

# IN SITU EVALUATION OF THE CARBONIZATION BEHAVIOR OF GRAPHITIZABLE CARBON PRECURSORS

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## ABSTRACT

Highly aromatic petroleum residues were carbonized in a high temperature high pressure cell mounted under a polarized light microscope in order to evaluate the appearance, development and type of the anisotropic mesophase. Kinetic parameters (formation and coalescence periods) were related to the nature of constitutive fractions (aromatics, resins, asphaltenes). The final type of anisotropic mesophase is determined by the nature of the starting material. However it is also sensitive to mixing and pretreatment processes such as desulfurization and thermal cracking. This technique can be used to select suitable carbon fiber feedstocks and to evaluate the effects of modifying agents, mixing and treatment processes. It has many advantages over traditional methods which measure the optical texture of polished surfaces.

## INTRODUCTION

The complex nature of petroleum residues used for the production of graphitizable carbons (e.g. needle coke, mesophase pitch carbon fibers) makes it difficult to find a single chemical analysis or physical property to rank potential feedstocks in terms of final product quality. It is known, however, that high aromaticity and low Conradson Carbon values are required<sup>(1)</sup>, and development of the liquid crystalline state intermediate (mesophase) is necessary<sup>(2,3)</sup>. Since the discovery of the nature of the mesophase intermediate by Brooks and Taylor<sup>(4)</sup> attempts have been made to characterize and correlate its description with the potential to produce graphitic carbons. Patrick<sup>(5)</sup> and Marsh<sup>(6)</sup> have developed two classifications in terms of the shape and size of optical texture of anisotropic cokes observed by polarized light microscopy using polished surfaces. These classifications are complemented by assignment of an arbitrary index (Optical Texture Index), related to the area of microstructural units<sup>(7)</sup>. The OTI can be implemented in point counting techniques to give an average number. Similar attempts have been made for Scanning Electron Microscope<sup>(8)</sup> and brightness histograms<sup>(9)</sup>. However, these methods require preparation of solid samples (in autoclaves) and extremely careful polishing before observations can be made. Alternatively, Perrotta<sup>(10)</sup> introduced a dynamic analysis based on in situ monitoring of mesophase development taking place in a micro-cell mounted on a hot stage polarized light microscope. It follows the actual transformation of pitch into anisotropic structures. The test can be performed in less than one hour, in comparison with several days required for previous methods.

This paper introduces a classification of mesophase structures for this dynamic test which is also applied to the evaluation of petroleum residues, constitutive HPLC (High Performance Liquid Chromatography) fractions and treated (distillation, desulfurization, thermal cracking, delayed coking) samples.

## EXPERIMENTAL

A high temperature (to 500 °C) high pressure (to 2000 psig) micro-cell (Figure 1) was designed<sup>(10-11)</sup> to fit a hot stage placed under a polarized light microscope. The cell arrangement includes a 2.9 mm o.d. by 1.25 mm cylindrical quartz pan (2 mg sample capacity) mounted on the bottom of the cell which is equipped for the flow of gases. A 5 mm o.d. by 2 mm soft copper O-ring is mounted on top of the pan and coupled with a 5 mm o.d. by 1.65 mm spinel crystal, sealed together tightly on a stainless steel cover. The cell is mounted on a Leitz 1618 hot stage incorporating a tungsten filament furnace that surrounds the bottom of the cell. The Leitz

Orthoplan microscope is equipped with interchangeable objectives (H 20X is the most convenient), a  $\lambda$  retarder plate and a polarizer. A color NEC camera is mounted on the microscope and connected to a PANASONIC video-recorder and a NEC Monitor to follow the carbonization reactions in situ. Temperature, pressure, time and size data are displayed on the screen. The cell is connected through 1/32" tubing to a gas system that supplies hydrogen or nitrogen at regulated pressures.

## RESULTS AND DISCUSSION

The development of mesophase starts with the appearance of sub-micrometer spherulites (Figure 2-a) that grow in size and occasionally also in number (Figure 2-b) and coalesce (Figure 2-c) until forming a bulk mesophase (Figure 2-d) that is characteristic of the nature (mainly the distribution of carbon atom types) of the feedstock. The time for the appearance of mesophase spherules and the coalescence period are recorded and related to the nature of the starting material and operating conditions.

