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Characterization of Petroleum Coke as an Additive in Metallurgical Cokemaking. Modification of Thermoplastic Properties of Coal

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It is often assumed that green petroleum coke behaves as an inert material in cocarbonization with coking coal blends and has no active behavior on the important thermoplastic properties of the coal blend. This paper investigates that assumption. The objective of this study is to clarify effects arising when different petroleum cokes are added to a single coal or an industrial blend. The effects studied include changes during the pyrolysis stages of the cocarbonization, using a bituminous coal. This was done to study if petroleum coke is totally inert at the plastic stage of a given coal or there is an influence at the plastic stage. A further aim is to show how conventional and nonconventional techniques for petroleum coke characterization relate to its activity with the plastic stage of coal. A range of six petroleum cokes was used. The petroleum cokes were studied in terms of (a) optical texture, (b) FTIR spectroscopy, (c) hydrogen donor ability, (d) thermogravimetric analysis of the pyrolysis stage, (e) free-swelling index, and (f) thermoplastic properties of blends made up of a bituminous coal and petroleum coke. Evidence for a significant activity of some petroleum cokes was assessed using the above techniques, which can be considered as nonconventional in petroleum coke characterization. A good correlation among the parameters obtained from the above techniques/methods was found, indicating that the presence of unreacted and partially carbonized material, the hydrogen donor ability, the relative proportion of methyl and methylene groups, the amount of volatile matter released at a temperature range between 400 and 500 °C, the temperature of maximum volatile matter evolution and, finally, the agglomeration degree of petroleum cokes can be considered as important factors in the plastic properties of cocarbonization systems with coking coals.

Introduction

The use of green petroleum coke as an additive in industrial coal blends is a practice often used by coke oven plants, depending on its availability in the market at prices lower than those of coking coals. The performance of metallurgical coke, produced from coking coal blends containing petroleum coke, was successfully tested in several blast furnaces.[1,2]

The amount of petroleum coke that may be incorporated in a coal/blend without impairing coke quality considerably depends mainly on its particle size and the rheological properties of the coal/blend. The limit of petroleum coke in a coal blend is considered to be about 5 wt % in Japan and is established as the quantity of petroleum coke needed to decrease the Gieseler fluidity of the coal/blend below 200 ddpm.[3] However, elsewhere the maximum limit of petroleum coke addition for the production of a coke of acceptable quality has been reported to be 20 wt %,[4] and in Argentina a petroleum coke addition of 40 wt % has been quoted.[5]

The benefits of petroleum coke addition on metallurgical coke quality produced using the preheating process have been studied by INCAR[6] and Inland Steel.[7]

In two studies using petroleum cokes of different volatile matter contents, it was found that when high-volatile petroleum coke was used, a better quality of metallurgical coke was obtained in terms of lower reactivity to carbon dioxide and lower fines production in microstrength tests[8] and a higher coke postreaction strength (CSR).[7]

Several studies reported on the use of petroleum coke in cokemaking with special reference to the importance of the characteristics of the coal/blend to which it is added and the optimum particle size of petroleum coke.[9] However, the problem remains of explaining why petroleum cokes with similar conventional parameters such as volatile matter or total carbon content have different behaviors when added to coking coal blends. The main objective of this study is to resolve this problem and at the same time gain knowledge of the role of petroleum coke added to the coal/blends and carbonized, using nonconventional methods/techniques. Analytical methods/techniques used for characterization

(1) Triska, A. A.; Schubert, C. D. *International Congress on Coke, Iron and Steel Industry;* Charleroi: 1966; pp 402–416.
(2) Lin C.; Garzella, J. 45th Ironmaking Conference Proceedings. *Trans. Iron Steel Soc. AIME* **1986,** *45,* 195–202.
(3) Matsubara, K.; Morotomi, H.; Miyazu, T. In *Petroleum-Derived Carbons;* Bacha, J. D., Newman, J. W., White, J. L., Eds.; ACS Symposium Series 303; American Chemical Society: Washington, DC, 1986; pp 251–268.
(4) Triska, A. A. *Blast Furn. Steel Plant* **1965,** June, 508–515.
(5) Madías, J.; Colombo, L.; Ruiz, O. *Rev. Metal. Madrid* **1988,** *24,* 8–15.
(6) Alvarez, R.; Alvarez, E.; Suárez, C.; Méndez de Andrés, F.; Fernández, E.; Sirgado, M. *Proceedings of the 1st International Cokemaking Congress,* Essen, Germany; European Cokemaking Committee; Verlag Glückauf: 1987; Vol. I, p E5.
(7) Valia, H. S. 51st Ironmaking Conference Proceedings. *Trans. Iron Steel Soc. AIME* **1992,** *51,* 443–447.
(8) Ruiz, O.; Romero-Palazón, E.; Díez, M. A.; Marsh, H. *Fuel* **1990,** *69,* 456–459.
(9) Alvarez, R.; Díez, M. A.; Menéndez, J. A.; Barriocanal, C.; Pis, J. J.; Sirgado, M. 54th Ironmaking Conference Proceedings. *Trans. Iron Steel Soc. AIME* **1995,** *54,* 405–413.

