

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231274996>

Characterization of Petroleum Coke as an Additive in Metallurgical Cokemaking. Influence on Metallurgical Coke Quality

ARTICLE *in* ENERGY & FUELS · MARCH 1997

Impact Factor: 2.79 · DOI: 10.1021/ef960124q

CITATIONS

29

READS

57

6 AUTHORS, INCLUDING:



[J. Angel Menéndez](#)

Spanish National Research Council

216 PUBLICATIONS 5,122 CITATIONS

SEE PROFILE



[Maria Antonia Díez Díaz-Estébanez](#)

Spanish National Research Council

122 PUBLICATIONS 1,039 CITATIONS

SEE PROFILE

Characterization of Petroleum Coke as an Additive in Metallurgical Cokemaking. Influence on Metallurgical Coke Quality

J. A. Menéndez, J. J. Pis, R. Alvarez, C. Barriocanal, C. S. Canga, and M. A. Díez*

Instituto Nacional del Carbón (INCAR), CSIC, Apartado 73, 33080 Oviedo, Spain

*Received August 5, 1996. Revised Manuscript Received November 29, 1996**

The relevance of petroleum coke activity during the plastic stage in cocrarbonization with a low-volatile bituminous coal was assessed by establishing differences in lowering of Gieseler maximum fluidity of the blend (bituminous coal and petroleum coke) and in metallurgical coke quality. Differences in fluidity of the blend were well correlated with parameters used in petroleum coke characterization such as hydrogen donor ability, the volatile matter released between 400 and 500 °C, and the ratio of methyl and methylene groups in aromatic clusters. The metallurgical cokes were produced in a laboratory oven from blends of petroleum coke-bituminous coal and, then, characterized in terms of abrasion strength and reactivity to CO₂. There is a clear relation between the chemical activity of petroleum coke in cocrarbonization systems with coal and improvements in metallurgical coke quality. The ability of petroleum coke to interact with coal during the plastic stage contributes to good bonding between components as evidenced by the quantitative study of interfaces by optical microscopy.

Introduction

Petroleum coke is used as an additive in metallurgical cokemaking, mainly because of its availability at prices cheaper than coking coals. Much work has been published on the incorporation of petroleum coke to coal blends, but most have focused on maximum limit of addition without impairing metallurgical coke quality, the influence of petroleum coke particle size in this limit, and the possible increase in total sulfur of the blend when high sulfur petroleum cokes are used.¹⁻³ However, little attention has been paid to the characterization of petroleum coke as an additive in cokemaking to explain why petroleum cokes with similar conventional parameters (elemental and proximate analyses) produced metallurgical cokes of different quality.

New methodology for characterization of petroleum coke to be used as an additive in cokemaking has been developed using optical polarized light microscopy, Fourier transform infrared (FTIR) spectroscopy, hydrogen donor ability test, free-swelling index test, and thermogravimetric analysis.⁴ For a given petroleum coke, a good correlation was observed between volatile matter released in the temperature range of 400 and 500 °C, structural features such as methylene groups in the structure of petroleum coke, and its ability to supply hydrogen to the reaction system.

The aim here is to show the different abilities of petroleum cokes to modify the plastic properties of a

Table 1. Main Characteristics of the Coking Coal A

moisture (wt %)	9.6	maceral composition (vol % mmf)	
ash (wt % db)	8.0	vitrinite	92.6
volatile matter (wt % db)	18.5	exinite	0.0
sulfur (wt % db)	0.94	semifusinite	2.5
Gieseler max fluidity (ddpm)	21	fusinite	4.9
Koppers-INCAR expansion (mm)	7		
mean reflectance of vitrinite, \bar{R}_0 (%)	1.37		
standard deviation of \bar{R}_0	0.20		

coking coal and subsequent modifications in metallurgical coke quality. Metallurgical cokes produced on a laboratory scale were characterized in terms of mechanical strength and reactivity to carbon dioxide at 1000 °C. An interface quality index was used to assess the relationship between the active role of the petroleum coke during the first stages of carbonization and the bonding between the components in the petroleum coke/metallurgical coke matrix. In addition, as the coking coal selected is a dangerously swelling coal, modifications in Koppers-INCAR contraction/expansion caused by petroleum coke addition were also studied.

Experimental Section

Table 1 lists the main characteristics of a Spanish low-volatile bituminous coal A with a low fluidity and low volatile matter content used as a basis in the preparation of blends of coal and petroleum coke. Five green petroleum cokes with volatile matter contents between 10 and 14 wt % and one calcined petroleum coke (R4) were used as additives. The conventional parameters of these petroleum cokes and those derived from the different techniques/methods employed to assess the chemical activity in cocrarbonization systems⁴ are presented in Table 2. The hydrogen donor ability (D_a) of petroleum cokes was established in terms of hydrogen transfer to anthracene in cocrarbonizing systems at 450 °C under an inert atmosphere. D_a was estimated from the amounts of 9,10-dihydroanthracene and tetrahydroanthracene formed in the

* Author to whom correspondence should be addressed.

© Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) Becken, W. H. In *Blast Furnace Coke Quality, Cause and Effect*; Liu, W. K., Ed.; McMaster Symposium 8; 1980; pp 7.1-7.13.

(2) Matsubara, K.; Morotomi, H.; Miyazu, T. In *Petroleum-Derived Carbons*; ACS Symposium Series 303; Bacha, J. D., Newman, J. W., White, J. L., Eds.; American Chemical Society: Washington, DC, 1986; pp 251-268.

(3) Koshkarova, M. E.; Danilyan, P. G.; Koshkarov, V. Ya.; Vdovichenko, N. S.; Mazuka, B. G.; Fedotov, V. E. *Coke Chem. USSR* 1981, No. 9, 34-38.

(4) Menéndez, J. A.; Pis, J. J.; Alvarez, R.; Barriocanal, C.; Fuente, E.; Díez, M. A. *Energy Fuels* 1996, 10, 1262-1268.

Table 2. Main Characteristics of the Petroleum Cokes Used

	petroleum coke					
	R2	RD	R1	EH	R3	R4
ash (wt % db)	0.9	0.3	0.4	0.6	0.4	0.0
VM (wt % db)	14.4	10.3	12.7	12.5	11.9	0.4
S (wt % db)	2.69	0.82	4.57	1.33	4.08	0.00
C (wt % db)	90.3	93.6	88.2	90.1	90.1	99.8
H (wt % db)	4.2	3.0	3.9	4.3	4.3	0.1
N (wt % db)	1.3	1.1	1.6	2.2	0.6	0.0
D_a (mg or r/r g of coke)	0.30	0.44	0.23	0.19	0.10	0.00
H_{al}	0.783	0.738	0.740	0.675	0.604	
H_{1375}/H_{1440} ratio	0.865	0.892	0.904	0.968	1.002	
VM ₄₀₀₋₅₀₀ (wt %)	4.12	3.49	2.98	1.75	1.45	0.02

Table 3. Gieseler Maximum Fluidity of Blends with Petroleum Cokes

coal A + additive	T_r (°C)	T_m (°C)	T_s (°C)	fluid range (°C)	Gieseler MF (ddpm)
coal A	438	481	504	66	21
6 wt % R2	432	478	501	69	18
10 wt % R2	444	478	504	64	14
6 wt % RD	442	478	500	68	16
10 wt % RD	442	481	498	56	13
6 wt % R1	445	481	504	59	17
10 wt % R1	445	473	499	54	12
6 wt % EH	445	478	500	55	14
10 wt % EH	442	476	496	54	11
6 wt % R3	445	478	500	55	13
10 wt % R3	445	481	501	56	10
6 wt % R4	445	477	501	56	12
10 wt % R4	445	478	500	55	9

above conditions by means of gas chromatography. The aliphatic hydrogen content (H_{al}) and the ratio of methyl and methylene groups (H_{1375}/H_{1440}) were semiquantitatively evaluated by FTIR spectroscopy. The amount of volatile matter released between 400 and 500 °C was determined from TG curves of pyrolysis at 1000 °C and a heating rate of 30 °C/min.⁴

Blends of coal A with the petroleum cokes at 6 and 10 wt % were prepared and subjected to Gieseler plasticity testing (ASTM D2639-74). To evaluate the apparent fluidity of a plastic coal, a modified constant torque Gieseler plastometer was used, which is described in the ASTM D2639-74 procedure. The instrument measures the rotation of a stirrer in a compacted 5 g coal/blend charge (<424 µm in size) while the coal is being heated from 300 °C at 3 ± 0.1 °C/min and records the fluidity in dial divisions per minute (ddpm). The sample of single coal A without petroleum coke is used as a reference (Table 3).

Carbonization Tests. A 400 g coal/blend sample, ground to <3 mm, was carbonized in an electrically heated oven under nitrogen on a laboratory scale. Samples were charged in a stainless steel crucible (115 mm height and 90 mm i.d.). The crucible was placed inside a refractory-lined electrically sole-heated oven, designed to carbonize at constant volume.⁵ A diagram of this carbonization setup can be seen in Figure 1. The bulk density of coal/blend charges was always 820 kg/m³, and carbonization tests were carried out at a heating rate of 5 K/min. The final temperature of the oven (1200 °C) was kept constant until reaching 1000 °C at 3 mm from the top of the coke charge. The coke quenching was performed under an inert atmosphere and afterward characterized following the methodology developed by INCAR.^{5,6}

Koppers-INCAR Contraction-Expansion Test. INCAR has developed and patented a laboratory method, Koppers-INCAR test, as previously described.⁷ The interpretation of

