Modification of coking behaviour of coal blends by plasticizing additives

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Abstract

Commercial coal-tar pitch (CTP) and pitch-like residue (RP)—a waste by-product of coking plants—were used as an additive to two coal blends in metallurgical coke production. The additives were characterized in terms of chemical composition, solvent analysis, ^{1}H NMR spectroscopy, extrographic fractionation, hydrogen transfer properties, thermogravimetric analysis and plastic properties. Both the thermal behaviour and hydrogen transfer properties of the additives are crucial for the coal plastic phase modification during co-carbonization. CTP improves the coking properties of coal blend, i.e. coking and swelling abilities, dilation and fluidity, whereas RP leads only to a fluidity enhancement. This is reflected in different yields, anisotropic carbon, microstrength and reactivity to carbon dioxide of the cokes produced at two different laboratory scales. The beneficial effect of the additives on the metallurgical coke quality not only depends on the properties of the additives themselves, but also the coking properties of the coal blend to which the plasticizing agent was added is a critical factor. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

High-quality metallurgical coke has been produced from good coking coals [1]. The price rise and reduced availability of prime coking coals on a world-wide scale has caused intensive studies of the behaviour of coal blends in the so-called co-carbonization process where lower rank coals with some additives were used instead of prime coking coals [2–4].

A wide variety of carbonaceous materials of different origin including coal tars, coal-tar pitches, petroleum residues and pitches, solvent refined coals, coal extracts and model organic compounds have been evaluated as an additive in co-carbonization with single coals and coal blends [5–9]. The ability of these additives to modify the coal structure has been determined mostly on a laboratory scale by monitoring the changes of optical texture, mechanical strength and reactivity to oxidizing gases of the resultant cokes.

It has been well established that the most important range of temperature during coal coking is 400–500°C, when the coal exists in the form of a plastic phase that finally resolidifies to give semi-coke [10–12]. The metaplast [13] and mesophase [14] theories explain the phenomena that govern coal-to-coke transformation [15,16]. The behaviour of coal blends in the plastic zone depends on the amount and the quality of bitumens existing in the parent coals and can be modified by incorporating into the blend bituminous additives. The additives play the role of plasticizing agent which by lowering the viscosity of plastic phase facilitate the mobility and ordering of the molecules into liquid crystals structures leading to the development of the anisotropic texture of coke [14–18].

In spite of many studies, the co-carbonization mechanism has not been fully understood, because of the high complexity of the chemical nature of the blend components and the physical and chemical interactions between the constituents during heat treatment. The relevant characteristics of bituminous additives for use as blend components are aromaticity, alkyl substitution, heteroatoms and reactive functional group concentration [19], the hydrogen shuttle ability [20–22] and chemical compatibility with coal [23].

Coal-tar pitch has been recognized as a suitable active plasticizing agent during the co-carbonization process [8,24–26]. The proper chemical composition, mainly of an aromatic nature [26], and good coking properties are all the advantages of coal-tar pitch as a blend component.

In the present work two bituminous materials, a commercial binder coal-tar pitch and a pitch-like residue from the benzol distillation column of the by-products of coking plants, were evaluated as additives to coal blends of varying capability of producing metallurgical coke. The effect of the characteristics of the additive on blend performance is evaluated based on typical laboratory scale experiments. Special attention is given to the evaluation of a waste by-product of coking plants as a possible additive to coking. The recycling in situ of the hazardous by-product is a practical aspect of the study.

2. Experimental

2.1. Additives

Two pitches were selected as additives: (1) a commercial binder coal-tar pitch (CTP) produced by the Blachownia chemical plant in Poland; and, (2) a pitch-like material (RP), a residue from the bottom of the benzol distillation column in a coking plant in Spain. The main characteristics of these pitches are shown in Table 1.

2.2. Coals/blends

Four bituminous coals of different rank from Polish and Spanish mines were used to prepare two coal blends with different coking properties. Two high-volatile bituminous coals from Ślask (S) and Kleofas (K) mines (ICC 633 and ICC 611, respectively), a medium-volatile coal (ICC 535) from the Jastrzębie mine (J) and a low-volatile coal (ICC 322) from the Figaredo mine (F). The basic characteristics of the coals are given in Table 2.

