



Novel coal-based precursors for cokes with highly oriented microstructures

P. Alvarez, N. Díez, R. Santamaría, C. Blanco, R. Menéndez*, M. Granda

Instituto Nacional del Carbón, CSIC, P.O. Box 73, 33080 Oviedo, Spain

ARTICLE INFO

Article history:

Received 22 July 2011

Received in revised form 7 September 2011

Accepted 8 September 2011

Available online 20 September 2011

Keywords:

Anthracene oil

Coke

Microstructure

ABSTRACT

The suitability of new environmentally-friendly coal-based products for the preparation of cokes with a highly oriented microstructure is investigated. These products (AO-A and AO-B) are obtained from two different stages of the processing of an industrial anthracene oil. The composition and degree of polymerization determine their ability to produce cokes with highly oriented textures. The transformation of AO-A into a highly oriented coke requires pyrolysis temperatures of 450–460 °C, residence times of 8–20 h and a pressure of 5 bar, whereas AO-B, which is more polymerized, requires lower temperatures (420–440 °C) and shorter residence times (8 h) without the application of any external pressure. The larger extent of highly oriented microstructures present in cokes from AO-A is explained from the greater hydrogen transfer capacity during the coking process.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Cokes with a preferential orientation in their microstructure (i.e. needle-like cokes) are in great demand because of their superb properties (e.g., thermal and electrical conductivity, stiffness, etc.). These premium cokes readily find application in the steel industry, since they are an essential raw material for making graphite electrodes, which are used in electric arc furnaces for metals smelting [1].

Feedstocks for the production of premium needle cokes are obtained from both petroleum and coal tar derivatives and include the distilled residues of low sulphur crudes, FCC-decant oil, naphtha cracked tar pitch and their blends [2–5]. Due to the great industrial demand for both feedstocks and cokes, a greater deal of effort has been devoted for reducing the production costs. To achieve this, the process employs additional materials such as low-cost by-products from coal and petroleum which, after an adequate pre-treatment (to favour the fluidity of the mesophase generated during the process and the gas evolution [6–8]), produce the necessary microstructural orientation. However, inconsistency in the composition and characteristics of the precursors may significantly affect the processing conditions and properties of the resultant coke.

We have recently reported on a low cost coal tar derivative, anthracene oil, that can be polymerized to produce a pitch-like material [9,10]. Anthracene oil is an industrial product that is readily available on the market and the quality and consistency of the

material obtained is guaranteed by the special distilling technology employed in its production. This makes anthracene oil a potential alternative for the production of different carbon materials at industrial scale. The special type of pitches obtainable from anthracene oil exhibit certain inherent characteristics, such as their low toxicity (compared to industrial coal-tar pitches), high beta resin content and total absence of particles and metals that make them easily transformable into cokes with highly oriented microstructure. Furthermore, the versatility of the processing conditions of anthracene oil gives rise to products with different composition and degree of polymerization, key issues in the development of mesophase and the orientation of the microstructure of the final coke.

This work explores the possibility of using two anthracene oil derivatives, obtained at different stages of the processing of anthracene oil, to produce cokes with highly oriented microstructure. The composition and pyrolysis behaviour of the two products are studied by elemental analysis, solubility tests, ¹H NMR spectroscopy and thermogravimetric analysis. The results obtained are used to select an adequate coking procedure for each derivative. Green cokes are examined under polarized light microscopy and the different microstructures observed are quantified. A relationship between the optical texture and the experimental conditions used in the preparation of the cokes is established.

2. Experimental

2.1. Materials used

Two anthracene oil derivatives (AO-A and AO-B) were used as precursors for the preparation of the cokes. AO-A was obtained

* Corresponding author. Address: Instituto Nacional del Carbón, CSIC, Department of Chemistry of Materials, P.O. Box 73, 33080 Oviedo, Spain. Tel.: +34 985 11 89 78; fax: +34 985 29 76 62.

E-mail address: rosmenen@incar.csic.es (R. Menéndez).

by thermal oxidative treatment of industrial anthracene oil (coal tar fraction that distills between ~ 270 and ~ 400 °C). This treatment involves heating to ~ 240 – 260 °C in the presence of air (air/anthracene oil ratio of 0.18/1). AO-B was obtained by thermal treatment of AO-A at temperatures of ~ 400 °C. This second treatment is addressed to obtain a pitch with a targeted softening point of 110 °C. During this second treatment, the oxygen introduced in the previous step is reduced and the degree of polymerization of the components is higher [10].

2.2. Characterization of the anthracene oil derivatives

2.2.1. Elemental analysis

Carbon, hydrogen, nitrogen and sulphur content of the samples was determined using a LECO-CHNS-932 elemental analyzer. Oxygen content was directly determined using a LECO-VTF-900 graphite furnace. Experiments were carried out with 1 mg of sample ground and sieved to <200 μm . The results were quoted as the mean of values from four determinations. In all the cases, the experimental error was $<0.5\%$ of the absolute value.