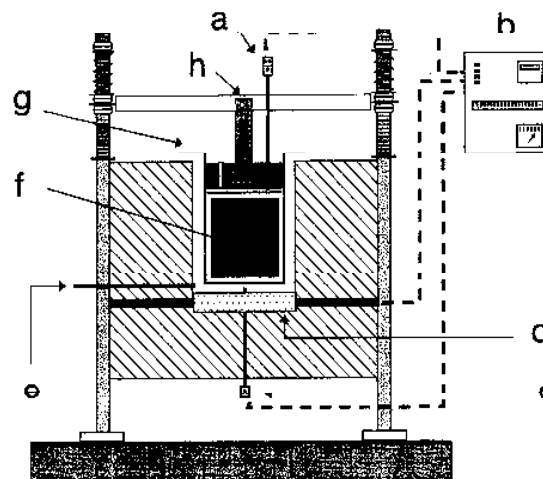


Figure 1. Scheme of the carbonization equipment: (a) thermocouple placed on the top of the coal charge; (b) temperature controller; (c) electric heating; (d) thermocouple placed on the sole of the oven; (e) nitrogen input; (f) coal sample; (g) reactor; (h) piston.

the graph obtained in this test can be summarized as follows: coals giving expansion or a contraction lower than 10 mm are dangerous during carbonization. The practical application of this laboratory test to measure expansion and contraction behavior during carbonization has been previously studied.⁸⁻¹⁰

Metallurgical Coke Characterization. Metallurgical cokes obtained were characterized in terms of mechanical strength and reactivity to carbon dioxide. Mechanical strength was assessed by an abrasion test on a laboratory scale: INCAR-MITREM.¹¹ Briefly, coke samples (75 g) between 5 and 15 mm are introduced in a mini-MICUM drum (110 mm length, 130 mm diameter). After 3000 revolutions at 33 rpm, an abrasion index is defined as the weight percentage of the coke sample below 1 mm.

Coke reactivity measurements were made following a procedure based on the INCAR-ECE method.¹² This test measures the rate of reaction of a 7 g coke sample sized between 1 and 3 mm, using CO₂ at 1000 °C for 1 h. The coke reactivity was calculated as the percentage of weight loss after 1 h of reaction.

Interface in Metallurgical Cokes. Samples for polarized light microscopy, consisting of coke particles sized 1–3 mm, were mounted in resin to form cylindrical blocks of 30 mm in diameter. The upper surface was smoothed using successively finer grades of silicon carbide papers and then polished with 0.3 and 0.05 mm alumina powder.

To assess the quality of the interfaces, metallurgical coke/petroleum coke, four different types of interfaces, according to the type and the degree of contact between particles, are defined as transitional (T), fused (Fu), fissured (Fi), and unfused (U). Table 4 shows the definition of each interface category, which has been previously described in detail.¹³ Relative abundance of the different type of interfaces was obtained by point-counting recording the quality of the interface nearest the cross-wire at 250 positions on the coke surface. A Leitz Laborlux x 12 POL microscope equipped with a one-

(8) Alvarez, R.; Miyar, E. A.; Canga, C. S.; Pis, J. J. *Fuel* 1990, 69, 1511–1516.

(9) Alvarez, R.; Pis, J. J.; Barriocanal, C.; Lázaro, M. *Cokemaking Int.* 1991, 3, 37–42.

(10) Alvarez, R.; Pis, J. J.; Barriocanal, C.; Sirgado, M. *Cokemaking Int.* 1992, 4, 16–18.

(11) Menéndez, J. A.; Pis, J. J.; Díez, M. A.; Barriocanal, C.; Cassi, M. D.; Parra, J. B.; Alvarez, R. *Rev. Metal. (Madrid)* 1995, 31, 235–241.

(12) Menéndez, J. A.; Alvarez, R.; Pis, J. J. *Rev. Metal. (Madrid)* 1993, 29, 214–222.

(13) Barriocanal, C.; Hanson, S.; Patrick, J. W.; Walker, A. *Fuel* 1994, 73, 1842–1847.

(5) Pis, J. J.; Cagigas, A.; Simón P.; Lorenzana, J. J. *Fuel Process. Technol.* 1988, 20, 307–316.

(6) Alvarez, R.; Díez, M. A.; Menéndez, J. A.; Barriocanal, C.; Pis, J. J.; Sirgado, M. *Ironmaking Conf. Proc.* 1995, 54, 405–413.

(7) Escudero, J. D.; Alvarez, R. *Fuel* 1981, 60, 251–254.