Initial coal blends based on prime coking coal J were prepared as follows: blend M1: 65 wt.% J + 20 wt.% S + 15 wt.% F; and blend M2: 50 wt.% J + 25 wt.% K + 25 wt.% F. The selected pitches were added to coal blends M1 and M2 to give the following blends:

M1A: 55 w.% J + 20 wt.% S + 20wt.% F + 5 wt.% CTP
M2A: 50 wt.% J + 18 wt.% K + 25 wt.% F + 7 wt.% CTP

Table 1
Characteristics of pitches used as additives

	CTP	RP
Ash (wt.% db)	0.3	0.9
Volatile matter (wt.% daf)	55.2	72.6
Softening point (°C)[a]	107	71
Toluene insolubles (wt.%)	29.4	21.8
Quinoline insolubles (wt.%)	9.4	1.0
Carbon (wt.% daf)	93.46	88.89
Hydrogen (wt.% daf)	4.10	4.54
Nitrogen (wt.% daf)	0.99	1.87
Sulphur (wt.% daf)	0.39	2.48
Oxygen (wt.% daf)[b]	1.06	2.22
$(H/C)_{at}$[c]	0.52	0.61
$N+S+O/C_{at}$[d]	0.019	0.047
Coke yield (wt.%)[e]	41.8	30.8

[a] Determined by the Mettler method.
[b] Determined by difference.
[c] Hydrogen/carbon atomic ratio.
[d] Heteroatom/carbon atomic ratio (N: nitrogen; S: sulphur and O: oxygen).
[e] Determined by thermogravimetric analysis at 1000°C.

Table 2
Basic characteristics of coals used for blend preparation

	Coal S (hvb)	Coal K (hvb)	Coal J (mvb)	Coal F (lvb)
Ash (wt.% db)	5.6	4.5	6.7	9.3
Volatile matter (wt.% daf)	36.2	36.2	28.5	17.4
Carbon (wt.% daf)	84.3	82.5	85.9	89.3
Hydrogen (wt.% daf)	5.4	4.9	5.0	4.4
Mean vitrinite reflectance (R_o) (%)	0.90	0.91	1.16	1.37
Petrographic analysis (%)				
Vitrinite	64.3	55.5	78.8	92.3
Liptinite	16.2	10.9	3.2	–
Inertinite	19.5	33.6	18.0	7.7
FSI	$6\frac{1}{2}$	$1\frac{1}{2}$	$8\frac{1}{2}$	4
RI	76	20	81	42
Audibert–Arnu total dilatation (%)	75	30	205	45
Gieseler maximum fluidity (ddpm)[a]	28	–	1752	2

[a] ddpm, Dial divisions per minute.

M1B: 55 wt.% J + 20 wt.% S + 20 wt.% F + 5 wt.% RP
M2B: 50 wt.% J + 18 wt.% K + 25 wt.% F + 7 wt.% RP

2.3. Extrography

The fractionation of pitches by extrography has been carried out according to the method elaborated by INCAR-CSIC [27]. Each pitch (4 g) (< 0.2 mm particle size) dissolved in dichloromethane were mixed with 40 g of silica gel which was previously activated by heating at 120°C and its activity adjusted by adding 4% of water. After evaporating the solvent, the residue was dried under nitrogen and placed in a glass column. At the bottom of the column, 20 g of unloaded silica gel was also placed to avoid the overlapping of the fractions. The separation into six fractions was performed using the following sequence of solvents: F1 eluted with *n*-hexane (150 ml); F2 with *n*-hexane–benzene (64:36 v/v, 220 ml); F3 with chloroform (225 ml); F4 with chloroform–dimethylether (95:5 v/v, 300 ml), F5 with chloroform–ethanol (93:7 v/v, 325 ml) and F6 with pyridine (325 ml). An additional fraction F7 was obtained by Soxhlet extraction of the material remaining on the silica gel with 300 ml pyridine.

2.4. ^1HNMR

Spectra were obtained in a Bruker 300 spectrometer for pitches dissolved in pyridine deutered using tetramethylsilane as a standard. Assignments of hydrogen types are based on the chemical shifts (δ) reported in the literature [28].

2.5. Hydrogen transfer properties

The hydrogen donor (D_a) and hydrogen acceptor (A_a) abilities of the pitches were assessed by co-carbonization with anthracene as the H-acceptor and tetraline as the H-donor, respectively. The ratio of pitch to the hydrogen acceptor and donor compounds was 1:1 w/w. The reaction was carried out in a sealed glass tube at 380°C with 1 h soaking time. After treatment, the residue from the co-carbonization with anthracene was extracted with a mixture of *n*-hexane and dichloromethane (3:1 v/v) and that from the co-carbonization from tetraline with *n*-hexane. The soluble fractions were analyzed by gas chromatography with flame ionization detector (FID). The amount of hydrogen transferred from pitch to anthracene (D_a) was calculated from the content of di plus tetrahydroanthracene and that of hydrogen transferred from tetraline to pitch (A_a) from the content of naphthalene in the reaction product. Both, D_a and A_a are expressed as mg of hydrogen per g of pitch.

