LIQUID CRYSTALS AND MASSIVE ANISOTROPY IN CARBONACEOUS MATERIALS

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Introduction

When carbon precursors are/or derived from geopolymers, they are macromolecules the elemental composition of which is C,H,O,N,S [1-4]. They give rise to sp^2 carbons either after coalification (natural process) or carbonization (industrial or laboratory process). There is two groups of precursors: the first one is under the dependence of cross-linking atoms (O and /or S). Among this group are essentially kerogens, coals and refinery residues such as vacuum (VR) or atmospheric residues (AR) of distillation. The second group is under the dependence of the ratio $(H/C)_{at.}$. It gathers asphaltenes extracted from rocks or oils (biodegraded and conventional) and pitches (isotropic or anisotropic derived from oil and coals).

Experimental

42 samples were studied, 22 for the first group, 20 for the second one. Natural samples were extracted from rocks by the "Institut Français du Pétrole" (IFP) process [5]. Asphaltenes were obtained from the toluene soluble fraction of oils and kerogens, n-heptane precipitated [6]. Refinery residues were studied as received, as well as pitches industrially prepared. Details about samples are given in [1,3,4,7-15].
Natural samples of increasing coalification were carbonized so as to simulate the natural process. Industrial precursors were also thermally converted. Heat treatment was performed at a $4°C.min^{-1}$ heating rate up to 1000°C. This range of heat treatment temperature (HTT) covers primary carbonization step and a part of secondary carbonization. 1000°C was chosen to observe the textures with enough contrast in imaging.
The textures were studied by optical microscopy (OM) at micrometric scale, by all modes of TEM (bright and dark-fields, lattice imaging and selected area electron diffraction [3]). The physicochemical characteristics were determined after elemental analyses, Conradson test following AFNOR norm NFT60-116, van Krevelen patterns [1,2], by measuring plasticity [2] or Vickers microhardeness [14], DTA, TGA, and infrared spectroscopy [1,3,7-9]. X-ray diffraction techniques were also used as a complement [3].

Results and Discussion

To classify the samples the Conradson test was chosen. The weight percent residues obtained after heat-treatment at 1000°C is plotted versus $H/C_{at.}$ of the precursor. This widely employed industrial test generally not suffer exceptions and samples align on a straight line (Fig. 1). The 42 samples studied (22 for the first group, 20 for the second one) satisfactorily align on the Conradson line, except isotropic industrial pitches (A 240, Nalon,…) for which the amount of residue is considerably too small.

First group of samples: In this group the precursors are geopolymers (fossil fuels) deriving from biopolymers, *i.e.* having the same elemental composition (C,H,O,N,S). The way followed to give rise to sp^2 carbonaceous matter is the same for coalification and carbonization. The macromolecular precursors break (softening) leading to Basic Structural Units formation [3,4,8]. BSU's have an aromatic core ($\leq$ 1nm) di or tricoronene-like in shifted configurations [16]. Their edges are saturated by various functional groups which determine the BSU's steric hindrance. Edge groups also govern the relations between BSU's and their surrounding medium (suspensive medium). The suspensive medium inside which BSU's are "floating" is made of the lightest molecules freed by macromolecule breakage [4]. Simultaneously the light molecules progressively release as volatiles (saturated hydrocarbons, then non-condensable gases). During coalification or carbonization BSU's concentrate and self-associate into individual liquid crystals. The liquid crystals produced (shapes, sizes, ordering) depend on the functional groups grafted on BSU edges and on the amount of available suspensive medium. In the case of refinery residues, the edge groups are in majority hydrogen and the suspensive medium is abundant $(H/C)_{at.} = 1.6$. The liquid crystals formed are mainly Brooks and Taylor mesophase with PAN-AM texture (mesophase A) [17-19] systematically associated to two other kinds of mesophase: B (1 µm in size) and C (200 nm in size) [4,20]. They are smaller and devoid of PAN-AM texture. B and C mesophases are egg-shaped but keep the same columnar order than mesophase A (this order is typical of many discotic liquid crystals [21]). The suspensive medium is abundant so that the volatile yield is large. Figure 1 shows that the representative points are at the extreme right.

As an increasing number of cross-linking atoms (O and S) is joined to a decreasing amount of $(H/C)_{at.}$ the size and ordering of liquid crystals degradate. Mesophase A disappears as well as B and C. They are replaced by Local Molecular Orientations (LMO) with digitized contours (200 nm down to 5 nm in size) [3,12]. As oxygenated cross-linking atoms saturate BSU's edges $(O/C_{at.} \sim 0.5)$, BSU's are frozen-in at random and no LMO is observable (oxidized sporopollenin). The mechanism responsible for this behavior is under the dependence of a unique parameter $F_{LMOat.}$ [3,12] measured at LMO occurrence. It is the ratio between cross-linkers (O and /or S) and the amount of suspensive medium, *i.e.* hydrogen still present. All samples of the first group, further named "F_{LMO} group" follow the same rule along the Conradson line (black symbols in Fig.1). F_{LMO} increases progressively from the right hand side to the left hand side of the figure as $(H/C)_{at.}$ of the precursor decreases. Correspondingly the residue at 1000°C increases. At the extrema (F_{LMO} nil or maximum), there is no softening point: the

samples are either initially viscous or always solids. As F_{LMO} increases, softening point decreases from 460° to 390°C.