Table 1. Main Characteristics of the Petroleum Cokes Used

	petroleum coke					
	R2	R1	EH	R3	RD	R4
ash (wt % db)	0.9	0.4	0.6	0.4	0.3	0.0
VM (wt % db)	14.4	12.7	12.5	11.9	10.3	0.4
S (wt % db)	2.69	4.57	1.33	4.08	0.82	0.00
C (wt % db)	90.3	88.2	90.1	90.1	93.6	99.8
H (wt % db)	4.2	3.9	4.3	4.3	3.0	0.1
N (wt % db)	1.3	1.6	2.2	0.6	1.1	0.0

of coal and carbon materials, which include optical polarized-light microscopy, FTIR spectroscopy, hydrogen donor ability test, thermogravimetric analysis, and free swelling index test, have been successfully adopted here in the characterization of petroleum cokes to be used as additive in cokemaking.

Experimental Section

Table 1 shows the typical properties of a set of industrial green petroleum cokes and one calcined petroleum coke (R4), which have been supplied by Repsol Derivados S.A. The petroleum coke R3 was obtained at laboratory scale (490 °C and 10 kg/cm^2).

In an attempt to demonstrate a certain degree of "activity" of the above petroleum cokes during the plastic stage of a coal, a characterization using Fourier transform infrared (FTIR) spectroscopy, hydrogen donor ability (D_a) test, thermogravimetric analysis, and free swelling index (FSI) test was carried out.

Optical Microscopy. Polished coke surfaces were examined using a polarized light microscope (Leitz Ortolux Z) fitted with crossed polars and a $\lambda/2$ wave retarder plate. An overall magnification of $\times$720 in oil immersion was used. The different structural features were evaluated by a point-counting procedure on 500 points, which were divided into categories from isotropic material to mosaics of various grain sizes and domain and flow domain anisotropy following a classification system described previously.[8] A category including mesophase spheres within an isotropic matrix (MI) was also quantified.

From the quantitative data and an increasing factor assigned to each textural component according to its size, an optical texture index (OTI) was calculated.[10] This index, which gives an indication of the degree of anisotropic development of a carbon material, was calculated using the expression

$$OTI = \sum F_i(OTI)/100$$

where F_i is the fraction of anisotropic unit in optical texture and $(OTI)_i$ is the factor for each anisotropic unit in the optical texture approximately proportional to the size of the unit.

FTIR Spectroscopy. FTIR spectra were obtained in a Perkin-Elmer 1750 spectrometer using standard pellets of KBr matrix (1:100 petroleum coke to KBr ratio) by co-adding 100 interferograms at a nominal resolution of 4 cm^{-1}. Spectra were corrected for scattering using two baselines (3800−1800 and 1800−660 cm^{-1}) and then standardized to 1 mg of petroleum coke dry ash free basis in the pellet before determination of the band areas and maximum absorbances. The semiquantitative study was carried out using the baseline method.

Hydrogen Donor Ability. Mixtures of petroleum coke and anthracene (1:1 w/w) were heated in sealed glass tubes under argon atmosphere to 450 °C at a heating rate of 5 °C/min with no soaking time.[11−13] After heating, the samples were extracted with CS$_2$ and the extracts analyzed by gas capillary

Table 2. Main Characteristics of the Coking Coal Used in Blend Preparation

ash (wt % db)	9.7	maceral composition (vol % dmmf)	
VM (wt % db)	23.7	vitrinite	70.0
sulfur (wt % db)	0.60	semifusinite	8.0
Gieseler max fluidity (ddpm)	874	fusinite	22.0
mean reflectance of vitrinite, $\bar{R}_0$ (%)	1.06		
SD of $\bar{R}_0$	0.10		

chromatography (GC).[13] The GC analyses were performed on a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a flame ionization detector (FID). Separations were carried out on a fused-silica capillary column (25 m × 0.22 mm) coated with SE-54 stationary phase. The temperature was programmed from 100 to 190 °C at 4 °C/min with helium as carrier gas at a flow rate of 1.5 mL/min and a splitting ratio of 1:50. The detector and injector temperatures were 300 °C. Compounds were identified by comparison of retention time data with those for standard compounds [anthracene and 9,10-dihydroanthracene (DHA)] and the data for tetrahydroanthracene (THA) from previous pitch studies.[13] For quantification, fluorene was used as an internal standard. The donor ability of the petroleum cokes (D_a) was calculated from the amount of DHA and THA formed from anthracene and expressed as milligrams of hydrogen per gram of petroleum coke.[13]

Thermogravimetric Analysis. TG/DTG measurements were carried out using a Setaram TAG24 thermal analyzer. Samples of each petroleum coke (25 mg) sized <125 μm were heated to 1000 °C at a rate of 30 °C/min flowing nitrogen at 50 mL/min and maintained at the maximum temperature to constant weight.

FSI. Good coking coals should swell during carbonization. The FSI is obtained by heating a sample of 1 g (<212 μm) in a standardized crucible to 820 °C for 2.5 min. The profile of the resulting coke is compared to standard profiles.[14,15] The FSI test can be applied to blends and mixtures for cocarbonization with reactive additives and in this study to check the ability of the petroleum cokes to agglomerate.

Gieseler Plastometry Test. Blends of a coking coal with volatile matter content of 23 wt % db and the different petroleum cokes (90:10 w/w) were prepared and subjected to the Gieseler plasticity test, following ASTM D2639-74 standard procedure. The parameters derived from this test are (i) the temperature at which the coal/blend starts to be fluid (T_s), (ii) the temperature of maximum fluidity (T_m), (iii) the temperature of resolidification (T_r), (iv) the temperature range covering the softening of a coal (plastic range), which is defined as the difference between the resolidification temperature (T_r) and the initial softening temperature (T_s), and (v) the maximum fluidity (MF) reported as dial divisions per minute (ddpm). MF is one of the most important parameter used for coking coal characterization.