2.6. Thermogravimetry (TG)

The single additives were subjected to thermogravimetric analysis in a Perkin-Elmer TGA7 thermobalance. A sample of 100 mg (< 0.425 mm in size) of each additive was heated at a rate of 3°C min^{-1} from room temperature to 1000°C. A N_2 flow of 95 ml min^{-1} was used to sweep out the volatile products.

2.7. Coking properties

For coking properties determination of coals and coal blends, four different tests were performed, according to standard procedures. Two of the tests used, the free swelling index (FSI) (ASTM D720) and Roga index (RI) (ISO 335-1974), are based on very rapid heating of coal itself or coal blended with inert components, respectively. In the second test the swelling is not free and the caking and agglomerating power of the coal can be measured. The other two tests used,—Audibert–Arnu dilatation (ISO 349) and Gieseler plasticity (ASTM D2639-74)—are based on slow heating. They are the most informative in terms of behaviour of coals in the plastic range. Audibert–Arnu dilatation gives information on swelling behaviour and the Gieseler plasticity test allows measurement of the fluidity that coking coals possess. As in the Roga test, the swelling determined by the Audibert–Arnu test is not free because the coal has first been compressed into a small cylinder. Systematic studies of the intercorrelation of the parameters deduced from the above tests demonstrated that plasticity and swelling are not equivalent characteristics [12] and the swelling parameters are not an alternative group of parameters for all types of coals. One of the tests based on rapid heating, the Roga test, is commonly used in Poland while the other, the FSI test, is used in Europe and the USA. The relationship of the RI and FSI depends on the coal rank and it can be considered acceptable for coals having a volatile matter content of more than 28 wt.% [11].

2.8. Carbonization procedure

Carbonization of samples was carried out in a Gray–King apparatus according to Polish standard PN-84/G-04519. For each carbonization experiment a sample of 20 g (< 0.2 mm in size) was placed in a quartz retort which was heated in a horizontal electrically heated oven at 5°C min^{-1} to 1000°C and with 15 min of soaking time in the atmosphere of evolved gases. The yield of carbonization products (coke, tar, gas and decomposition water) was obtained. The type of coke was determined according to Gray–King test comparing the resultant coke shape to the standards.

Carbonization experiments were also carried out in an electrically-heated oven (400 g capacity) under a nitrogen atmosphere. Mixtures of coal blends (< 3 mm in size) and the additive (< 1 mm). The bulk density of the charge was always 820 kg m^3 and carbonization tests were carried out at a heating rate of 5°C min^{-1}. A description of the oven and heating experimental conditions applied are given elsewhere [29,30].

2.9. Coke microscopic analysis

Each coke lump obtained in the Gray–King oven was sectioned parallel to the retort axis at the half of its length in order to mount it in the epoxy resin block and, after conventional polishing, to examine the optical texture under a reflected polarized-light microscope. For the study of cokes produced at a larger laboratory-scale, coke samples of 0.6–1.18 mm in size (the same used for the microstrength test) were used. Quantitative assessments were carried out using a point counting technique based on 500 points for Gray-King cokes and 250 points for the other cokes. For each coke samples, two analyses of coke types were performed.

2.10. Coke mechanical strength

Coke microstrength was determined according to the Ragan and Marsh test [31]. While cokes from the Gray–King oven were subjected to 100 rotations, those produced at a larger laboratory-scale were subjected to a more severe treatment (800 rotations). The weight percent of coke fines (< 0.212 mm in size), R3 index, was used as an indicator of the abrasion of the examined coke [32].

2.11. Coke reactivity towards CO_2

Reactivity towards CO_2 of cokes produced at a larger laboratory-scale was measured following a procedure based on the ECE-INCAR method [33,34]. Briefly, 7 g of coke (1–3 mm in size) were reacted at 1000°C for 1 h using CO_2 at a flow rate of 120 ml min^{-1}. The coke reactivity (R_{ECE}) was calculated as the percentage of weight loss after reaction.

3. Results and discussion

3.1. Preparation and characterization of basic coal blends

The initial coal blends M1 and M2 of different coking properties are a three-component mixture of prime coking coal J, high-volatile bituminous coal (S or K) and low-volatile bituminous coal F used as a leaning component. The M1 is a rich blend of excellent coking properties for metallurgical coke production. These properties are due to the high proportion of prime coking coal J (65 wt.%), the use of high-volatile coal S of relatively good coking properties (20 wt.%) and a moderate contribution of coal F (15 wt.%). The M2 blend is characterized by poorer coking properties in comparison with the former blend. It contains a lower proportion of coal J (50 wt.%) and equal proportions of high- and low-volatile coals (25 wt.% each). In addition, a high-volatile coal K of very poor coking properties and a high inertinite content (Table 2) was added, instead of coal S used in the formulation of blend M1.