From F_{LMO} 0.01 (Kerosen Shale) up to F_{LMO} = 0.40 (Lignite), the HTT of LMO occurrence varies from 480°C ($H/C_{at.}$= 0.73) to 450°C ($H/C_{at.}$= 0.52). It results that HTT for LMO occurrence is almost constant, whereas $H/C_{at.}$ decreases noticeably. Following anterior data on kerogens [3,4,8,9], an HTT value of 475°C was chosen for LMO occurrence. Above LMO occurrence HTT, the liquid crystals coalesce and grow. Solidification into semi-cokes occurs at 100% anisotropy. From F_{LMO} 0.01 to F_{LMO} 0.40, HTT for solidification decreases from slightly above 500°C down to 450°C for $H/C_{at.}$ relatively constant, near 0.5, which is the coronene formula. At solidification, the LMO final size decreases as F_{LMO} increases.

Second group of samples (open symbols in Fig. 1). They are mainly asphaltenes extracted from oils and kerogens. The other samples are pitches (oil and coal derived). Except pitches, asplaltenes follow the Conradson rule in the same manner as F_{LMO} group. However, the second group being devoid of cross-linkers, F_{LMO} is nil or negligible, so that the properties only depend on $H/C_{at.}$. Since 475°C was chosen for LMO occurrence, it is thus tempting to choose $H/C_{at.}$ at 475°C as the leading parameter, but it is impossible since $H/C_{at.}$ at 475°C is constant (0.65 - 07). The deciding parameter is thus $H/C_{at.}$ of the precursors (Fig. 1). The second group is named "$H/C_{at.}$ group".

As for F_{LMO} group, the properties steadily vary but at the opposite. Softening point decreases from 460°C (Kerosen Shale: $H/C_{at.}$= 1.4) down to less than 120°C (A240: $H/C_{at.}$= 0.68). LMO occurs at 480°C for Kerosen Shale ($H/C_{at.}$= 1.4) and at 450°C for the 14618 asphaltene ($H/C_{at.}$= 0.74). The precursor of pitch C ($H/C_{at.}$= 0.58) is already initially 100% anisotropic, *i.e.* there is no LMO occurrence. In the case of isotropic or anisotropic pitches, 100% anisotropy is not the solidification point. Brittle solids semi-cokes occur at a little above 500°C for Kerosen Shale, at 490°C for 14618 asphaltene ($H/C_{at.}$= 0.55) and at 600°C for pitch C ($H/C_{at.}$= 0.41). Initially isotropic pitches, such as A240, come back on the Conradson line when they are 100% anisotropic. Their representative points are close to those of industrial anisotropic pitches (pitch C, Mitsubishi AR). A characteristic morphology [22-24] occurs in samples of the $H/C_{at.}$ group before solidification. Instead of lamellae where the aromatic layers are oriented systematically face-on relative to the interface with gas (volatiles), well extended lamellae limited by disclinations [25] are produced, where aromatic layers are systematically edge-on relative to the interface with gas. They recover the rule followed by individual liquid crystals relative to the suspensive medium. The usual face-on orientation observed in the pore walls of A240 pitch [14] was attributed to flow orientations [26]. The edge-on orientation is mainly due to wettability.
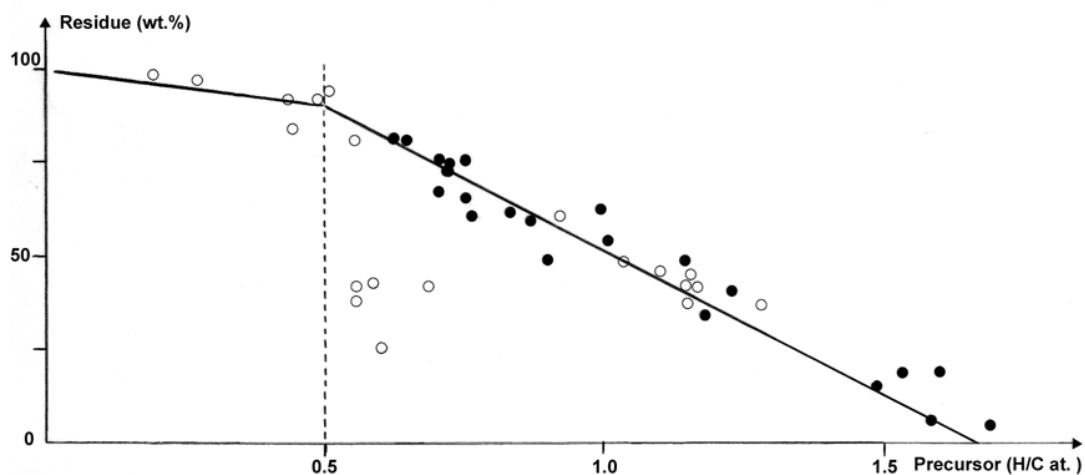
Figure 1. Plot of the Conradson test residues (weight percent) obtained after heat-treatment at 1000°C versus $H/C_{at.}$ of the precursor. Black circles correspond to samples of "F_{LMO} group"; open circles correspond to samples of "$H/C_{at.}$ group".

Conclusions

The recognition of two groups of carbonaceous matter having opposite trends could help to understand the mechanisms of coalification and carbonization. Its suggests that the interactions between BSU's edge-groups and the surrounding medium are the leading thread. Infrared spectroscopy of F_{LMO} group samples shows, on the one hand, the importance of cross-linkers. On the other hand, the utmost importance of the ratio aliphatic CH groups over aromatic CH ones is underlined [4,7-9]. In the absence of cross-linkers, the role of hydrogen has to be cleared-up, the work is in progress.

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