Table 4. Classification of Different Interfaces between Petroleum Coke and Metallurgical Coke Matrix¹³

interface	appearance
transitional (T)	fissureless interface with no clearly defined boundary; appearance changes gradually from that of one component to that of the other and gives rise to a distinct intermediate material at the interface
fused (Fu)	fissureless interface with a clearly defined boundary and without intermediate material between components
fissured (Fi)	fissures, small in comparison to the length of the boundary, are present at the interface between components
unfused (U)	fissuring at the interface extends along almost the whole boundary between components

wave retarder plate and a total magnification $\times 1000$ oil immersion was used.

From the interface counting, an interface quality index (Q), which relates good bonding and nonbonding at the boundary between particles, can be calculated as

$$Q = (T + Fu)/(Fi + U)$$

where T, Fu, Fi, and U are the percentages of transitional, fused, fissured, and unfused metallurgical coke/petroleum coke interfaces, respectively.

Results and Discussion

The presence of unreacted pitch and "isotropic sacks" in green petroleum cokes has been considered a source of volatile matter production, and the extent of their movement within the blend with coals may improve the caking ability of the blend.¹⁴ In an earlier paper, this assumption was demonstrated using a set of petroleum cokes.⁴ Although there is no relation between the amount of unreacted pitch and partially reacted material (mesophase spheres within an isotropic matrix) present in green petroleum cokes, the use of different techniques such as FTIR spectroscopy, donor ability test, thermogravimetric analysis, and free-swelling index provides useful information about the different activities of the petroleum cokes during pyrolysis. Higher hydrogen donor ability of petroleum coke in terms of hydrogen transfer to anthracene (D_a) was related to a higher amount of hydroaromatic and naphthenic structures, donor-hydrogen components (lower value of the H_{1375}/H_{1440} ratio), and a higher amount of volatile matter released between 400 and 500 °C (VM₄₀₀₋₅₀₀; Table 2). These characteristics for a given petroleum coke are indicative of a certain chemical activity during the plastic stage of a coking coal. On this basis a different behavior of the petroleum cokes studied within coccarbonization systems with coal was proposed according to the following classification from the higher to the lower chemical activity degree: R2 > RD > R1 > EH > R3 > R4. The calcined petroleum coke (R4) was used for comparison purposes because it has no chemical activity during the coking process.

Plastic Properties of the Blends. Certain types of coals, generally known as bituminous coals, when heated, soften, become plastic, and coalesce into a coherent mass that swells and resolidifies to form a solid porous residue (coke). Physical changes occurring in coal when heated in the temperature range of 350–500 °C are known as plastic properties. It is established that not all bituminous coals are suitable for producing an adequate metallurgical coke. Coking coals are a subclass of bituminous coals having volatile matter contents between 18 and 32 wt %. This type of coal becomes fluid when heated to 350–500 °C in the absence of air and resolidifies into coke with good mechanical strength. The plastic stage is probably the

most important step of the coking process. The most widely accepted test to measure the plastic behavior of a coal or a coal blend is the Gieseler plastometer test.

In an attempt to demonstrate the relevance of the differences in chemical and physical properties of the petroleum cokes according to the classification previously proposed,⁴ the petroleum cokes were added (6 and 10 wt %) to a low-volatile bituminous coal A having a low Gieseler maximum fluidity (MF; 21 ddpm). All of the additions of petroleum cokes lead to a lower MF, but in different ways according to the type of petroleum coke added (Table 3). In spite of the small differences in fluidity of the blends, the lowering in Gieseler MF is clearly related to the above established order. Taking into account the parameters derived in the characterization of the petroleum cokes, a reasonable correlation between the fluidity levels of the blends (coal A + 10 wt % petroleum coke) and hydrogen donor ability (D_a) at 450 °C was found (Figure 2a), indicating different behaviors of the petroleum cokes due to structural differences. The blend made up with the calcined petroleum coke (R4), which has no ability to supply available hydrogen ($D_a = 0$), has the lowest Gieseler MF (9 ddpm) in the series. On the other hand, the blend containing green petroleum coke R2 presents the highest Gieseler MF (14 ddpm). Additional parameters in the characterization of these petroleum cokes such as the relative abundance of methylene groups semiquantified by FTIR (H_{1070}/H_{1440} ratio) and the volatile matter released in the temperature range of 400 and 500 °C (VM₄₀₀₋₅₀₀) by thermogravimetric analysis also show a good relationship with Gieseler MF (Figure 2b,c). These results are in agreement with those found in blends prepared with a coking coal with a higher MF.⁴ Then, the decrease in MF by adding petroleum coke is related to its properties, particularly to the presence of hydroaromatic systems providing hydrogen donor ability. This can be considered to influence, critically, the development of the plastic zone of coal carbonization.