The purpose of using bituminous additives is different for each blend. In the case of M1, the intention is to save prime coking coal by its partial substitution by bituminous additive. For M2 the purpose is to improve the coking properties of the blend to obtain a good quality metallurgical coke.

3.2. Characterization of pitches used as additives

The main characteristics of pitches selected as additives to coal blends are given in Table 1. Pitch-like residue RP is characterized by a lower softening point, higher volatile matter content, but distinctly lower carbonization residue yield and a practical lack of quinoline insolubles (Table 1). A near three times higher heteroatom content, in particular sulphur, of RP (6.57 wt.%) than CTP (2.44 wt.%) indicates higher thermal reactivity of the former. Comparison of the H/C atomic ratios could suggest a less aromatic structure for RP than that for CTP (Table 1). This is in contrast with the ^{1}H NMR data (Table 3). While basically both additives are highly aromatic materials of rather similar distribution of hydrogen atoms, a slightly higher content of aromatic hydrogen is observed in RP. Therefore, the

Table 3
Hydrogen atom distribution in pitches by ^{1}H NMR

Hydrogen type	Chemical shift (ppm)	CTP	RP
H_{ar}[a]	9.0–6.0	82.4	86.6
H_f	4.5–3.4	3.3	2.2
$H\alpha$	3.4–2.0	11.5	9.0
H_N	2.0–1.4	1.1	1.0
$H\beta+\gamma$	1.4–0.5	1.7	1.2

[a] H_{ar}, aromatic hydrogen; H_F, fluorene-type hydrogen; $H\alpha$, aliphatic hydrogen in the α-position; H_N, naphthenic-type hydrogen; $H\beta+\gamma$, aliphatic hydrogen in the β- and γ-positions.
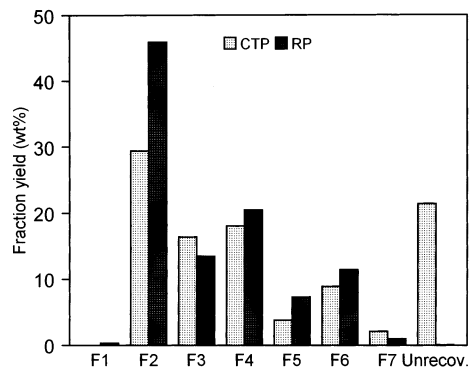
Fig. 1. Distribution of the extrographic fractions of the pitches used as additives. F1, aliphatic compounds and light aromatic hydrocarbons; F2, polycyclic aromatic hydrocarbons with molecular weight < 300 amu; F3; polycyclic aromatic hydrocarbons with molecular weight > 300 amu and neutral nitrogen compounds; F4, F5 and F6, highly polar compounds (basic nitrogen compounds, phenols, amides and polyfunctional constituents); F7, highly polar compounds; Unrecov, material remaining on the silica gel after Soxhlet extraction with pyridine.

degree of condensation of constituting molecules seems to have a strong influence on the H/C atomic ratio [35].

Extrography fractionation data indicate an essential difference in the composition of both pitches (Fig. 1). CTP shows a rather typical binder coal-tar pitch distribution of extrography fractions [27,36,37]. In general, aliphatic compounds (F1) are not present in the pitches. Polycyclic aromatic hydrocarbons with molecular weights < 300 amu (F2) make the highest contribution in both substances, especially in RP (45.9 versus 30% for CTP). Fraction F3 composed of aromatics hydrocarbons with molecular weight > 300 amu and neutral nitrogen compounds has a slightly larger proportion in CTP compared with RP. Higher contents of F4, F5 and F6 in RP suggest that RP is richer in highly polar compounds (basic nitrogen compounds, phenols, amides and polyfunctional constituents) which are concentrated in these fractions. This is in agreement with the higher heteroatom content in RP indicated by elemental analysis (Table 1). Soluble compounds in boiling pyridine (F7) constitute a minor part of the pitches.

Large amount of unrecovered material in the case of CTP (21.4 wt.%), much higher than for RP (0.1 wt.%), can be attributed to the quinoline insoluble material and high molecular-weight highly polar compounds irreversibly adsorbed on the silica gel [38].