2.2.2. Solubility

Toluene insoluble (TI) content was determined according to the Pechiney B-16 (series PT-7/79 of STPTC). *N*-Methyl-2-pyrrolidinone insoluble (NMPI) content was determined in a similar way to that described for the quinoline insoluble (ASTM D2318 standard), but using *N*-Methyl-2-pyrrolidinone instead of quinoline.

2.2.3. Carbon yield

The carbon yield of the samples was determined according to Alcan method (ASTM D4715-87 standard).

2.2.4. Softening point

The softening point of the anthracene oil derivatives was determined using a Mettler Toledo instrument according to the ASTM standard D3104-87.

2.2.5. Liquid-state ^1H NMR spectroscopy

Experiments were carried out in a 400 MHz AMX Bruker NMR spectrometer, using sample solubilized in CDCl_3 in a proportion

of 20 wt.% and placed in a 5 mm NMR tube CDCl_3 . Tetramethylsilane (TMS) was used as the chemical shift reference.

2.2.6. Thermogravimetric analysis

TG/DTG curves were obtained by using a 2960 STD TA Instruments thermal analyzer. About 15 mg of sample (<200 μm of particle size), placed in a platinum crucible (2.8 mm height and 7.5 mm i.d.), was heated to 1000 °C at 10 °C min^{-1} under a nitrogen flow of 150 mL min^{-1} .

2.3. Preparation of the green cokes

About 300 g of AO-A, or AO-B, sieved and ground to <200 μm , was placed in an aluminium crucible (130 mm height and 58 i.d.), vertically positioned in a stainless steel autoclave and then pyrolyzed using a heating rate was 10 °C min^{-1} and following a multi-step procedure which experimental conditions are detailed in Fig. 1. The pyrolysis of AO-A required in all cases an initial pyrolysis step under a nitrogen pressure of 5 bar. This pressure was subsequently reduced to 1 bar (second pyrolysis step) and kept constant until the sample was cooled down to room temperature to yield the samples AO-A1, AO-A2, AO-A3. The application of an extra third step, consisting of a depressurization down to the atmospheric pressure and holding the temperature until cooling down, led to sample AO-A4. In the case of AO-B all pyrolysis steps were carried out under a nitrogen flow of 100 mL min^{-1} in similar batches to yield samples AO-B1, AO-B2 and AO-B3.

2.4. Polarized light microscopy of the anthracene oil-based green cokes

Samples of green cokes were embedded in epoxy resin and then ground, using two grades of silicon carbide paper (600 and 1200 grits), and polished successively with two grades of alumina solution (0.3 and 0.5 μm). Microscopy analysis was conducted using a Zeiss Axioplan microscope. The microscope was equipped with an adjusted eye-piece, one-wave retarder plate to record the optical texture of the samples and infinity-corrected oil immersion objectives of $5\times$ and $50\times$. Representative photographs of the samples were taken by using a Leica DC100 camera fitted to the microscope.

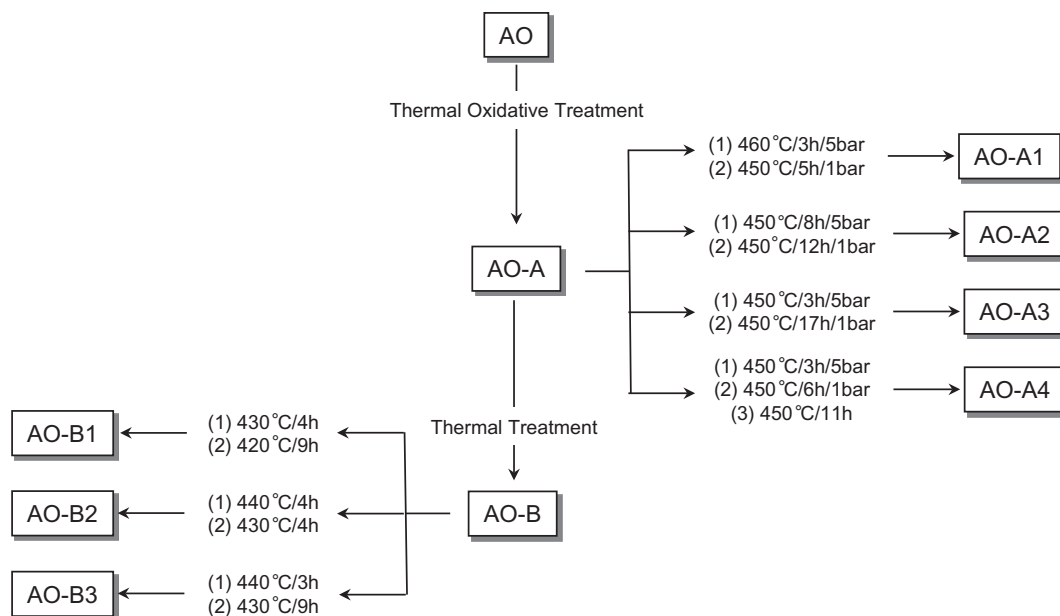


Fig. 1. Schematic illustration of the preparation of the anthracene oil-based pitches and green cokes.