A wide range of feedstocks have been evaluated in order to observe the widest range of mesophase structures to be included in the classification. This includes the case where coalescence of mesomorphic structures did not develop, leading only to isolated small spherulites, indicating no bulk formation of graphitizable carbon. Figure 3-a represents the smallest size of coalesced anisotropic structures (less than 1  $\mu\text{m}$ ) called fine grained mosaics, characteristic of low grade anode coke. Figure 3-b represents an improvement in the extension of aromatic layers where basic anisotropic structures can reach 50  $\mu\text{m}$ , coalesced in what is named as coarse flow mosaic. Figure 3-c represents the case of extended flow domain mosaics characterized by homogeneous anisotropic structures with internal disclinations (defects caused by the folding patterns of the aromatic layers). Larger sizes (ranging from 50 to over 500  $\mu\text{m}$ ) correspond to higher degrees of graphitizability. This type of structure is characteristic of high quality needle coke. Finally, Figure 3-d represents the case of non-restricted flow domain mosaic: the actual size is imposed by the geometrical configuration of the micro-cell but the fluid nature of the material would make it spread over larger surfaces if available. This is characteristic of good feedstocks for carbon fiber production.

In addition to characteristic size and shape of the final mosaic, there are typical kinetic parameters (mesophase formation and coalescence period) associated with each material (Table 1): longer coalescence periods appear to be associated with granular and coarse flow mosaics, but no relation is observed with formation time.

To further explore this aspect, one of the feedstocks (FCC Decanted Oil) was fractionated (HPLC) into four constitutive fractions: saturates, aromatics, polar aromatics and asphaltenes. Each one of the fractions was evaluated under the same carbonization conditions (700 psig hydrogen, 50 ° C/min, 30-450 ° C). Figure 3 shows the differences in the final mosaic: the restricted (250  $\mu\text{m}$ ) flow domain mosaic of the original feedstock (Figure 3-a) is increased largely (430  $\mu\text{m}$ ) for the aromatic fraction (Figure 3-b), but reduced for the polar aromatic (Figure 3-c) and asphaltene (Figure 3-d) fractions, while the saturates fraction volatilizes completely and does not form mesophase. In addition, the asphaltene fraction exhibited a fast formation time similar to that of the feedstock (Table 2), while polar aromatic and aromatic fractions were characterized by longer times. The opposite tendency was observed for the coalescence period. This can be interpreted to mean that the asphaltenes fraction (even though in very small concentration), by initiating its mesophase development, provides the path for catalyzing/promoting the development of mesophase of other fractions, with a final result that is dependent upon the interactions of carbon atom types present in the reacting material.

Research was also performed to evaluate the ability to modify the carbonization process of a particular material (FCC Decanted Oil). Mixing with other feedstocks generally result in a balanced compromise: when mixed with Lube Oil Extract (Figure 4-a) that exhibits no bulk mesophase but isolated spheres, the final mosaic (Figure 4-b) was a collection of poorly coalesced and small anisotropic regions; when mixed with a conversion residue (Figure 4-c) that exhibits coarse flow, the final mosaic was an agglomerate (Figure 4-d) of several flow domain regions. Distillation (Figure 5 a-b) also alters the final mosaic: higher cut point residues tend to result in larger anisotropic structures. On the other hand, hydrodesulfurization (Figure 5-c) significantly reduced the size of the final mosaic. Operating the carbonization process at higher pressures (1500 psig) results in larger mosaics.

Thermal treatments (Figure 6 a-d) considerably increase the size of the final mosaic, particularly at long times and relatively low temperatures, producing a pitch that transforms into

non-restricted (fluid) flow domain (Figure 6-c), suitable for carbon fiber production; however increasing the severity of the process results in a heterogeneous and solid bulk mesophase (Figure 6-d).

### CONCLUSIONS

In situ monitoring of mesophase development by hot stage polarized light microscopy has been complemented with a classification of final mosaic structures and applied to elucidate the effect of constitutive fractions, mixtures and pretreatment processes upon the carbonization behavior of petroleum residues, providing a technique for selecting graphitizable carbon (needle coke, carbon fibers) precursors.