It is well known that the chemical composition of the additives strongly influences cocarbonization systems, therefore, hydrogen transfer reactions play a very important role in all thermal processing of coals and pitches. Indeed, hydrogen donor ability (D_a) is considered as one of the most relevant characteristic of materials used as an additive to a coking blend [21,39]. The mobile hydrogen stabilizing free radicals created on the decomposition of coal organic matter

prevents their recombination and in that way enhances the fluidity of the plastic phase. CTP and RP show very similar and relatively low hydrogen donor ability (2.4 and 2.3 mg H g^{-1} CTP and RP, respectively). This fact can be attributed to a similar and low proportion of naphtenic systems and methyl hydrogens [40,41] in the pitch structure (Table 3). In contrast, the evaluation of hydrogen acceptor ability gives a distinctly higher value for RP (4.6 mg H g^{-1} pitch) than for CTP (1.0 mg H g^{-1} pitch). This is consistent with the results of elemental analysis showing increased content of heteroatoms in the former pitch (Table 1) and the extrographic data indicating a higher proportion of fractions containing heteroaromatic compounds (Fig. 1). Heteroatoms are considered to be mainly hydrogen acceptor centers in the pitch structure. All the above properties suggest that RP should be considered as a less suitable additive to the coal blend than CTP.

A TG analysis confirms the results obtained by extrography. Comparing the TG/DTG profiles of the two additives, CTP seems to generate volatile matter at a much higher temperature (Fig. 2). This fact is in agreement with a higher proportion of compounds with higher molecular-weight, implying the higher ther-
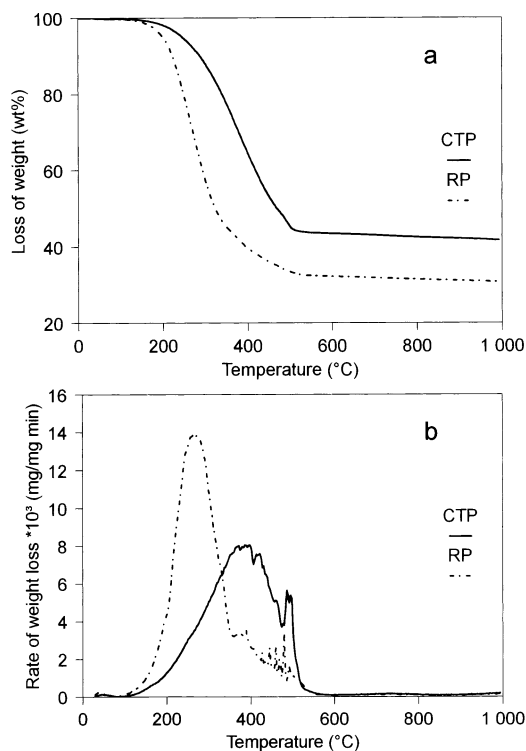

Fig. 2. TG/DTG curves of the two pitches used as additives. (a) Weight loss vs. temperature and (b) weight loss rate vs. temperature.
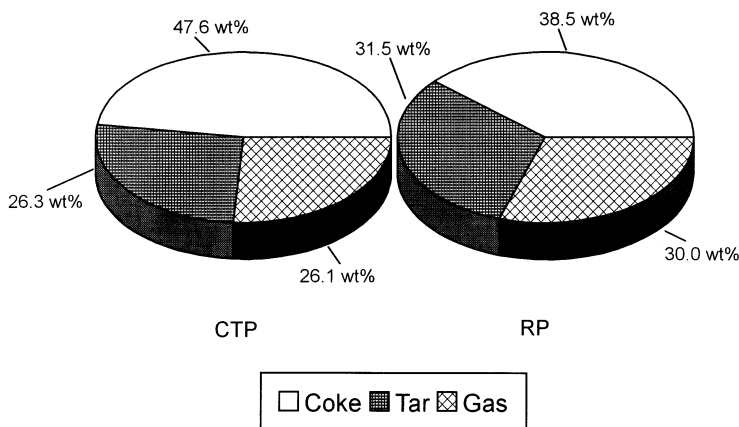
Fig. 3. Yield of products obtained in the carbonization of the pitches in a Gray–King apparatus.