Table 1
Nomenclature to describe the optical texture in the green cokes.

Category	Description of optical texture	Size		Optical texture index (OTI)
		Length (μm)	Width (μm)	
Iso	Isotropic	No optical activity		0
1	Fine-grained mosaic	<1.5		1
2	Medium-grained mosaic	1.5–5		3
3	Coarse-grained mosaic	5–10		7
4	Supra-mosaic	Aligned mosaics		10
5	Small domain	10–60		20
6	Domain	>60		30
7	Medium-flow anisotropy	<30	<5	7
8	Coarse-flow anisotropy	30–60	5–10	20
9	Flow domain anisotropy	>60	>10	30

The shape and size of the anisotropic units, observed as isochromatic areas, were quantified by polarized light microscopy according to the terms defined in Table 1 [11]. An optical texture index for each green coke was calculated using the formula:

$$OTI = \sum f_i \times (OTI)_i$$

where f_i represents the fraction of the anisotropic unit in the optical texture and $(OTI)_i$ the assigned factor for each anisotropic unit in the optical texture according to values reported in Table 1.

The quantification was performed on a series of green coke images, which were taken by polarized light microscopy using a magnification of 5×. The montage of the images resulted in a single image of the whole sample in which anisotropic units were examined to define the OTI value of each green coke. The results were quoted as the mean of values from three determinations. In all the cases, the experimental error was <1 vol.% of the absolute value of each individual optical component.

3. Results and discussion

The two anthracene oil derivatives used in this work (AO-A and AO-B) are the two main intermediates in a recently proposed procedure to transform anthracene oil (AO) into pitch, and are readily available at industrial scale. The first derivative, AO-A, is an oil obtained by the thermal oxidative treatment of AO. The subsequent thermal treatment applied to AO-A gave rise to AO-B, a pitch-like material with a softening point of 110 °C. As observed in Table 2, both derivatives exhibit characteristics that, initially, make them attractive as precursors for the preparation of coke with highly oriented microstructure. These characteristics include a low sulphur content (below 0.5 wt.%) and the absence of solid particles (ash and primary QI). However, their composition is very different, even

Table 2
Elemental composition and main characteristics of the anthracene oil derivatives.

Sample	Elemental analysis (wt.%)					C/H	SP	TI	NMPI	CY
	C	H	N	S	O					
AO-A	91.6	5.4	1.0	0.5	1.5	1.41	Oil	1	0	9
AO-B	93.3	4.5	1.1	0.5	0.6	1.73	110	23	3	51

C/H, carbon/hydrogen atomic ratio.

SP, Mettler softening point (°C).

TI, toluene insoluble content (wt.%).

NMPI, N-Methyl-2-pyrrolidinone insoluble content (wt.%).

CY, Alcan carbon yield (wt.%).

when they come from the same raw material (AO). This will have an effect on their further processing for obtaining highly oriented microstructures.

During the thermal oxidative treatment to produce AO-A, the oxygen causes an initial polymerization/condensation of the AO components, which is confirmed by the increase in the toluene insoluble material and carbon yield of AO-A (Table 2) with respect to AO (0 wt.% of TI and 0 wt.% of CY). At the same time, some oxygen is incorporated (1.5 wt.% for AO-A). This polymerization/condensation of the components progresses during the subsequent thermal treatment to produce AO-B, through the formation of molecular moieties able to generate a solid sample at room temperature (softening point of 110 °C), with a carbon yield much higher than that of AO-A (9 and 51 wt.% for AO-A and AO-B, respectively) as well as an increase in the solubility parameters up to 23 and 3 wt.% for TI and NMPI, respectively. This thermal treatment also produces a significant reduction in the oxygen content (down to 0.6 wt.%) as well as in the hydrogen content (5.4 and 4.5 wt.% for AO-A and AO-B, respectively). The type of hydrogen may affect the fluidity of the reaction media, the development of the mesophase and, therefore, the microstructure of the final coke. The ¹H NMR analysis of AO-A and AO-B shows structural differences between both samples. Thus, the higher Har/Hal ratio of AO-B (Table 3) suggests that the polymerization/condensation reactions involved in the thermal treatment occur at the expenses of the aliphatic hydrogen. Moreover, the type of this hydrogen is not the same in both samples. Based on works carried out by others, the ¹H NMR spectral regions can be analyzed by dividing the spectra into regions according to the nature of each type of hydrogen (see Table 2) [12]. As it can be seen, AO-A exhibits higher proportion of aliphatic hydrogen and, in particular, those which are located in methyl or methylene α to an aromatic ring and α to an aromatic ring (Ha), in methyl or methylene α to an aromatic ring which can be attached in γ to an aromatic ring (Hα1) and in methyl or methylene β to an aromatic ring (Hβ1). It can be also noted that AO-B not only exhibit higher amount of aromatic hydrogen but also higher proportion of aromatic hydrogen in sterically hindered positions, in angular PAH's in very pericondensed PAH's or next to heteroatoms or H-N (higher proportion of Har2/Har1).

