CARBONIZATION OF AN AROMATIC PETROLEUM RESIDUE

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INTRODUCTION

The production of carbonaceous mesophase is receiving increasing attention because they permit the manufacture of new carbon materials, such as high density isotropic graphite, without the use of the binder needed when producing conventional fine-grain graphites. The characteristics of the mesophase are determined by both the precursor and the experimental conditions used in the carbonization process [1]. There is ample information in the literature on the production of carbon mesophase from pure compounds, petroleum or coal-tar pitches [2,3]. Consequently, the adequate selection of the precursor and an in-depth knowledge of the carbonization mechanism are essential for the preparation of new carbon materials. This work presents the results corresponding to the carbonization process of an aromatic petroleum residue, analyzing the effect of the three main parameters (pressure, temperature and residence time) on the development of mesophase. The study was mainly centered on the early stages of mesophase development (formation of semicoke), with the aim of analyzing the possibility of using this material in the preparation of high density isotropic graphite.

EXPERIMENTAL

The petroleum residue is highly aromatic and completely soluble in toluene. The carbonization process was carried out in a small laboratory pilot plant, which permits an adequate control of the evolution of solids, liquids and gases during the process. The residue was carbonized at temperatures ranging from 420°C to 460°C, pressures between 0.1 MPa and 1.0 MPa, and residence times from 0 to 6 hours. The heating rate from room temperature to reaction temperature was 15°C/min, the residence time starting when the desired temperature was reached.

The advance of the carbonization was followed by measuring the toluene insoluble (TI), polarized light optical microscopy and diffuse reflectance infrared spectroscopy (DRIFTS). From the IR peaks, the area of the peak centered at 2925 and the one centered at 3050 cm^{-1} (corresponding to the C-aliphatic H and C-aromatic H bonds) are calculated; the ratio of the two areas is

defined as "n" in this work. This parameter may be taken as a qualitative measure of the evolution of aromaticity of the semicoke.

RESULTS AND DISCUSSION

Table 1 includes data for the characterization of the semicokes and it is shown that the carbonization variable affecting the yield to a larger extent is the pressure. On the other hand, large differences in yield are observed at the end of the heating ramp (zero residence time), with parallel differences in the distilled material; this indicates that distillation is the main phenomenon taking place during this stage. This difference in distillation will condition the carbonization process since the light material remaining at 1.0 MPa will modify the viscosity and reactivity of the reaction system with respect to that at 0.1 MPa. The carbonization temperature affects the process to a lower extent, although important differences are observed in the yield and distilled material. However, the residence time of carbonization has little effect on yield.

The advance in carbonization, measured as the development of TI at 0.1 and 1.0 MPa, is shown in Figure 1. Since some TI material is formed during the heating ramp, to a larger extent the higher the temperature and the lower the pressure, polymerization must be taking place at temperatures below the carbonization temperature. As expected, the amount of TI increases with increasing residence time, although the slope of the plots decreases with increasing residence time.

The percentage of anisotropy in the semicoke is very important from the point of view of applications [4] and, as Table 1 shows, it increases with increasing temperature and residence time. It also increases with decreasing pressure (if the other variables are kept constant). If the percentage of anisotropy is plotted as a function of TI (Figure 2) it is possible to see that the only variable having a significant effect is the carbonization pressure, since only two different lines are given for the two pressures used. On the other hand, Figure 2 shows that there is a minimum value of TI needed for the development of mesophase and this is not reached during

the heating ramp. A given residence time at the carbonization temperature is needed for the development of anisotropy; thus, if the pressure is 1.0 MPa anisotropy starts to develop for lower values of TI and at a lower rate than if the pressure is 0.1 MPa. The carbonization pressure modifies the viscosity and the reactivity in such a way that if the pressure is high the viscosity is low, allowing for molecular ordering at lower values of TI, this favoring the development of anisotropy. The lower rate of development of anisotropy can be explained by the presence of low molecular weight material at high pressure which limits the molecular stacking in the mesophase formation.

The parameter "n" (which provides chemical information on the evolution of carbonization) of Table 1 shows that the aromaticity increases with increasing temperature and residence time and decreasing pressure. When comparing the effect of pressure for semicokes of similar degree of carbonization (similar TI) the effect of pressure is the opposite, lower aromaticity at lower pressure. This could be explained if one considers that the fraction of light material being distilled at lower pressure (but it would remain at higher pressure) is essentially aromatic, the remaining fraction being richer in aliphatic components.

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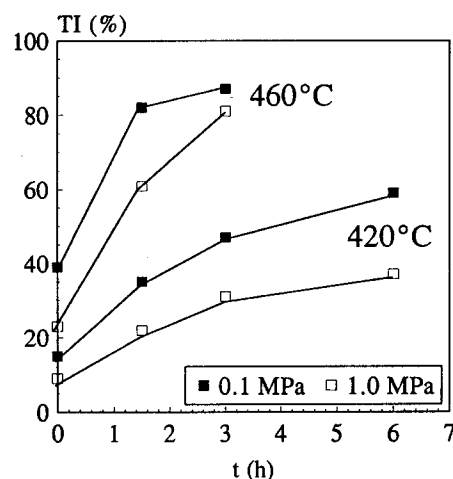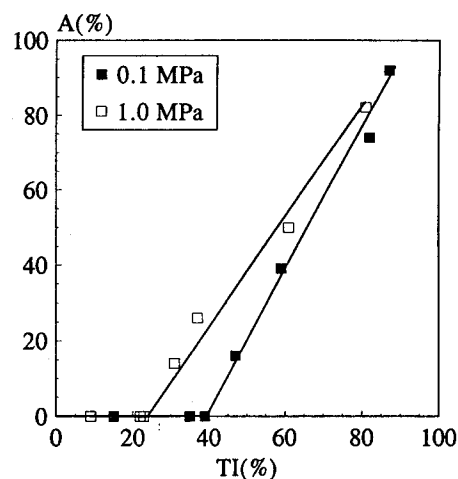

Fig.1 Evolución of TI with residence time.

Fig.2 Evolution of anisotropy with TI.

Table 1. Experimental data for Semicokes.

		420°C 0.1MPa.				420°C 1.0 MPa.				460°C 0.1MPa.			460°C 1.0MPa.		
Time(h.)		0	1.5	3	6	0	1.5	3	6	0	1.5	3	0	1.5	3
Carb. yield (%)		31	29	28	27	46	44	43	44	25	23	23	38	39	40
"n"		3.59	2.74	2.05	1.52	3.65	2.78	2.26	1.73	2.55	0.85	0.66	2.93	1.03	0.43
TI (%)		15	35	47	59	9	22	31	37	39	82	87	23	61	81
O.M.	I.(%)	100	100	84	61	100	100	86	74	100	26	8	100	50	18
	A.(%)	0	0	16	39	0	0	14	26	0	74	92	0	50	82