mal stability of this pitch. The effectiveness of the additive to modify the co-carbonization system can be related to the quantity and composition of the volatile matter released by the additive as well as the stage at which the volatile matter is released [42,43]. The volatile matter should be evolved just before the resolidification of the mass takes place [44]. If the volatile matter is produced earlier, the compounds leave the reaction system without any interaction, thus they cannot contribute to maintaining the fluid system. However, on the other hand, if the volatile matter is evolved too close to the resolidification temperature, the viscosity of the system is too high and then the volatile matter will be trapped within the system giving rise to too brittle coke with high porosity [44]. For co-carbonizing systems at 350°C, i.e. the temperature close to the onset of coal softening, the weight loss is much higher for RP (79.2 wt.%) than that of CTP (38.4 wt.%). This means that when RP is added to a coal or coal blend only about 21 wt.% of the total amount of volatile matter could be released during the plastic phase of the co-carbonization system. The lightest part of RP is being evolved from the reaction system before the organic coal matrix starts to decompose. In addition, very reactive additives such as RP gives lower coke yields at 1000°C (30.8 versus 41.8 wt.% for CTP in thermogravimetric analysis). This is in agreement with data derived from the mass balance of the carbonization carried out in a Gray–King apparatus. The lower coke yield is accompanied by a higher amount of tar and gas produced by this additive RP (Fig. 3).

From data in Table 4, it is also seen that RP produces a better developed optical texture towards domain and leaflet anisotropic components as a consequence of its very low QI content (Table 1) which favours the growth and coalescence of mesophase.

3.3. Influence of additives on coking behaviour of coal blends

The influence of the additives on the properties of the coal blends depends on

Table 4
Optical texture of the coke produced from pitches at 1000°C in a Gray–King apparatus

	CTP	RP
Medium-grained mosaics (%)	18.8	7.6
Coarse-grained mosaics (%)	68.6	39.4
Domain (%)	10.3	22.9
Leaflet anisotropy (%)	2.3	30.1
Isotropic (%)	0.0	0.0

the pitch and coals properties [42,43]. Table 5 shows the data for the thermoplastic properties, i.e. swelling and fluidity of the blends studied. The addition of CTP to both blends (M1A and M2A) produces an increase of the swelling capacity given by the FSI and the total dilatation. Pitch addition would enhance the ability of the coals in the blends to engulf the inert particles during the process, leading to a more coherent coke with better bonding between particles. CTP is able to replace, in theproperties of the M2A. On the other hand, RP induces a decrease in this capability. M1B still maintains the swelling FSI and RI and total dilatation values amount tested, a prime coking coal in the case of M1A and to improve the coking

Table 5
Characteristics and yield of carbonization products of blends M1 and M2 with and without pitch addition

	M1	M1A	M1B	M2	M2A	M2B
Additive	–	CTP	RP	–	CTP	RP
Proximate analysis						
Moisture (wt.%)	1.5	1.5	1.6	2.1	2.9	1.9
Ash (wt.% db)	6.8	6.7	6.8	7.0	6.7	6.6
Volatile matter (wt.% daf)	28.4	29.6	30.0	29.6	29.8	30.5
Coking properties						
RI	75	74	75	63	72	65
FSI	8	8.5	7.5	6	7	5
Audibert–Arnu total dilatation (%)	64	97	44	43	73	22
Gieseler test						
Softening temperature (°C)	414	408	405	421	404	403
Maximum fluidity temperature (°C)	457	468	456	462	450	452
Resolidification temperature (°C)	478	493	488	474	495	490
Plastic range (°C)	64	84	83	53	91	87
Maximum fluidity (ddpm)	821	1162	848	202	914	541
Gray–King carbonization products						
Coke (wt.%)	74.6	74.3	72.5	74.7	74.6	72.0
Tar (wt.%)	6.2	8.1	9.5	7.6	8.3	11.0
Gas (wt.%)	16.7	15.3	15.1	15.6	14.8	14.4
Water (wt.%)	2.5	2.3	2.9	2.1	2.3	2.6

within the limits of a good quality coal/blend for cokemaking, which is not the case for M2B, prepared on the basis of a blend with poorer coking properties.

Another test widely used in the coking industry to assess the coking properties is the Gieseler test that measures the plasticity developed by a coal/blend during heating. The use of both additives increases the maximum fluidity (MF) of the two initial blends, with a greater effect for the commercial coal-tar pitch than for the pitch-like residue. Another effect is the widening of the plastic range due to a decrease in the softening temperature, and in the case of M2 a noticeable increase in the resolidification temperature (Table 5). The plastic stage of the coking process is the most vital in the transformation of coal to coke. Indeed, without this fluidity, coke formation cannot occur. During this stage, the breakage of cross-linkages is involved leading to mobility and the production of some low molecular-weight compounds which will be evolved as gas components, while other hydrocarbons will form the highly complex mixture constituting the coal tar. Those of even higher molecular-weight remain to form semicoke on solidification, the process occurring by joining up of adjacent aromatic clusters possibly through a free radical condensation mechanism [2,4,20]. The enhancement of the fluidity induced by the additives (CTP and RP) will modify this process leading to coke with a different texture and properties, as will be seen later.