These results suggest that the polymerization/condensation reactions involved in the thermal treatment of AO-A to give rise to AO-B occur with the consumption of oxygen and aliphatic hydrogen leading to a polymerized product composed by highly aromatic and sterically hindered molecules.

It is expected that these differences in composition will affect the pyrolysis behaviour of the samples. The coking conditions will be therefore settled for each individual precursor according to its behaviour.

3.1. Microstructure of green cokes from AO-A

The experimental conditions required for the preparation of coke with highly oriented microstructure will be selected from the data obtained from the pyrolysis behaviour of the parent product AO-A. The thermogravimetric analysis (Fig. 2) shows that AO-A undergoes a significant removal of volatiles in a short range of temperatures (between 200 and 400 °C), the carbonaceous residue being <10 wt.% at temperatures above 400 °C. This indicates the convenience of using pressure during pyrolysis in order to mitigate the elimination of gases and to increase the yield of the process.

To determine the optimum conditions for mesophase formation and development, some preliminary experiments were carried out. The pyrolysis of AO-A at 460 °C/3 h/5 bar gave rise to a product with some incipient mesophase, in the form of microspheres (Fig. 3a, position A). A slight increase in the temperature and/or residence time (e.g., 460 °C/5 h/5 bar) resulted in a non-plastic

Table 3¹H NMR analysis of the anthracene oil derivatives.

Sample	Har		Har2/Har1	Hal						<i>I</i> _{Ar}
	Har2	Har1		Hf	Ha	Hα1	Hβ2	Hβ1	Hγ	
AO-A	0.068	0.790	0.086	0.004	0.037	0.085	0.006	0.009	0.000	6.1
AO-B	0.088	0.798	0.110	0.025	0.025	0.050	0.010	0.005	0.000	7.8

Har, aromatic hydrogen.

Har2, aromatic hydrogen in sterically hindered position, in angular PAHs, in very pericondensed PAHs or next to heteroatoms.

Har1, other aromatic hydrogen.

Hal, aliphatic hydrogen.

Hf, aliphatic hydrogen in methylene α to two aromatic rings.

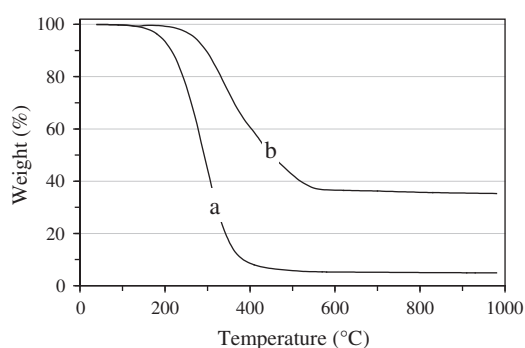
Ha, aliphatic hydrogen in methyl or methylene α to an aromatic ring and β to an aromatic ring.

Hα1, aliphatic hydrogen in methyl or methylene α to an aromatic ring which can be attached in γ to an aromatic ring.

Hβ2, alicyclic hydrogen β to two aromatic rings.

Hβ1, aliphatic hydrogen in methyl or methylene β to an aromatic ring.

Hγ, aliphatic hydrogen in methyl or methylene γ to an aromatic ring.

*I*_{Ar}, Aromaticity index (Har/Hal).**Fig. 2.** Thermogravimetric curves of the (a) AO-A and (b) AO-B.

product (Fig. 3b) with a poor microstructural orientation. This suggests that, once the formation of mesophase initiates, it rapidly progresses leading to a non-plastic and poorly oriented material.

In order to improve the microstructural orientation of the cokes from AO-A, the experimental conditions were modified to favour the fluidity of the mesophase and the gas evolution during the process, which are two main factors in the whole process [13,14]. The idea is to extend the temperature zone of maximum fluidity which would result in a better orientation of the microstructures [15]. Bearing this in mind, AO-A was pyrolyzed in two consecutive steps. The first step, carried out under a nitrogen pressure of 5 bar, led to the formation of large macromolecules and/or incipient mesophase, especially in the form of small microspheres, whereas the

second step, carried out under milder conditions (lower temperature and pressure), favoured the growth and orientation of the mesophase. A summary of the conditions used and the optical textures of the green cokes obtained are shown in Table 4 and Fig. 4, respectively.

