73.8	13.9	12.3

The chemical composition of the primary tars obtained at 600 ºC was determined by GC-FID-MS and FTIR. In complex mixtures, an evaluation of the different chromatographic regions or hydrocarbon families is a common practice and is used to explain the differences in fluidity induced by the addition of several organic additives to coal [13-14].

In terms of chemical families, tars are mainly composed of phenol derivatives (14-18%, except for A5HDPE with about 8%), aliphatic compounds -paraffinic and olefinic hydrocarbons- (20-36%) and aromatic hydrocarbons and their highly-alkylated derivatives. The latter fraction is the most abundant in the tar, 46-67%, and it is mainly constituted by the hydrocarbons range from benzene to those containing three aromatic rings such as phenanthrene and anthracene.

The aliphatic hydrocarbons, both the long-chain saturated and unsaturated types, dominate the tar obtained from the blend with HDPE (Figure 1). This tar contains a greater amount of this family of hydrocarbons. The amount and the distribution of aliphatic compounds in the A5HDPE tar resembles that obtained of single coal HVC which has a higher amount of aliphatic compounds, representing about 35% of the chromatographiable fraction of the tar. In general, the amount of aliphatic compounds evaluated by GC is consistent with the aliphatic hydrogen content estimated by FTIR.

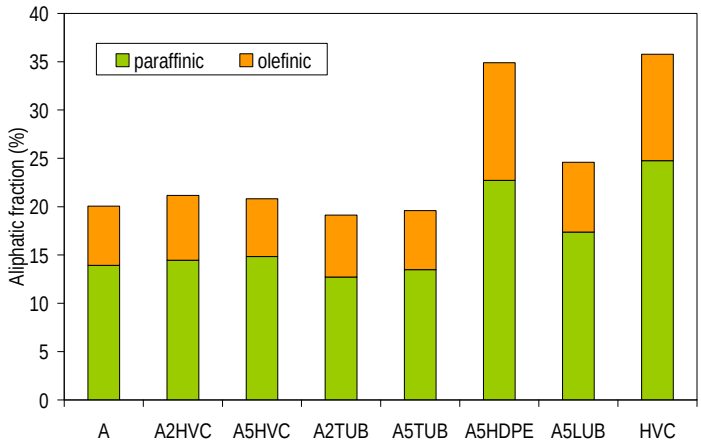

Figure 1. Distribution of aliphatic hydrocarbons, paraffinic and olefinic compounds, in the tars obtained at 600 ºC.

Three chromatographic regions were also defined in the chromatograms on the basis of the compositional ranges used to characterize coal and petroleum fuels: a lighter fraction of tar which includes the low-boiling point compounds with a retention time lower than that of *n*-dodecane (C12); an intermediate fraction which is composed of medium-boiling point compounds with a retention time between that of C12 and *n*-nonadecane (C19); and the heaviest molecular-weight hydrocarbons which elute from C19 to the end of the chromatogram [11-12]. The tars are dominated by the intermediate fraction C12-C19 (Figure 2), except for the A5HDPE tar that contains a similar percentage of this fraction to the heaviest hydrocarbons (>C19), and a very low

proportion of the lighter fraction (<C12). In the case of the tar from A5LUB heavier hydrocarbons were also expected, due to the composition of the lubricating oil added from C20 to C40. However, the predominant hydrocarbons in this tar are those with a moderate volatility (C12-C19) as a consequence of the distillation of the oil components and their fragmentation during co-pyrolysis.

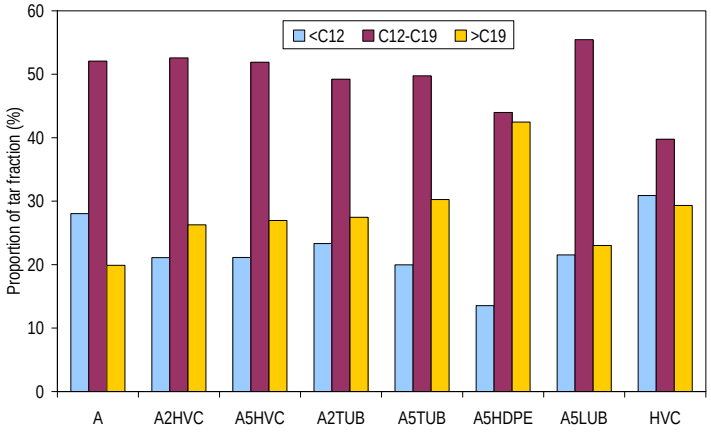

Figure 2. Distribution of the fractions of tars produced in Gray-King pyrolysis at 600 ºC.