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Table 1. Classification of delayed coking feedstocks for anode and needle coke.  
(Based on dynamic hot stage microscopy at 450 °C, 50 °C/min and 700 psig hydrogen)

Material	Aromaticity <sup>13</sup> C nmr wt%	Mesophase formation min	Coalescence period min	Optical Texture Size, μm	Uses
Lube Oil Extract	29.30	5	No	Spheres	None
Heavy Crude Oil	37.30	11	11	<1	Anode
Conversion Residue	41.43	9	13	10-50	Anode
FCC Decanted Oil	52.73	2	3	250-500	Needle
Petroleum Pitch A-240	88.61	18	-	>500	Needle, Fibers

**Table 2.** Mesophase development of FCC Decanted Oil HPLC fractions.  
(Based on dynamic hot stage microscopy at 450 °C, 50 °C/min and 700 psig hydrogen)

Material	Yields wt %	Mesophase formation min	Coalescence period min	Optical Texture Size, $\mu\text{m}$
FCC Decanted Oil	-	2	3	250
<b>HPLC Fractions</b>				
Saturates	26.8	No	No	-
Aromatics	67.3	12	3-10	430
Polar Aromatics	4.7	9	25	50
Asphaltenes	1.2	2	>37	<1

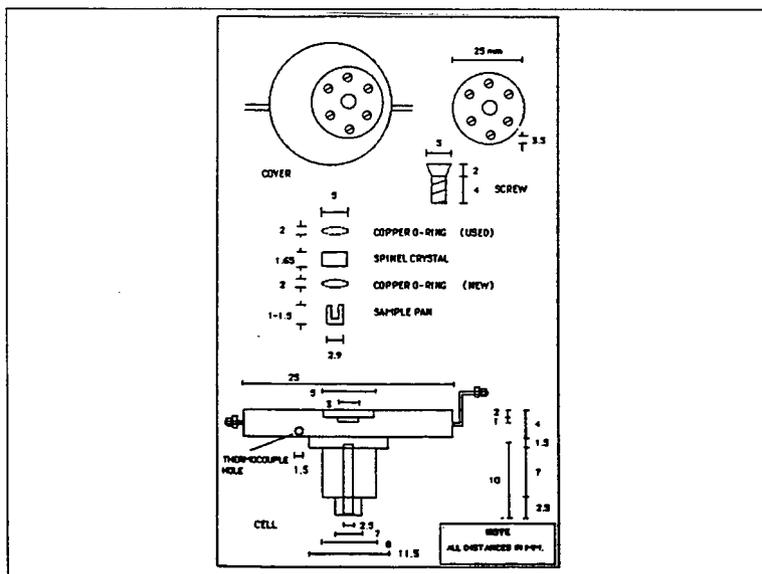


Figure 1. High Temperature High Pressure Micro-cell

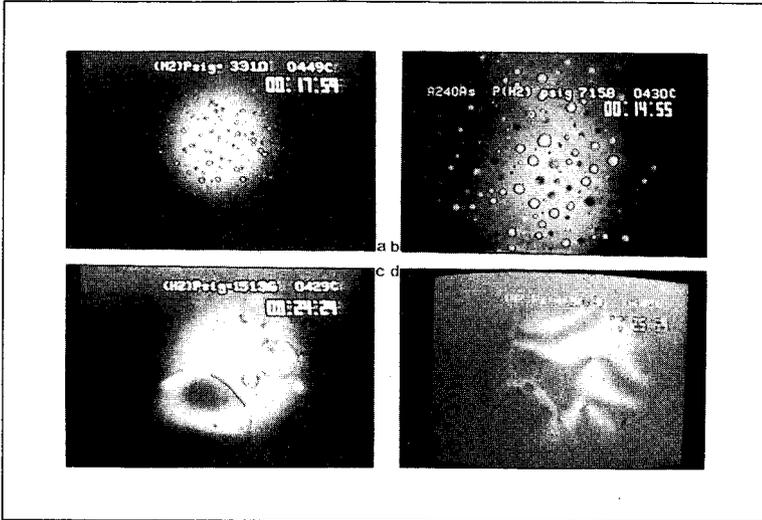


Figure 2. Evolution of mesophase development: (a) appearance, (b) growth, (c) coalescence, (d) final mosaic (screen size: 475  $\mu\text{m}$ )