The two-step procedure used in this work improves the microstructural orientation of the green cokes in all cases. The quantification of the main microstructural features was made according to the OTI values, known to be good indicators of the microstructural orientation of the cokes which directly correlates with the thermal expansion coefficients of the resultant cokes [16]. The values obtained varied from 25.05 to 26.97 (Table 4), well inside the range of those reported for other cokes exhibiting highly oriented microstructure [11].

It should also be mentioned that prolonged residence times in the second step of the pyrolysis (AO-A3, OTI of 26.97) gave rise to green cokes with a higher OTI values than when the prolonged residence time is applied in the first step (AO-A2, OTI of 26.31). Additionally, total depressurization during the second step led to a green coke with a lower OTI value (AO-A4, OTI of 25.89) than when this step was carried out at 1 bar of nitrogen pressure (AO-A3, OTI of 26.97). These facts could be related with the proper percolation of the gas bubbles that deforms the planar liquid-crystal components and causes their arrangement into an uniaxial geometry characteristic of a precursor of coke with highly oriented microstructure, that is, at the specific point of solidification and with a proper extent [17]. Before or after this specific point, the evolution of gases was found to be detrimental for the formation of a coke with highly oriented microstructure [18].

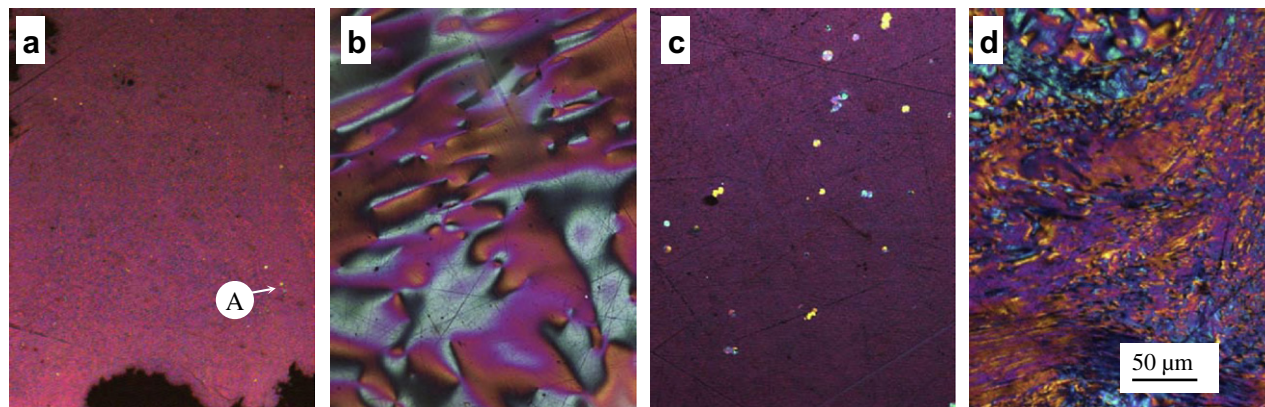
**Fig. 3.** Polarized light micrographs of the pyrolysis products obtained from AO-A at (a) 460 °C/3 h/5 bar, (b) 460 °C/5 h/5 bar and from AO-B at (c) 440 °C/4 h, (d) 440 °C/6 h, showing representative microstructure orientation.