Koppers-INCAR Contraction-Expansion. According to coal classification as in the Koppers-INCAR test, coal A is a dangerous coal, presenting expansion at the end of the test (Figure 3a). Due to the partially inert nature of petroleum coke, it is an effective additive in dissipating wall pressure developed during the carbonization process and reducing expansion of the system.^{15,16} This is in agreement with the reduction in expansion of blends of coal A and the petroleum coke studied. Parts b and c of Figure 3 show, as an example, the reduction of the expansion after 10 wt % addition of petroleum cokes R2 and R4. The addition of 10 wt % of R4 produces the greatest decrease in expansion of all the cokes studied. This greater reduction is still not enough to make the blend with petroleum coke safe to be industrially carbonized. Nevertheless, in complex blends commonly used in cokemaking, this reduction

(14) Ruiz, O.; Romero-Palazón, E.; Díez, M. A.; Marsh, H. *Fuel* 1999, 78, 456–459.

(15) Case, E. R. *Ironmaking Conf. Proc.* 1986, 45, 195–202.
(16) Loison, R.; Foch, P.; Boyer, A., Eds. *Coke, Quality and Production*; Butterworth: London, 1989; pp 405–410.

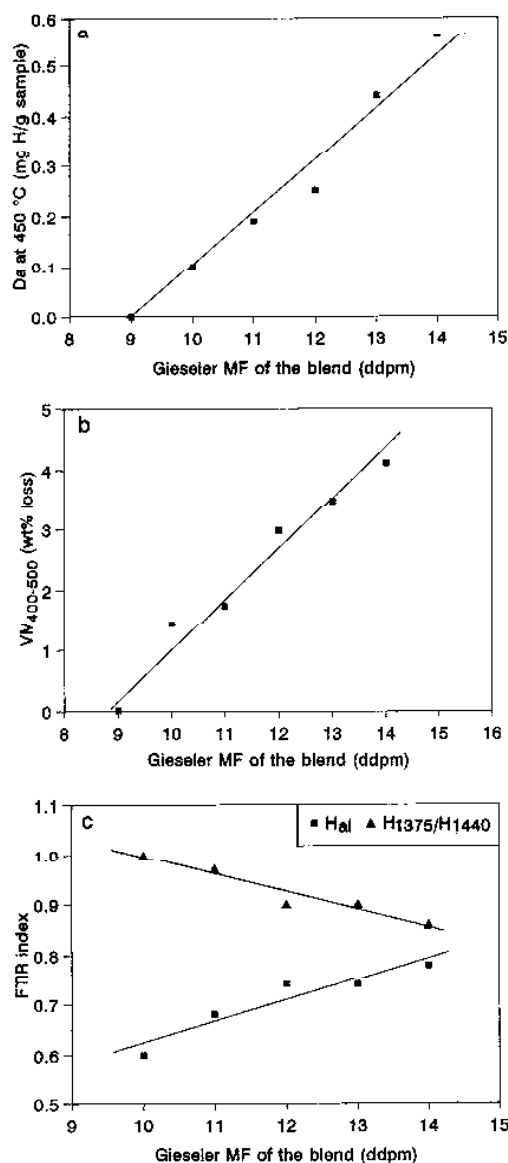


Figure 2. Relation between the Gieseler maximum fluidity of blends and (a) hydrogen donor ability (D_a) at 450 °C, (b) volatile matter release between 400 and 500 °C, $VM_{400-500}$, and (c) FTIR indices, relative aliphatic hydrogen content ($H_{al} = H_{al}/H_{ar} + H_{al}$) and ratio of methyl to methylene groups (H_{1375}/H_{1440}) of petroleum cokes.

allows the use of higher proportions of good coking coals as coal A, which has limitations due to its dangerous behavior. Although differences between the Koppers-INCAR expansion values of blends with R2 and R4 are small, they can be explained by the active/inert nature of the petroleum coke added. Calcined petroleum coke R4 has a totally inert nature, and it causes a diluent effect on the dangerous coal A. As an inert, it is believed that it does not change in volume and the space available for the coal to swell/expand is therefore increased. The inert, by absorbing a certain proportion of tar, reduces the fluidity and the expansion of the coal and improves the permeability of the plastic layer and hence modifies its dangerous character.¹⁶ If petroleum coke has a partially active role during the coccarbonization,

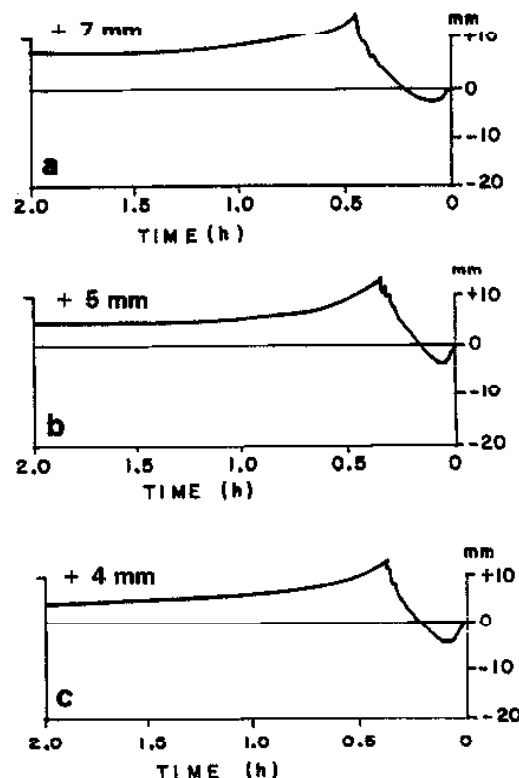


Figure 3. Koppers-INCAR curves of (a) coal A, (b) coal A + 10 wt % R2, and (c) coal A + 10 wt % R4.