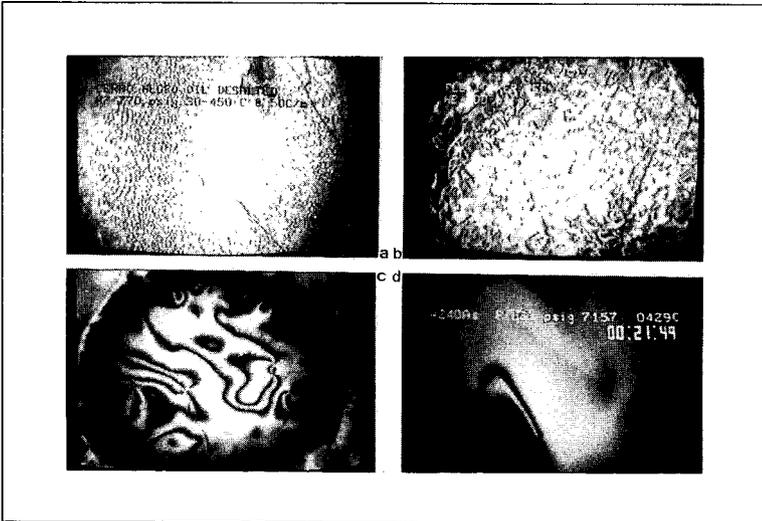


Figure 3. Classification of final mosaic: (a) fine grain, (b) coarse flow, (c) flow domain, (d) fluid flow domain (screen size: 475  $\mu\text{m}$ )

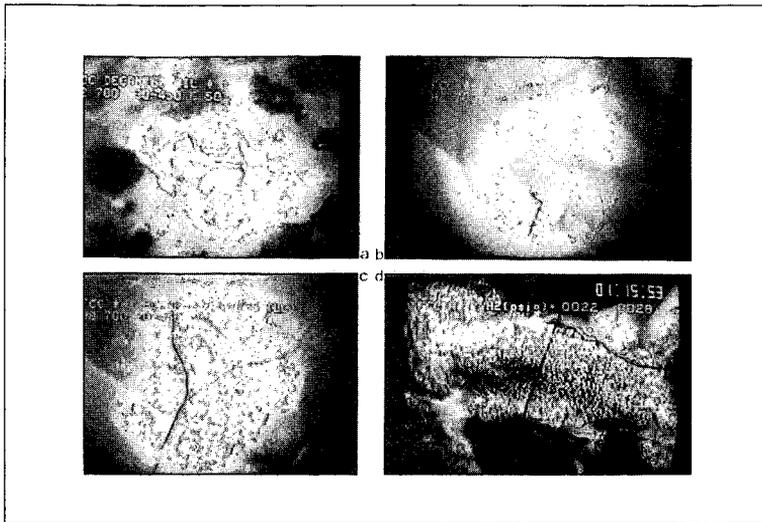


Figure 4. Final mosaics of HPLC fractions: (a) FCC Decanted Oil, (b) Aromatics, (c) Polar aromatics, (d) asphaltenes (screen size: 475  $\mu\text{m}$ )