Table 4

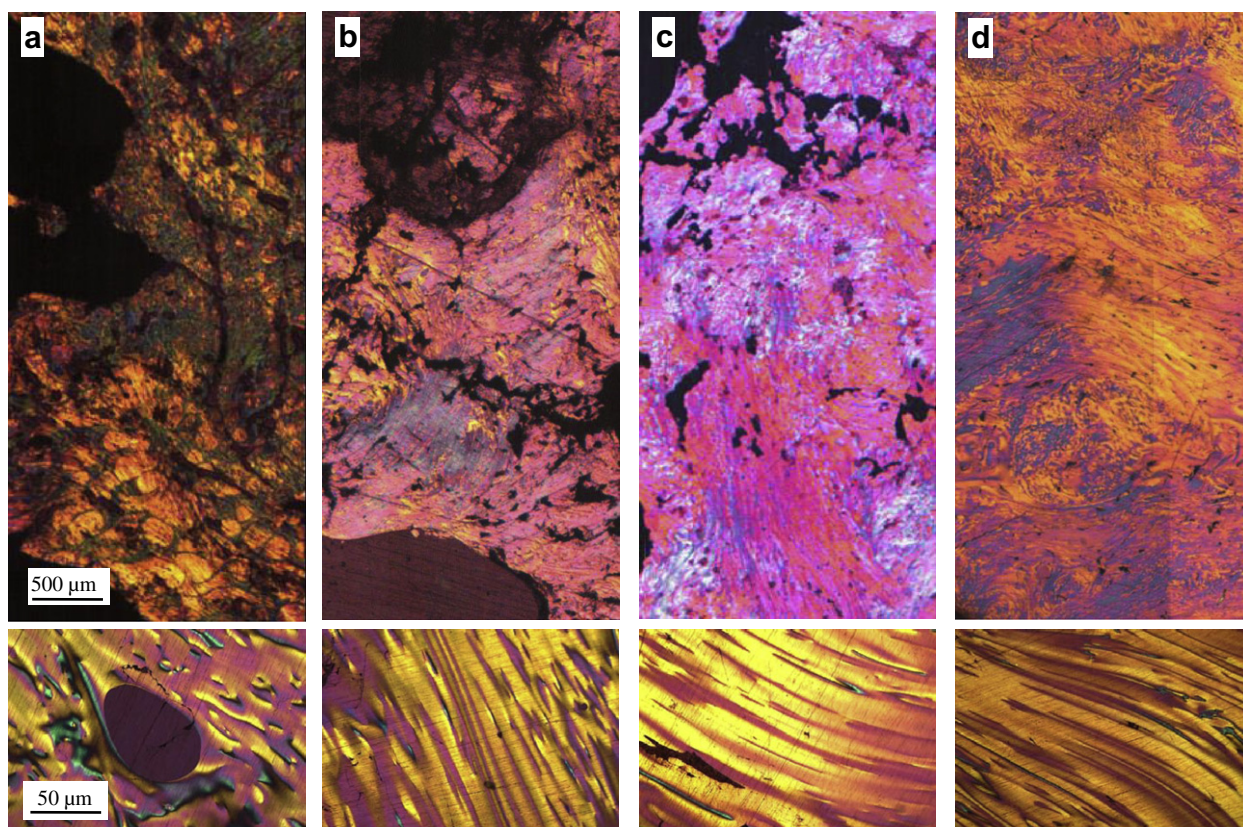
Experimental conditions, yield of the process and optical texture index of the semi-cokes prepared from AO-A and AO-B.

Sample	Treatment	PY	Optical texture (vol.%)										
			Iso	1	2	3	4	5	6	7	8	9	OTI
AO-A1	460 °C/3 h/5 bar + 450 °C/5 h/1 bar	26	1	3	1	3	0	13	19	4	6	50	25.05
AO-A2	450 °C/8 h/5 bar + 450 °C/12 h/1 bar	32	0	1	0	6	0	7	25	4	4	53	26.31
AO-A3	450 °C/3 h/5 bar + 450 °C/17 h/1 bar	30	0	1	0	3	0	3	15	5	6	67	26.97
AO-A4	450 °C/3 h/5 bar + 450 °C/6 h/1 bar + 450 °C/11 h	28	1	1	0	1	0	12	13	3	14	55	25.89
AO-B1	430 °C/4 h + 420 °C/9 h	67	28	0	4	2	0	17	12	5	0	32	–
AO-B2	440 °C/4 h + 430 °C/4 h	55	0	0	2	8	0	21	24	8	7	30	22.98
AO-B3	440 °C/3 h + 430 °C/9 h	65	7	1	4	3	0	20	18	0	6	43	–

PY, process yield (wt.%).

Iso, isotropic material.

OTI, optical texture index.

**Fig. 4.** Polarized light micrographs of the green cokes (a) AO-A1, (b) AO-A2, (c) AO-A3 and (d) AO-A4.

3.2. Microstructure of green cokes from AO-B

The pyrolysis behaviour of AO-B, determined by thermogravimetric analysis, substantially differs from that observed in AO-A. The thermogravimetric curve of AO-B (Fig. 2) indicates that this sample generates coke with a relatively high yield at atmospheric pressure (carbon yield of ~40 wt.% at 1000 °C). Taking into account that this sample includes in its preparation an additional thermal treatment compared to AO A, the possibility to produce green cokes avoiding the use of pressure (milder conditions than AO-B) is an advantage. For this sample, the initiation of mesophase occurs at about 440 °C, with a residence time of 4 h (Fig. 3c). However, increasing the reaction time in two more hours, the resultant green coke rapidly progresses to a green coke with a poorly oriented microstructure (Fig. 3d) [19]. Again and similarly to AO-A, the further uniaxial orientation of this liquid crystal structures formed in AO-B can be improved by modifying the coking conditions. The

conditions applied to produce the green cokes are summarized in Table 4.

Temperatures between 430 and 440 °C and residence times shorter than 8 h are sufficient to form anisotropic green cokes with improved oriented microstructures (AO-B2, Fig. 5b). Less severe reaction conditions led to samples AO-B1 and AO-B3 which still contain unreacted pitch in the amounts of 28 and 7 vol.% respectively, as established from the quantification of the isotropic material.