Although no clear relationship was found between any parameter relating the chemical composition of all the tars studied and the reduction in fluidity of the parent blend, there is a tendency towards an increase in the heavier hydrocarbon fraction (>C19) as the fluidity decreases (Figure 3). However, other chemical families present in the two tars A5HDPE and A5LUB should be considered to explain the different behaviour.

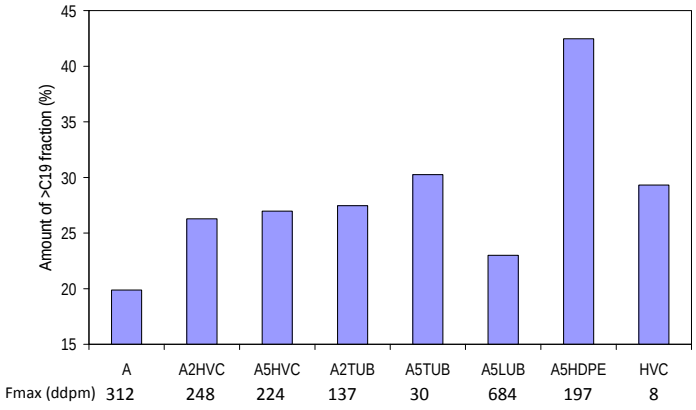

Figure 3. Variation of the amount of heavy fraction (>C19) in the tars obtained at 600 ºC with the parent blend fluidity.

The development of the fluidity of the coal in the presence of the additives clearly influences the structure of high-temperature cokes. The decrease in the Gieseler maximum fluidity in the parent blend results in a less organized carbon structure with various forms of structural defects and imperfections in the graphitic microcrystallites as is reflected by the increase in the D/G band ratio of the cokes obtained at 900 ºC (Figure 4). The exception to the general trend is the coke produced from the blend with the lubricating oil (A5LUB, not included in the graph). The increase in the fluidity of the coal blend from 312 ddpm to 684 ddpm when the lube oil gives rise to a coke with a similar carbon structure to that of the coal blend.

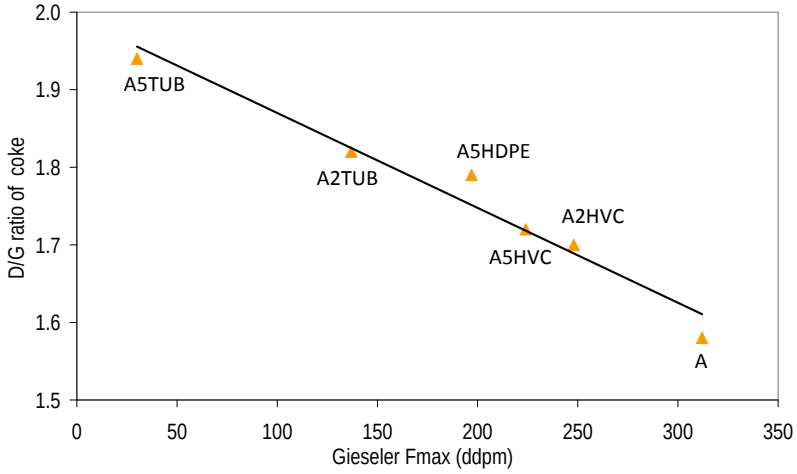

Figure 4. Variation of the band area ratio (D/G) for cokes obtained at 900 ºC (D and G bands at 1320 and 1595 cm^{-1}, respectively) with Gieseler maximum fluidity of the parent blends.

4. Conclusions

All the additives tested increase the volatility of the products by limiting the coke-forming processes and consequently enhancing the formation of tar and gas fractions. Gray-King pyrolysis provides useful information on the effect of the additives on the distribution of coke, tar and gas. HDPE and lubricating oil mainly contributed to the formation of a tar with heavier hydrocarbons, whereas the other two additives are mainly recovered as the non-condensable fraction. The degree of inhibition in Gieseler fluidity induced by the additives is related to the more disordered structure of the cokes produced at high-temperature as was detected by Raman spectroscopy.

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