The main characteristics of the coking coal used for blends preparation are given in Table 2.

Results and Discussion

The main characteristics of a set of five green and one calcined (R4) petroleum cokes used in this study are presented in Table 1. The calcined petroleum coke was used as a reference for an inert additive to coking coal blends. The green petroleum cokes had a narrow range in volatile matter content (10.3−14.4 wt % db) and a wide range in sulfur content between 0.82 and 4.57 wt

(10) Oya, A.; Quian, Z.; Marsh, H. *Fuel* **1983**, *62*, 274−278.
(11) Yokono, T.; Marsh, H.; Yokono, M. *Fuel* **1981**, *60*, 607−611.
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(14) ASTM. Method D720, Test for Free-Swelling Index of Coal; ASTM: Phildelphia, PA, 1991.
(15) Collin, G.; Bujnowska, B. *Carbon* **1994**, *32*, 547−552.

Table 3. Optical Texture Components (in Percentage) and OTI Values of the Petroleum Cokes

	R2	R1	EH	R3	RD	R4
fine mosaic	0.5	0.6	0.4	0.0	0.1	0.1
medium mosaic	2.4	4.7	1.8	4.0	1.6	4.8
coarse mosaic	12.3	21.5	56.9	4.6	9.9	2.7
small domain	25.5	32.6	27.7	43.4	26.3	0.0
domain	21.2	28.0	4.8	45.4	38.4	41.3
flow domain	12.5	8.9	1.0	2.6	21.0	51.1
isotropic	12.8	0.6	3.8	0.0	0.4	0.0
mesophase spheres/ isotropic matrix	12.8	3.1	3.6	0.0	2.3	0.0
OTI	16.1	19.2	11.3	23.5	23.8	28.0
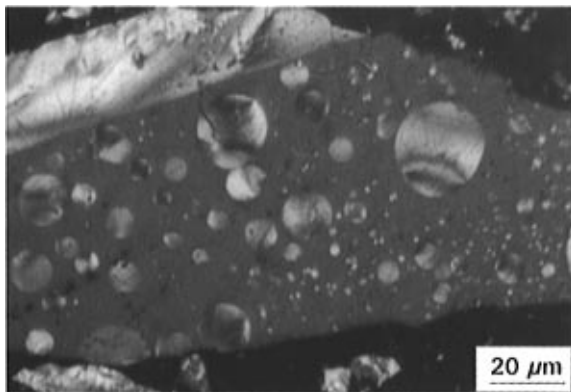
Figure 1. Optical micrograph of petroleum coke R2 showing the partially carbonized material composed of mesophase spheres within an isotropic matrix (MI).

% db, which may be a restrictive parameter in the use of petroleum coke for cokemaking.

Optical Microscopy. Percentages of optical texture components within the petroleum cokes and the calculated OTIs are in Table 3. The petroleum cokes studied varied in both anisotropic content and the size of anisotropic units. This is reflected in the variation of OTI values from 11.3 to 28.0, which were derived from the quantitative data and the specific factors attributed to each anisotropic optical texture.

With some exceptions, R3 and R4, unreacted isotropic like pitch material and mesophase spheres can be seen, either isolated or coalescing, within isotropic matrix (MI) as a consequence of petroleum cokes not having been completely carbonized in the delayed coker (Figure 1). Green petroleum coke R3 was produced on a laboratory scale under controlled experimental conditions to give an anisotropic solid residue and to avoid the presence of uncarbonized material. For R2, the abundance of such components clearly shows a lower "degree of carbonization" and a higher "degree of chemical activity," suggesting the presence of organic compounds that can be extracted with organic solvents of high extractive ability, such as quinoline. In fact, R2 has up to 10 wt % of quinoline-soluble material. The above optical texture components within petroleum cokes offer a potential source of volatile matter release in the transition to anisotropic features, which would improve the caking ability in cocarbonizations with coals.[8] If so, when petroleum coke containing partially carbonized material is used as an additive in cokemaking, it could modify physical and chemical mechanisms during the plastic stage of a coking coal and so influence the plastic properties of the blend. Then, the ability of such additives to promote the formation of small reactive molecules, to modify chemical condensation and
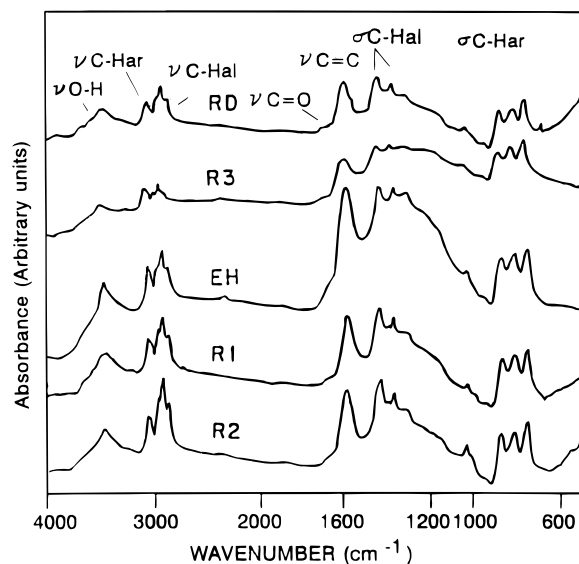
Figure 2. FTIR spectra of green petroleum cokes.

dehydrogenation reactions, and to use transferable hydrogen to generate mesogens to create mesophase in the cocarbonization system can be defined as the "*chemical activity*" of a given petroleum coke. Although R2, with the highest volatile matter content (14.4 wt % db), may be considered as the most reactive and petroleum cokes R3 and R4 as inerts during the plastic stage of the cocarbonization system with coal, no apparent relationships between the occurrence of such optical texture components and conventional parameters of the petroleum coke such as volatile matter content and H/C atomic ratio were found.