The process yield of the green coke AO-B2 was 55 wt.% (Table 4), higher than the yield of green cokes obtained from AO-A at all the studied conditions. This must be due to the extra thermal treatment at which AO-B was subjected during its preparation. The quantification of the microstructural features of the green coke AO-B2 shows an OTI value of 22.98, in the range of cokes with highly oriented texture [17] and lower than those obtained for cokes from AO-A. It is not possible to quantify the OTI in samples

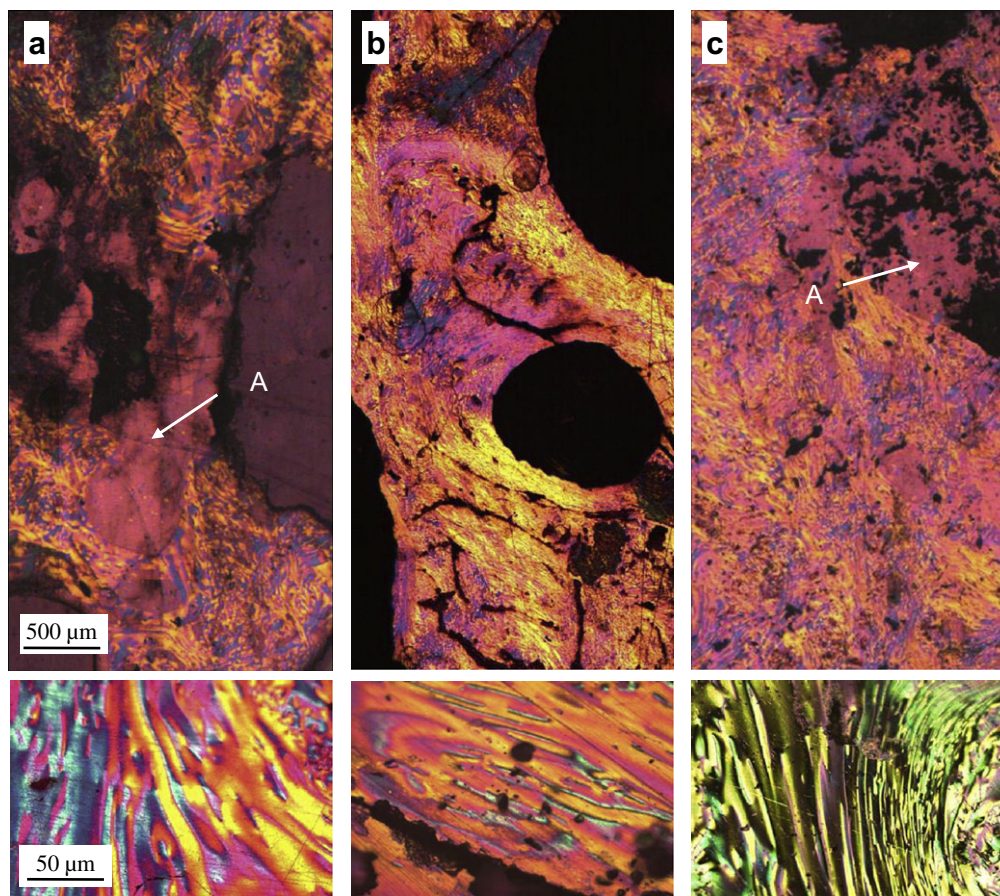


Fig. 5. Polarized light micrographs of the green cokes (a) AO-B1, (b) AO-B2 and (c) AO-B3.

AO-B1 and AO-B3 as both still contain certain amount of partially reacted material (isotropic, Fig. 5a and c; position A). It can be also observed that AO-B3 exhibits a large proportion of flow domains (number nine in Table 4) and similar or even lower proportion of mosaic-like structures (numbers 1–4 in Table 4). It seems therefore that an initial temperature of 440 °C during 3 h (to favour the initial formation of mesophase) followed by longer residence times (higher than 9 h) at slightly lower temperature (430 °C) may contribute to enhance the quality of the green cokes to be obtained from AO-B. The lower temperature during the second step of the pyrolysis (once the mesophase is initiated) allowed the development of more oriented bulk mesophase through the moderation of the pyrolysis reactions [20].

Comparing the capability of both precursors to form longer range orientations of the microstructures, it can be stated that, despite the more rigorous experimental conditions required for AO-A, this sample is able to attain higher degree of microstructural orientation than AO-B, under the experimental conditions used (higher OTI values, Table 4). This behaviour can be related with the ability of AO-A to transfer hydrogen during pyrolysis, which contributes to the enlargement of the size of the optical texture in the coke. Hydroaromatic rings and naphthenic rings in hydroaromatic moieties, which are more abundant in AO-A (Table 2), are considered to be the main hydrogen donor groups [15]. On the other hand, oxygen acceptor sites are thought to deplete the supply of donor hydrogen and leave radicals free to recombine. The thermal reactivity of the samples will be, therefore, dependent on both the amount of reactive species and the ability of the samples to stabilize free radicals by hydrogen transfer. Bearing this in mind, it seems apparent that the capability of hydrogen transfer in AO-A will determine the reactivity of this derivative during the coking

process. This effect could be also enhanced by the use of pressure required during the pyrolysis of AO-A.