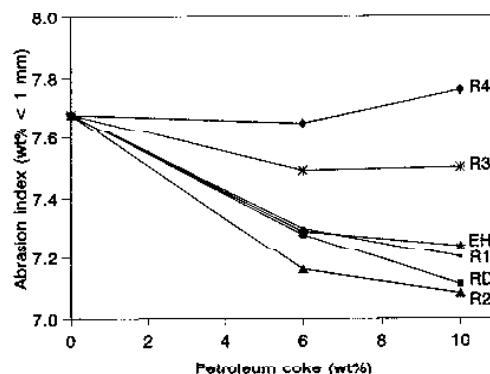


Figure 4. Variation of abrasion index of metallurgical cokes produced from blends made with petroleum cokes.

two effects can take place in different extension. As an inert material it has a diluent effect, but the partially active material causes increased evolution of volatile matter, and then it contributes to less reduction in the expansion of the coal (Figure 3). This is the case of the most active petroleum coke studied, R2.

Metallurgical Coke Quality Parameters. Table 5 contains data of coke yield, abrasion, and reactivity to carbon dioxide at 1000 °C (INCAR-ECE reactivity) for resultant cokes from blends of coal A with petroleum cokes. The petroleum coke addition produces a slight increase in coke yield from 77 wt % for the single coal A to 77.7–79.2 wt % when petroleum coke is added. On the other hand, the addition of 6 and 10 wt % of petroleum coke causes a decrease in coke fines (< 1 mm size) produced in the INCAR-MITREM abrasion test together with a decrease in reactivity to CO_2 in relation to the metallurgical coke produced from the single coal A.

(17) Barriocanal, C.; Hanson, S.; Patrick, J. W.; Walker, A. *Fuel Technol. Transact.* **1995**, *25*, 1–10.

Table 5. Yield and Properties of Metallurgical Cokes Obtained

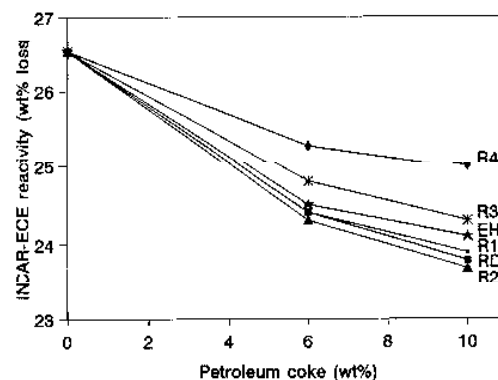
coal A + additive	coke yield (wt %)	abrasion index (wt % < 1 mm)	reactivity (wt % loss)
coal A	77.0	7.7	26.5
6 wt % R2	77.8	7.2	24.3
10 wt % R2	78.3	7.1	23.7
6 wt % RD	78.2	7.3	24.4
10 wt % RD	79.0	7.1	23.8
6 wt % R1	77.7	7.3	24.4
10 wt % R1	78.2	7.2	23.9
6 wt % EH	77.9	7.3	24.5
10 wt % EH	78.4	7.2	24.1
6 wt % R3	78.1	7.5	24.8
10 wt % R3	78.4	7.5	24.3
6 wt % R4	78.5	7.6	25.3
10 wt % R4	79.8	7.9	25.0

With 6 and 10 wt % petroleum coke additions, abrasion is lower using petroleum cokes of lower carbonization degree and increases with the increase in the carbonization extent (Figure 4). There is a nonquantitative relationship between the above established order of chemical activity/carbonization degree with a decrease in abrasion index. Greater differences are seen, first, for cokes produced from the blend of coal A and petroleum coke R2 with the lower carbonization degree and, consequently, the higher chemical activity during the plastic stage of the coking system and, second, when petroleum coke R3 with the lower chemical activity and R4 with nonchemical activity and the higher carbonization degree are used. At the 6 wt % additions of RD, R1, and EH differences in the abrasion index are not very relevant because the influence of petroleum coke type is also related to other additional factors influencing coke abrasion. On the other hand, different effects can be observed when the calcined petroleum coke R4 is added. The 6 wt % addition causes a slight decrease in abrasion index. However, by increasing the levels of addition of R4 at 10 wt %, the abrasion index of the produced coke increases, being of worse metallurgical quality than the original from coal A. These findings suggest that coal A can agglomerate a limited amount of R4, which can be considered as an optimum amount in the blend. However, the fact that this coking coal A is not able to agglomerate a higher amount of the calcined petroleum coke (10 wt %) may be partially due to its low fluidity.