FTIR Spectroscopy. Figure 2 shows the FTIR spectra of the green petroleum cokes. The calcined petroleum coke (R4) is not used in this spectroscopic study because of its low absorption characteristics to baseline levels. The FTIR spectra typically display an absorption band near 3045 cm^{-1} due to aromatic C—H stretching vibrations, the pattern of absorption bands between 900 and 700 cm^{-1} which arise from the out-of-plane vibration of aromatic C—H bonds, and bands corresponding to aromatic C=C bonds near 1600 cm^{-1}. On the aliphatic side, the spectra consist of a pattern of absorption bands corresponding to saturated C—H stretching vibrations of alkyl substituents and methylene groups in hydroaromatic compounds (region between 2980 and 2750 cm^{-1}) and those corresponding to the C—H bending vibrations of methylene (1440 cm^{-1}) and methyl (1375 cm^{-1}) groups. It can also be noted that, basically, the functionalities are related to the existence of carbonyl groups (shoulder at 1670 cm^{-1} corresponding to C=O vibration modes), hydroxyl groups (3400 cm^{-1}), and aryl O groups (1300–1100 cm^{-1}). In general, the FTIR spectra are similar with regard to functionality, and differences are quantitative rather than qualitative.

In an attempt to provide additional evidence for the extent of carbonization and the degree of activity of the petroleum cokes in cocarbonization systems with coal, two FTIR indices are considered. First is the aliphatic hydrogen content (H_{al}), which is defined as the ratio between the area under the bands in the region between 2980 and 2750 cm^{-1} due to aliphatic C—H bonds (area$_{2980-2750}$) and that corresponding to aliphatic
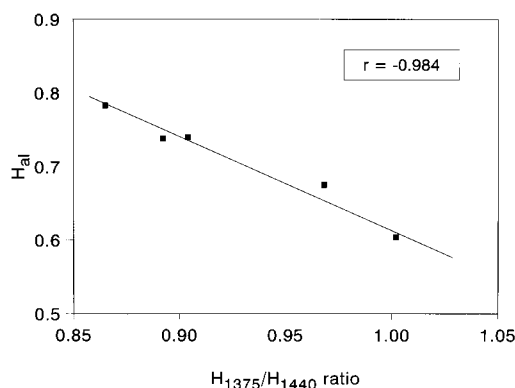
Figure 3. Relationship between aliphatic hydrogen content (H_{al}) and the H_{1375}/H_{1440} ratio for green petroleum cokes.

Table 4. Indices Derived from FTIR Semiquantitative Analysis for the Petroleum Cokes

petroleum coke	H_{al}	H_{1375}/H_{1440}	petroleum coke	H_{al}	H_{1375}/H_{1440}
R2	0.783	0.865	R3	0.604	1.002
R1	0.740	0.904	RD	0.738	0.892
EH	0.675	0.968			

(area$_{2980-2750}$) and aromatic (area$_{3100-2980}$) C−H bonds:

$$H_{al} = \text{area}_{2980-2750}/(\text{area}_{3100-2980} + \text{area}_{2980-2750})$$

The second FTIR index reflects the changes in intensity of the band centered near 1375 cm^{-1} due to methyl groups (H_{1375}) relative to that of methylene groups near 1440 cm^{-1} (H_{1440}).

The data of the FTIR indices from the semiquantification are given in Table 4. It can be observed that a decrease in aliphatic hydrogen content (H_{al}) is accompanied by a decrease in the methylene groups. The latter is reflected by an increase in the H_{1375}/H_{1440} ratio (CH$_3$/CH$_2$ groups ratio). In fact, a good linear correlation was found between H_{al} content and H_{1375}/H_{1440} ratio with a coefficient of 0.984 (Figure 3).

Petroleum cokes are composed of polynuclear aromatic hydrogen-deficient structures with few alkyl side chains as substituents and naphthenic groups.[16,17] It can be assumed that most of the methyl groups exists in α-position to aromatic rings and the presence of long chains is unlikely in these materials. The methylene groups detected may exist in the form of methylene/ethylene bridges and in hydroaromatic systems. Although no direct information on the type of the methylene groups can be derived from FTIR, taking into account these considerations, it can be deduced that the most abundant aliphatic groups in petroleum cokes with lower H_{al} content are methyl groups in the α-position to aromatic rings and that they have fewer methylene groups, most likely in indane or fluorene structures. On the other hand, the higher H_{al} contents may be due to higher abundances of cluster systems containing hydroaromatic rings. The presence of such hydroaromatic systems in petroleum cokes may be responsible for the chemical activity during the coking process, as discussed below.