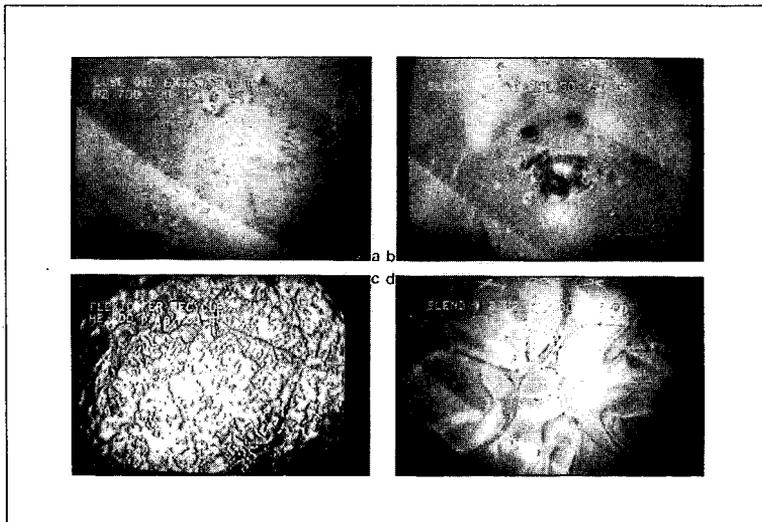


Figure 5. Final mosaics of mixtures: (a) Lube Oil Extract, (b) 70% FCCDO & 30% LOE, (c) Conversion residue, (d) 70% FCCDO & 30% CR (screen size: 475  $\mu\text{m}$ )

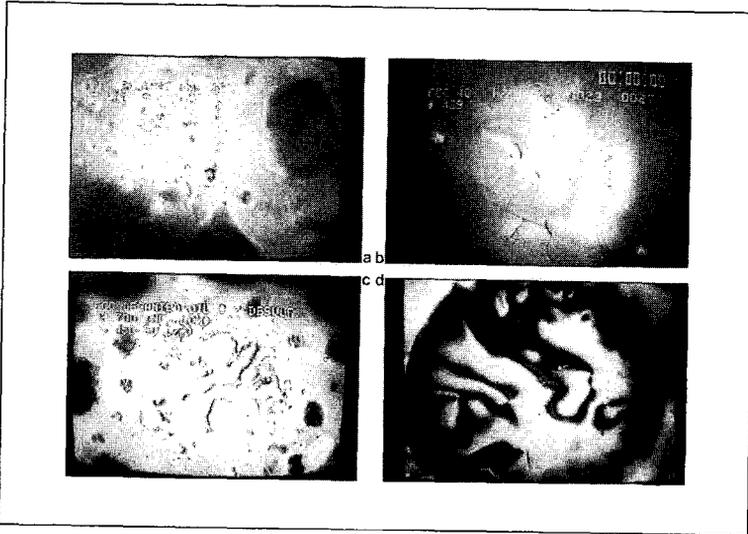


Figure 6. Final mosaics of pretreated materials: (a) Distillation bottoms 63%, (b) Distillation bottoms 40%, (c) Desulfurized, (d) High pressure carbonization (screen size: 475  $\mu\text{m}$ )

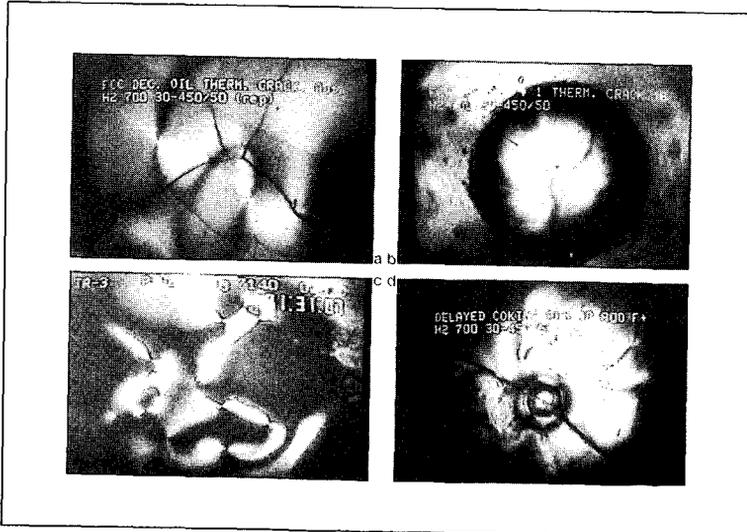


Figure 7. Final mosaics of pretreated materials: (a) Autoclave thermal cracking, (b) Pilot plant thermal cracking, (c) Severe thermal cracking (long time), (d) Delayed coking residue (screen size: (a) 190  $\mu\text{m}$ , (b-d) 475  $\mu\text{m}$ )