From the modification of the thermoplastic properties of the blends induced by the two additives a higher efficiency of CTP can be deduced. This fact can be easily explained by taking into account the results of the pyrolysis of the single additives carried out in a thermobalance (Fig. 2). At 400°C, the conversion of RP is 87.1 wt.%, while only about 61 wt.% of CTP reactes. In addition, the temperature at which the maximum release of volatile species during pyrolysis of CTP (398°C) is close to the softening temperature of the coal blend (Table 5). The volatile matter released by the additive near the softening temperature of the blend will help to plasticize the coal mass, having a solvent effect which will decrease the softening temperature (Table 5). It can be considered that the plastic stage of the blends measured with the Gieseler plastometer occurs in the temperature range between 400 and 500°C (Table 5). CTP evolves more than 30 wt.% of total volatile matter in this temperature range while RP losses approximately 9 wt.%. The volatile matter released in this temperature interval by the additive will effectively interact with the coal in the plastic range and, therefore, have the possibility of modify this stage of the coal [42,43]. The higher efficiency of CTP as an additive is also associated with a higher coke yield of the blend obtained in a Gray–King apparatus (Table 5). As expected, the use of both pitches produces a decrease in coke yield which is especially slight when using CTP, and an increase in tar yield that is more noticeable in the case of blends containing RP (Table 5). From the point of view of maximizing productivity of metallurgical coke, the use of CTP is more suitable.

Table 6
Microscopic analysis of optical texture and mechanical strength indices of cokes obtained from blends M1 and M2 with and without pitch addition in the Gray–King oven

	CM1	CM1A	CM1B	CM2	CM2A	CM2B
Additive	–	CTP	RP	–	CTP	RP
Isotropic carbon (%)	20.9	18.6	20.3	30.3	24.7	26.6
Anisotropic carbon (%)	79.1	81.4	79.7	69.7	75.3	73.4
ΣA_{calc} [a]	–	79.7	82.1	–	73.4	75.1
$R3$ index (wt.% < 0.2 mm) [b]	10	7	9	8	9	9

[a] ΣA_{calc}, Total anisotropic carbon content (A) estimated from single components of the blend.
[b] $R3$, Microstrength index after 100 rotations.

3.4. Influence of additives on texture and properties of cokes from the Gray–King oven

The extent of interaction between coal constituents and the additive during co-carbonization can be monitored by changes in the optical texture of the resultant cokes. The presence of CTP reduces the amount of isotropic carbon and promotes the anisotropy development (Table 6). This means that CTP creates better conditions for structure ordering during the plastic stage. As a result a large size of anisotropic units and a more extended range of anisotropic carbon in cokes from M1A and M2A blends are also observed. Experimentally determined higher content of anisotropic carbon structures (ΣA) in cokes from blends M1A and M2A than calculated one (ΣA_{calc}), on the base of the contribution of individual components, can be observed. This proves that CTP interacts chemically with coal constituents which singly carbonized do not fuse and give an isotropic coke [24,30].

However, the optical texture of cokes from M1B and M2B indicates that RP incorporation into the coal blend does not encourage anisotropy development as in the case of CTP (Table 6). This means that the conditions for anisotropic structure formation during co-carbonization are less favourable, probably because of a high heteroatom content in RP and a small amount of volatile matter released during the plastic stage. A higher content of isotropic carbon is observed in coke from a coal blend with RP addition compared with CTP. The comparison of the total amount of determined and estimated anisotropic carbon for cokes from M1B and M2B proves that RP is not as effective as CTP in terms of the development of the optical texture.

Pitch addition to the coal blend results in a better mutual fusibility of the coal particles that improves bonding between the coke components and consequently has a positive effect on the coke strength. But the high fluidity of the plastic phase also leads to higher coke porosity, resulting in a negative effect on the coke strength [2,4,45]. In summary, the pitch addition acts in two opposite directions, so the overall effect for an improvement in coke strength should be a balance between them. The results of this work show that the bituminous additives used have a differentiated effect on the strength of the resultant cokes measured by a mi-

crostrength test under mild conditions (Table 6). It is emphasized that the microstrength indices obtained using a very small initial particle size (0.6–1.2 mm) and a low number of rotations mainly represent a comparative measurement of the strength of the carbon matrix of coke free of macro-defects, i.e. cracks and fissures. For the M1 blend, both additives cause a slightly improvement in mechanical properties demonstrated by a decrease in the R3 index. The extent of the changes is slightly lower when RP is used. In the case of M2 both additives cause a deterioration in mechanical properties. Surprisingly, the addition of CTP leads to a coke of slightly low strength (Table 6). Apparently CTP is not able to modify coking properties of the M2 blend towards an improvement in coke microstrength. The explanation of the unexpected result is that coke from the M2 blend shows very good strength due to a dense structure (coke type G in the Gray–King assay). CTP addition to the M2 blend increases fluidity during the plastic stage resulting in a developed macroporosity of the resultant coke (coke type $> G_3$ in the Gray–King assay).