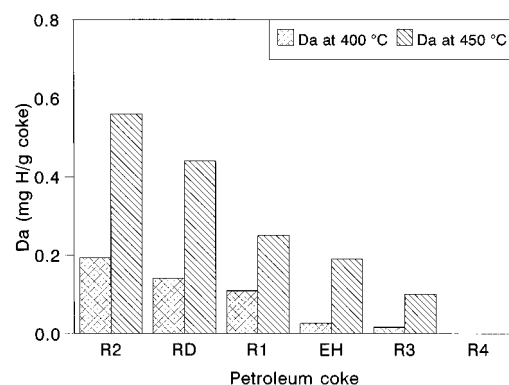Using the above two FTIR indices, an increasing order of carbonization degree or a decreasing order of thermal−

(16) Michel, D.; Pruski, M.; Gerstein, B. C. *Carbon* **1994**, *32*, 31−40.

(17) Pruski, M.; Gerstein, B. C.; Michel, D. *Carbon* **1994**, *32*, 41−49.

Figure 4. Hydrogen donor ability (D_a) at 400 and 450 °C of green petroleum cokes.

chemical activity of the green petroleum cokes can be established:

$$R2 < RD < R1 < EH < R3 < (R4)$$

It is obvious that the calcined petroleum coke (R4) has the highest graphitization level and, consequently, the higher carbonization degree in this series of petroleum cokes.

Hydrogen Donor Ability (D_a). During the carbonization process two types of opposite and simultaneous reactions occur: cracking and aromatization/condensation. The equilibrium between these two reactions depends on the hydrogen available in the reaction system.[18,19] Thus, at least to some degree, the ability of the green petroleum cokes to modify cocarbonization systems with coal can be attributed to the presence of hydroaromatic rings that exhibit a hydrogen donor ability. Here, the petroleum coke can interact with the fluid coal system as a donor and acceptor material. For this reason, another approach to check if the petroleum cokes studied have an active role within the plastic zone of the carbonization system is the hydrogen donor ability (D_a) test. This test has been successfully applied in studies of cocarbonization systems of coking coals and pitches for determining the ability to act as "hydrogen shuttles" in the carbonization system and to affect the optical texture components of the metallurgical cokes produced.[11,12,20−22] The D_a was determined with anthracene at temperatures of 400 and 450 °C, which correspond to the plastic range of a coking coal. Figure 4 shows the hydrogen donor ability values of the petroleum cokes at 400 and 450 °C. As expected, the calcined petroleum coke R4 does not have any chemical activity at the above temperatures, indicating the inert role that this type of material has in the fluid system. However, all of the green petroleum cokes have the ability to donate hydrogen to anthracene, the highest being that of the petroleum coke R2 (0.56 at 450 °C) and the lowest being that of R3 (0.10 at 450 °C). The two green petroleum cokes with similar volatile matter contents, R1 (12.7 wt % db) and EH (12.5 wt % db), are clearly differentiated by FTIR spectroscopy, hydrogen

(18) Lewis, I. C. *Carbon* **1982**, *20*, 519−529.

(19) Loison, R., Foch, P., Boyer, A., Eds. In *Coke Quality and Production*; Butterworth: London, 1989; pp 108−110.

(20) Yokono, T.; Obara, T.; Iyama, S.; Sanada, Y. *Carbon* **1984**, *22*, 623−624.

(21) Yokono, T.; Obara, T.; Sanada, Y. *Carbon* **1986**, *24*, 29−32.

(22) Yokono, T.; Takahashi, N.; Sanada, Y. *Energy Fuels* **1987**, *1*, 360−362.
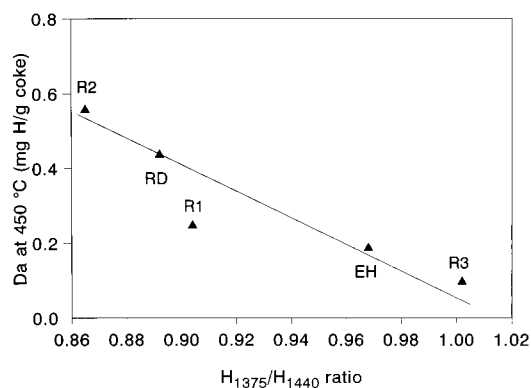
Figure 5. Relationship between D_a at 450 °C and the H_{1375}/H_{1440} ratio of green petroleum cokes.

Table 5. Volatile Matter Released of the Petroleum Cokes from TG Studies

	R2	R1	EH	R3	RD	R4
VM below 150 °C (wt %)	0.24	0.20	0.50	0.41	0.28	0.09
VM 150−400 °C (wt %)	2.14	1.53	1.16	2.13	1.89	0.00
VM 400−500 °C (wt %)	4.12	2.98	1.75	1.45	3.49	0.02
VM 500−750 °C (wt %)	6.84	7.12	5.99	5.21	6.51	0.12
VM 750−1000 °C (wt %)	2.76	2.76	4.49	3.60	2.50	0.32
calcined residue (wt %)	83.89	85.41	86.11	87.21	85.34	99.45
$T_{max}{}^a$ (°C)	503	548	621	644	525	

^{a} Temperature of maximum evolution of volatile matter on the basis of DTG curve.

donor ability test, and additional techniques used in this study as discussed below. This means that the two petroleum cokes, having the same amounts of volatile matter, differ in the structural features promoting the formation of volatile components. The ability of petroleum cokes is always low in comparison with materials considered as active in the coking process such as pitch or coal with low fluidity that exhibits D_a of 1.15 mg of H/g of coal at 450 °C.