With regard to reactivity to CO₂, similar conclusions can be drawn. Although the calcined petroleum coke R4 produces a decrease in reactivity to CO₂, the order of magnitude is lower than that produced by the green petroleum cokes with some degree of chemical activity during the plastic stage (Figure 5). Once more, the established order of the petroleum cokes relating to chemical activity or carbonization degree is in agreement with the reduction in reactivity to CO₂ of resultant metallurgical cokes.

Although the present results demonstrate the effects of chemical activity of petroleum coke on quality parameters of metallurgical cokes produced from blends with a Spanish low-volatile coal, similar trends for blends made with coking coals with a higher fluidity could be expected.

Interface Quality Index. Table 6 shows the percentage of each interface defined in Table 4 and the interface quality index (*Q*) for the resultant cokes from blends made with 10 wt % petroleum coke addition. The results indicate that when petroleum coke is used as an additive in metallurgical coke production, the inter-

**Figure 5.** Variation of reactivity to CO₂ at 1000 °C (INCAR-ECE reactivity test) of metallurgical cokes produced from blends made with petroleum cokes.**Table 6. Percentage of Each Interface Type^a for the Resultant Cokes Produced from Blends with 10 wt % Petroleum Coke**

petroleum coke	T (%)	Fu (%)	Fi (%)	U (%)	<i>Q</i> ^b
R2	3.6	59.6	24.8	12.0	1.7
RD	0.0	61.6	27.2	11.2	1.6
R1	0.4	46.8	38.4	14.4	0.9
EH	0.0	49.6	40.4	10.0	1.0
R3	0.0	38.0	44.8	17.2	0.6
R4	0.0	31.6	50.4	18.0	0.5

^a T, transitional; Fu, fused; Fi, fissured; U, unfused. ^b *Q*, interface quality index.

action between components is quite different depending on the petroleum coke added. So, as the chemical activity of petroleum coke during the plastic stage increases, there is an increase in fused interface (Fu), showing a clearly defined boundary without intermediate material between components, and a decrease in the amount of fissured interface (Fi). In addition, evidence of mutual interaction between particles of petroleum coke and metallurgical coke (transitional interface, T) is clearly shown for addition of the most reactive petroleum coke in the series (R2). The quality of the interfaces, apart from differences on shrinkage between metallurgical and petroleum coke, depends on the capability of the two materials to make contact and to form a good bond. Therefore, an important factor to take into account in the incorporation of a petroleum coke into the metallurgical coke matrix is the degree of chemical activity/inertness in the coking process.^{14,18} This can be evaluated as the ability to influence the fluidity of the blend and, then, the plastic stage of the process, which can be measured as the hydrogen donor ability (*D_a*) at 450 °C.⁴ For this series of petroleum cokes the relationship between *D_a* at 450 °C and the interface quality index *Q* is shown in Figure 6 which relates higher *D_a* of a petroleum coke to better quality of the interfaces involving that petroleum coke. This fact confirms the point stated above which supports the idea of the importance of the ability of the additive, petroleum coke in this case, to form a good bond with the coke matrix. The higher the *D_a*, the higher the chemical activity in the plastic stage, and thus the bonds between the two materials will be of better quality (Figure 6). The interface quality index (*Q*) is also linearly related to VM₄₀₀₋₅₀₀ (*r* = 0.908) and *H*₁₃₇₅/*H*₁₄₄₀ ratio (*r* = 0.852).

(18) Forrest, M.; Marsh, H. *Fuel* 1981, 60, 429-433.

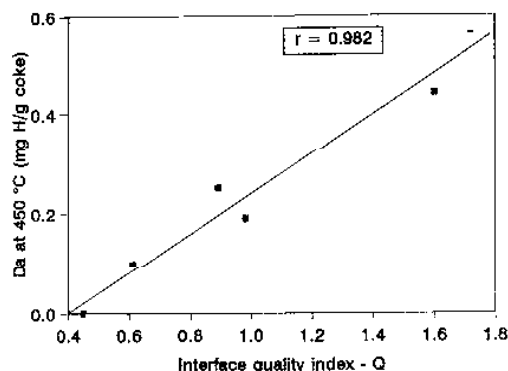


Figure 6. Relation between the interface quality index (Q) of metallurgical cokes and hydrogen donor ability (D_a) at 450 °C of the petroleum cokes.