4. Conclusions

Anthracene oil derivatives, obtained at different stages of anthracene oil processing to produce pitch-like materials, can be transformed into cokes with highly oriented microstructure. The stage at which the precursors are obtained greatly affects their pyrolysis behaviour and, therefore, the microstructural orientation of the resultant cokes. Thus, the production of high quality cokes would require severer pyrolysis conditions when using the derivative with the lower degree of processing (AO-A). However, the higher hydrogen transfer capacity of this derivative favours the development of microstructures with longer range orientations.

Acknowledgements

The research leading to these results has received funding for the European Union's Research Fund for Coal and Steel research programme under Grant Agreement number RFCR-CT-2009-00004. The MICINN (CONSOLIDER INGENIO 2010, Ref. CSD2009-00050, MAT2010-16194, and Ramon y Cajal research contract of Dr. P. Álvarez) is also acknowledged.

References

- [1] Hackley RC. Manufacture of graphitizable petroleum coke. US patent 2922755 1960.
- [2] Shea Jr SL. Production of coke from petroleum hydrocarbons. Great Lakes Carbon Co. US patent 2775549 (1959), Chem Abstr 1957;51:5392d.

- [3] Stokes CA, Guercio VJ. Feedstocks for carbon black, needle coke and electrode pitch. *Erdol Kohle-Erdgas-Petrochemie* 1985;38:31–4.
- [4] Scott CB, Folkins HO. Effects of major processing variables on carbonization. *J Met* 1972;24:111.
- [5] Mochida I, Oyama T, Korai Y, Qing Fei Y. Study of carbonization using a tube bomb: evaluation of lump needle coke, carbonization mechanism and optimization. *Fuel* 1988;67:1171–81.
- [6] Zhang HP. Formation mechanism of needle coke from heavy aromatic hydrocarbons. *Tansu jishu* 2004;23:28–33.
- [7] Mochida I, Fujimoto K, Oyama T. In: Thrower PA, editor. *Chemistry and physics of carbon*, New York: Marcel Dekker; 1994. p. 111–212.
- [8] Rodriguez-Reinoso F, Santana P, Romero Palazon E, Diez MA, Marsh H. Delayed coking: industrial and laboratory aspects. *Carbon* 1998;36:105–16.
- [9] Alvarez P, Granda M, Sutil J, Menéndez R, Fernández JJ, Viña JA, et al. Characterization and pyrolysis behaviour of novel anthracene oil derivatives. *Energy Fuel* 2008;22:4077–86.
- [10] Alvarez P, Granda M, Sutil J, Santamaría R, Blanco C, Menéndez R, et al. Preparation of low toxicity pitches by thermal oxidative condensation of anthracene oil. *Environ Sci Technol* 2009;43:8126–32.
- [11] Oya A, Qian Z, Marsh H. Structural study of cokes using optical microscopy and -ray diffraction. *Fuel* 1983;62:274–8.
- [12] Díaz C, Blanco CG. NMR: a powerful tool in the characterization of coal tar pitch. *Energy Fuels* 2003;17:907–13.
- [13] Hoover DS, Davis A, Perrota AJ, Spackman W. In: *Extended abstracts 4th biennial conference on carbon*. American Carbon Society. 1979. p. 393.
- [14] Brooks JD, Taylor GH. In: Walker Jr PL, Thrower PA, editors. *Chemistry and physics of carbon*, New York: Marcel Dekker; 1968. p. 243.
- [15] Yokono T, Marsh H, Yokono M. Hydrogen donor and acceptor abilities of pitch:¹ H NMR study of hydrogen transfer to anthracene. *Fuel* 1981;60:607–11.
- [16] Mochida I, Korai Y, Oyama T. Semi-quantitative correlation between optical anisotropy and CTE of needle-like coke grains. *Carbon* 1987;25:273–8.
- [17] Mochida I, Maeda K, Takeshita K. Structure of anisotropic spheres obtained in the course of needle coke formation. *Carbon* 1977;15:17–23.
- [18] White JL. In: Deviney ML, ÓGrady TM, editors. *Petroleum derived carbons*. ACS symposium series no. 21. American Chemical Society. 1976. p. 287.
- [19] Alvarez P, Sutil J, Santamaria R, Blanco C, Menendez R, Granda M. Mesophase from anthracene oil-based pitches. *Energy Fuels* 2008;22:4146–50.
- [20] Mochida I, Qing Fei Y, Korai Y, Fujimoto K, Yamashita R. Carbonization in the tube bomb leading to needle coke: III. carbonization properties of several coal-tar pitches. *Carbon* 1989;27:375–80.