As expected, D_a values determined at 400 °C (a temperature of the beginning of the plastic stage in the coking process) are lower than D_a values determined at 450 °C. Although the D_a values at 400 °C are in a narrow range, the differences being very small, a similar trend was found for all petroleum cokes studied (Figure 4).

Hydrogen donor ability does not appear to correlate well with H_{al} content itself and depends rather on the relative amount and the type of alkyl substituents as methyl or methylene groups. This can be seen in the linear correlation between D_a and the H_{1375}/H_{1440} ratio (Figure 5), suggesting that the intensity of the absorption band near 1440 cm^{-1} is mainly related to methylene groups in hydroaromatic systems.

Thermogravimetric Analysis. Another way to differentiate green petroleum coke behavior during the pyrolysis process is to use TG/DTG curves. Table 5 contains percentages of volatile matter released in specific temperature ranges, relating to loss of water during pyrolysis (below 150 °C), the plastic range of a given coal (400−500 °C), and the pre- (150−400 °C) and postplastic stages (500−750 and 750−1000 °C). In Table 5, the temperatures at which the maximum release of volatile matter occurs (T_{max}), on the basis of DTG curves of the green petroleum cokes, are listed.

In the 150−400 °C interval the higher weight loss corresponds to R2 and R3, indicating a lower degree of carbonization. The next temperature interval, between
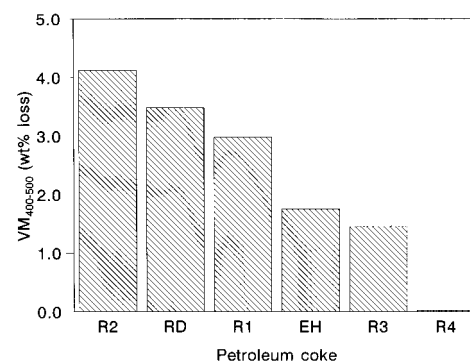

Figure 6. Percentage of volatile matter released between 400 and 500 °C (VM$_{400-500}$) for the petroleum cokes.

400 and 500 °C (VM$_{400-500}$), is more important due to the similarity with the plastic stage range of coals. Therefore, it is to be expected that the higher the amount of volatile matter released in this interval of temperature, the higher the chemical activity of petroleum coke in the carbonization process.

Figure 6 shows the percentage of volatile matter released between 400 and 500 °C for the six petroleum cokes studied. According to these values the following order from higher to lower chemical activity during the coking process is established:

$$R2 > RD > R1 > EH > R3 > R4$$

Again, this behavior may be attributed to chemical differences between the petroleum cokes and, consequently, a different role during the cocarbonization with coal can be expected. It is interesting to note that again the above order of these petroleum cokes corresponds to that established from FTIR and D_a data. It is known that the modification of the cocarbonization system by pitch (derived from coal and petroleum) can be associated with hydrogen transfer reactions (hydrogen shuttling) which involve movement of hydrogen from the pitch to stabilize certain of the free radicals. This stabilization prevents formation, at too early stage, in the process of a composite coal−coke and allows the pitch to interact chemically with the coal, so extending the zone of maximum fluidity in the cocarbonizing system. Then, as the fluidity increases with increasing temperature of pyrolysis, a stage is reached at which the hydrogen becomes consumed and is evolved as volatile matter. The presence of naphthenic systems apparently promotes the above hydrogen transfer reactions.[23−25] The point emerging is that there is a certain similarity in the mechanism of pitch and "reactive" petroleum coke interaction with coal. The results obtained from TG, FTIR, and D_a suggest that the volatile matter evolved between 400 and 500 °C may be associated with an enhanced ability of the petroleum coke to transfer hydrogen to the system due to a higher concentration of hydroaromatic systems.

In addition, a good linear relationship was found between the amount of VM$_{400-500}$ and the temperature of maximum evolution of volatile matter (T_{max}) (Figure 7). The higher the VM$_{400-500}$, the lower the temperature

(23) Mochida, I.; Marsh, H. *Fuel* **1979**, *58*, 626−632.
(24) Marsh, H.; Neavel, R. C. *Fuel* **1980**, *59*, 511−513.
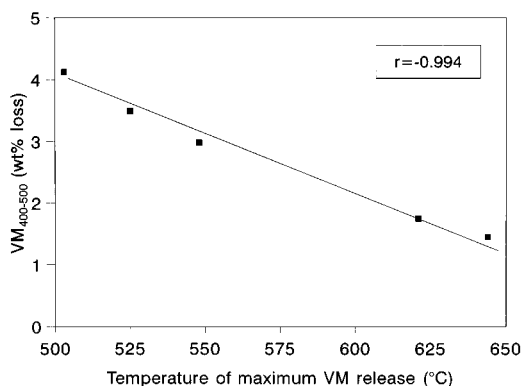(25) Marsh, H.; Clarke; D. E. *Erdoel Kohle, Erdgas, Petrochem.* **1986**, *3*, 113−122.