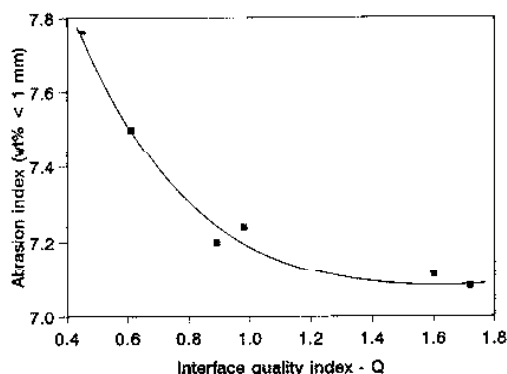


Figure 7. Relation between the interface quality index (Q) and the abrasion index of metallurgical cokes.

Good bonding between particle components of the two materials (petroleum coke and coke matrix) is an essential factor for improving coke strength.^{14,18–21} For this series of cokes the variation of abrasion with the interface quality index (Q) is shown in Figure 7, illustrating less fissuring at the interfaces of metallurgical and petroleum cokes with increasing quality index Q . When there is no interaction at the interface and, consequently, no bonding between the two materials, crack propagation is facilitated. This is the case of R4. An example of such an interface is shown in Figure 8a at position A. On the other hand, panels b and c of Figure 8 show SEM micrographs of the resultant cokes produced from the blends with the petroleum cokes R1, with an intermediate chemical activity, and R2, with the higher chemical activity during the coal plastic stage. In this case, the mutual interaction between the petroleum coke particle and the coke matrix is shown at position A, indicating the active role of certain components within petroleum coke.

Conclusions

Modification of carbonization systems by addition of different types of petroleum cokes to a Spanish low-volatile coal is clearly related to the metallurgical coke quality. The presence of unreacted isotropic-like pitch and partially carbonized material is a source of volatile active species which supply hydrogen to the cocarbon-

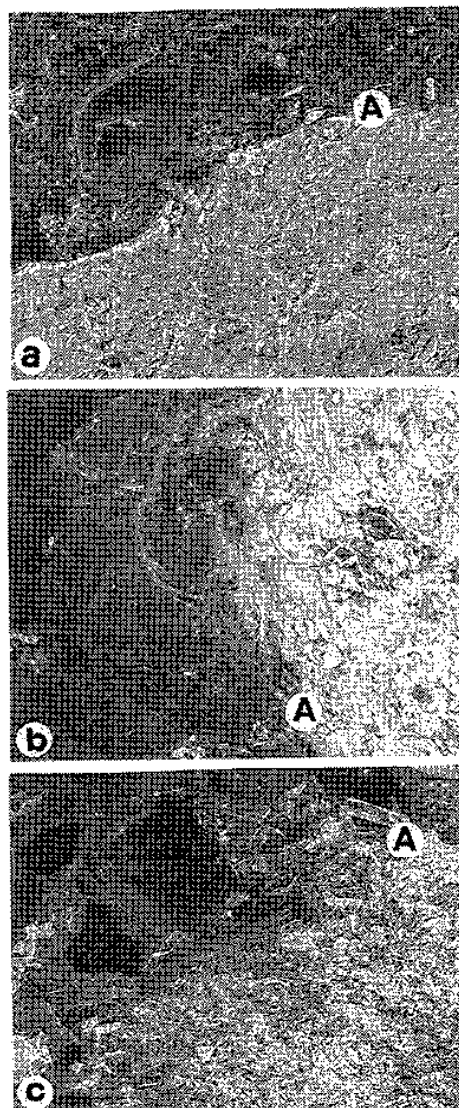


Figure 8. SEM micrographs of resultant cokes showing interface between petroleum coke and metallurgical coke matrix (position A). The petroleum coke used as additive was (a) R4, (b) R1, or (c) R2.

ization system during the plastic stage of coal. This allows a better interaction between carbon components from coal and petroleum coke. The carbonization degree (chemical activity) established for six petroleum cokes used as additives to a bituminous coal can explain the decrease in Gieseler MF of the blends and the improvements in metallurgical coke quality. A good correlation was found between the hydrogen donor ability of the green petroleum cokes and the abrasion resistance, the reactivity toward carbon dioxide of resultant metallurgical cokes, and the quality of the interfaces of both materials, petroleum and metallurgical cokes. If green petroleum cokes are to be added to coal blends, then a prior characterization of the activity of petroleum coke during the plastic stage of coal, as it was demonstrated, is a prerequisite.

Acknowledgment. We thank Repsol Derivados S.A. for financial support.

EF000124Q

(19) Qian, Z.; Marsh, H.; Clarke, D. E. *Fuel* 1985, 64, 125–128.

(20) Grint, A.; Swietlik, U.; Marsh, H. *Fuel* 1979, 58, 642–650.

(21) Mouchal, L.; Marsh, H.; Grint, A. *Fuel* 1978, 57, 600–605.