3.5. Comparison of properties of cokes produced at different laboratory-scale

Table 7 shows the yield, anisotropic carbon, microstrength index (R3) and reactivity towards CO_2 of cokes produced in the larger laboratory-scale oven. The coke yield present a similar trend to that obtained in the Gray–King experiments. However, it can be observed that a slight higher yield for cokes with RP addition obtained at the larger scale tested, mainly due to the bulk density applied (820 kg m^{-3}) that allows a better chance for volatile matter to be incorporated within the coal. In the case of Gray–King experiments, the blend is placed in a silica tube without appreciable packing of particles.

For cokes obtained from blends of M1 microstrength tests were carried out using 100 rotations (the same used for the Gray–King cokes) and also more realistic and severe conditions (800 rotations). The use of both types of additives increase the production of coke fines when more severe experimental conditions were applied— 800 instead of 100 revolutions (Table 7). That is, in the opposite direction to values

Table 7
Coke yield, anisotropic carbon, microstrength and reactivity indices of cokes produced from blends M1 and M2 with and without pitch addition in a larger laboratory-scale oven

	CM1	CM1A	CM1B	CM2	CM2A	CM2B
Additive	–	CTP	RP	–	CTP	RP
Coke yield (wt.%)	74.6	74.4	73.0	75.1	74.4	73.1
Anisotropic carbon (%)	70.4	78.0	75.0	63.0	70.0	65.2
$R3$ index (wt.%<0.2 mm)[a]	9.4	8.4	8.9	nd	nd	nd
$R3$-800 index (wt.%<0.2 mm)[a]	43.4	45.7	49.8	50.7	45.4	50.1
R_{ECE} (wt.% loss)[b]	14.6	12.5	15.1	20.4	17.5	20.3

[a] $R3$, microstrength index after 100 rotations; and $R3$-800, microstrength index after 800 rotations;
[b] R_{ECE}, reactivity to carbon dioxide determined by ECE test; nd, not determined.

obtained after only 100 rotations. This means that at a low number of rotations, the microstrength index most closely reflects the 'stabilization' of cokes, but not the 'strength' of carbon material in cokes and the stresses that can be created by agglomeration between particles.

For cokes produced from blends of M2 in the larger scale oven and subjected to a more realistic and severe mechanical treatment, when CTP was added a better resistance to fines production was obtained.

In summary, experimental conditions of coke production such as the particle size of the coal, the size and shape of the reactor, the bulk density of the charge, and the heating regime have a decisive effect on the yield, structure and properties of the cokes. Larger scale experiments in a vertical retort can create completely different conditions of transport of mass and heat leading to coke of different morphology and mechanical properties.

Referring to CO_2 reactivity, CTP addition always lowers the coke reactivity in all cases while RP addition slightly increases reactivity of the coke from blend M1, remaining the same in the case of CM2B. A decrease in isotropic carbon (Table 7) as well as a decrease in surface area available for reaction with carbon dioxide should moderate the reactivity. It is important to point out the existence of a correlation between this reactivity index and that most frequently employed by the industry, the Nippon Steel Corporation procedure [46]. In conclusion, the addition of CTP causes an increase in anisotropic carbon, a decrease in percentage of fines and reactivity to carbon dioxide which are all beneficial for metallurgical cokes used in the blast furnace. In the case of the addition of RP, the beneficial effects are only noticed for coal blends of low fusibility.

4. Conclusions

Laboratory scale results show that CTP is a good plasticizing agent in coal blends. It can replace a good coking coal in a coal blend as well as improve markedly the coking properties of a worse quality blend. RP can be considered rather as a poorer plasticizing additive than CTP. However, the advantages for using this material as an additive are the in situ recycling with a coal blend of poor coking properties.

The difference in the modifying ability of both pitches can be explained by distinct differences in their chemical composition and properties, nearly three times higher heteroatom content, higher content of relatively low molecular-weight aromatic and polyfunctional compounds in RP compared to CTP.

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