Figure 7. Relationship between volatile matter released between 400 and 500 °C ($VM_{400-500}$) and the temperature of maximum volatile matter evolution for petroleum cokes.
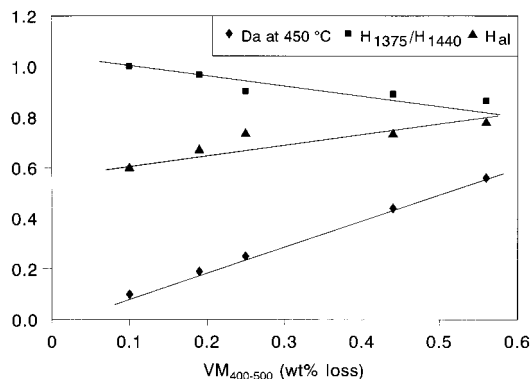

Figure 8. Relationship between the volatile matter released between 400 and 500 °C ($VM_{400-500}$) and D_a at 450 °C, H_{1375}/H_{1440} ratio, and aliphatic hydrogen (H_{al}) for the green petroleum cokes.
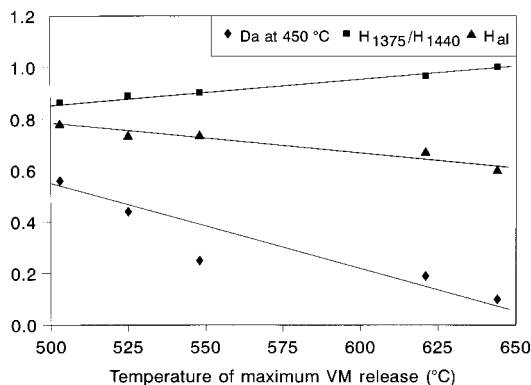

Figure 9. Relationship between the temperature of maximum volatile matter evolution (T_{max}) and D_a at 450 °C, H_{1375}/H_{1440} ratio, and aliphatic hydrogen (H_{al}) for green petroleum cokes.

of maximum evolution of volatile species during low-temperature pyrolysis of the petroleum cokes.

The weight loss in the temperature range between 500 and 750 °C is the highest, and it represents between 40 and 49 wt % of the total volatile matter released during pyrolysis up to 1000 °C. Finally, at temperatures in the 750–1000 °C range, the volatile matter released decreases, being still high for EH and R3 which exhibit the higher carbonization degree.

The two above parameters derived from thermogravimetric analysis correlate well with the H_{1375}/H_{1440} ratio and D_a as in Figures 8 and 9, respectively. However, no clear relationship has been found between amounts of isotropic pitch material and mesophase spheres within an isotropic matrix quantified by optical micros-
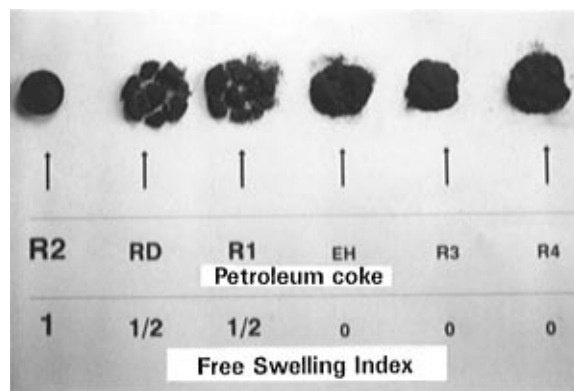

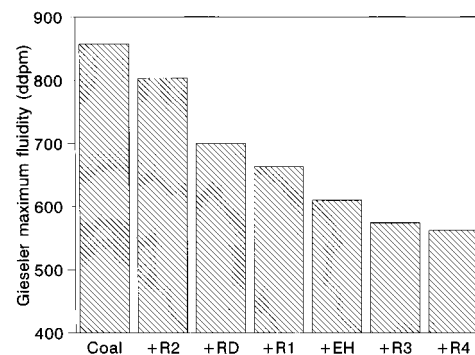**Figure 10.** Profiles and FSI values of the residues of the petroleum cokes.

Figure 11. Variation of the Gieseler maximum fluidity for a single coking coal and its blends with petroleum coke at 10 wt % addition.

copy. This fact suggests that the active role in hydrogen transfer reactions of the mesogenic molecules within these components is the most important factor.

FSI. FSI data are also in agreement with the order established using the characterization techniques above quoted. Figure 10 shows the profiles of all petroleum coke residues obtained in the FSI test. It is seen that R2 with a lower carbonization degree gives a residue in the FSI test with a low but certain degree of agglomeration (FSI = 1). RD and R1 have a lower ability to agglomerate (FSI = 0.5). Finally, EH, R3, and R4, with a higher degree of carbonization, do not show any ability to agglomerate (FSI = 0).

Thermoplastic Behavior of Blends of a Coking Coal and Petroleum Cokes. The Gieseler maximum fluidity (MF) values of a single coking coal and the blends made from this coal and 10 wt % of the petroleum cokes studied are shown in Figure 11. The addition of petroleum coke produces a decrease in MF in the blend due to the lack or small proportion of low molecular weight and hydrogen-containing species available for contributing to the generation of fluidity in the cocarbonization system. However, the type of petroleum coke added is a key factor for explaining the different values of MF in these blends. Thus, calcined petroleum coke R4, which has a high degree of carbonization and no ability to agglomerate, produces the biggest decrease in MF. This fact clearly confirms the expected inert role that this material plays in the fluid system. On the other hand, R2, with a lower degree of carbonization, produced the smallest decrease in MF because the presence of mesogenic molecules contributes to the chemical activity of the blend. The extent of the decrease in MF in these blends is in agreement with
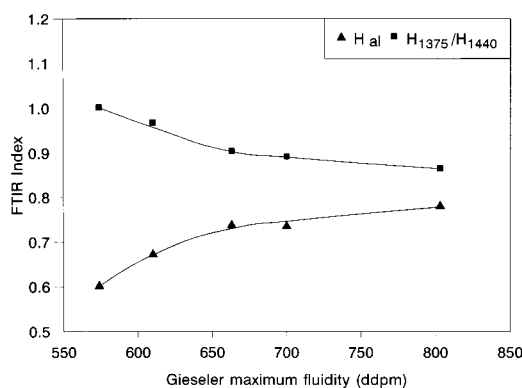
Figure 12. Relationship between Gieseler maximum fluidity of blends and FTIR indices of the green petroleum cokes.
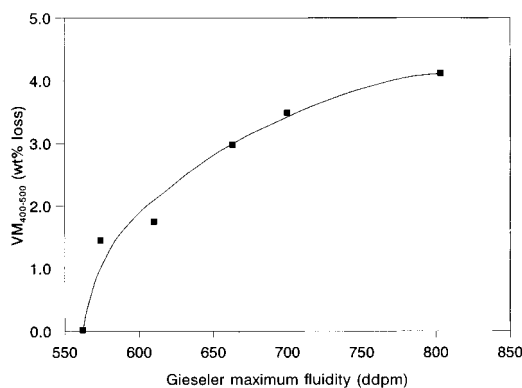

Figure 13. Relationship between Gieseler maximum fluidity of blends and the volatile matter released between 400 and 500 °C ($VM_{400-500}$) of the petroleum cokes.

the classification proposed from higher to lower chemical activity of the petroleum cokes during the coking process (R2 > RD > R1 > EH > R3 > R4).

Figure 12 shows the contribution of the hydroaromatic species in petroleum coke to the maximum fluidity developed in the cocarbonizing systems. Thus, a lower H_{1375}/H_{1440} ratio in petroleum cokes corresponds to a higher MF in the blend. Similarly, the removal of low molecular weight substances, originally present in the petroleum coke and liberated during heating within the plastic range ($VM_{400-500}$), leads to a decrease in MF in the blend (Figure 13).

With regard to the other parameters from the Gieseler test, no relevant changes were found ($T_s = 405 \pm 2$ °C; $T_m = 457 \pm 2$ °C; and $T_r = 489 \pm 2$ °C). Figure 14 shows an example of the Gieseler fluidity curves of the single coking coal and its blends with three selected petroleum coke—the most chemically active coke (R2), a moderately active coke (R1), and an inactive coke (R4) during the plastic stage. The profiles of the evolution of Gieseler fluidity with temperature suggest a dependence on chemical activity of the petroleum cokes. In fact, a relatively quicker evolution of fluidity begins at a lower temperature for blends with R2 and R1 in comparison with the single coal and the blend with R4. After the maximum, the gradual decrease in fluidity clearly
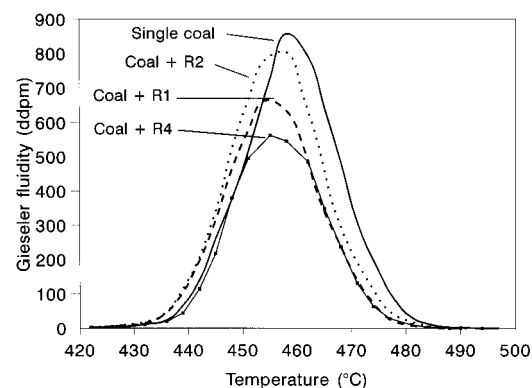

Figure 14. Evolution of Gieseler fluidity with temperature for a single coal and its blends with petroleum cokes of different chemical activity (R2, R1, and R4).

differentiates the single coal, the blend with R2, and those blends with R1 and R4. These results together with the MF values indicate that the characterization of petroleum coke proposed is adequate for detecting the different behaviors of petroleum cokes during the plastic interval of a coking coal. The plastic behavior in carbonization systems is an important factor to determine the quality of the resultant metallurgical cokes. The relevance of the differences in petroleum coke activity during the plastic stage in relation to the quality parameters of metallurgical cokes prepared in a laboratory oven are demonstrated in an additional study.

Conclusions

This study clearly indicates that not all green petroleum cokes have identical behaviors in the cocarbonization with a coking coal. Differences arise because of differences in feedstocks used and in the pyrolysis operation within the delayed coker. Different extents of nonpyrolyzed pitch feedstock were found in these green petroleum cokes. Calcined petroleum coke behaves as an inert diluent to the carbonizing coal. The most important properties of the green petroleum cokes are their hydrogen donor ability associated with extents of pitch residue and the volatile matter release between 400 and 500 °C and the chemical composition of the pitch residue. The ratio of methyl and methylene groups has an important role in the chemistry of the plastic zone of the cocarbonization system. This is where the anisotropic optical texture of the metallurgical coke is established, via the formation of liquid crystal systems. Hydrogen donor ability extends the formation of an anisotropic optical texture. Green petroleum coke can be considered not totally inert material during the plastic stage of a given coking coal. The procedure described in this work may be useful to select petroleum cokes as additives in cokemaking.