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Activated carbons prepared from thermally and chemically treated petroleum and coal tar pitches

E. Daguerre[a], A. Guillot[a,]*, F. Stoeckli[b]

[a]*C.N.R.S.-I.M.P., Institut de Science et Génie des Matériaux et Procédés, 52 avenue de Villeneuve, 66860 Perpignan Cedex, France*
[b]*Institut de Chimie de l'Université, avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*

Abstract

Petroleum and coal tar pitches have been treated thermally at 400°C and 470°C, extracted with toluene and subsequently activated with CO_2 at 900°C. With one exception, the development of the micropore widths and volumes in the resulting carbons follows the trend observed for carbons based essentially on precursors of vegetable origin. On the other hand, petroleum pitch treated at 400°C leads to an active carbon which follows the pattern observed for cokes, semi-cokes and pyrolyzed tyres. It is suggested that the difference between the two types of active carbons is due to the large amount of compounds with low molecular weight left in the petroleum pitch after thermal soaking.

Keywords: A. Pitch, Activated carbon; D. Microporosity

1. Introduction

Active carbons can be produced from a variety of carbonaceous materials, by physical or chemical activation. It is well known that their structural properties (micropore volume, pore size distribution and external surface area) depend on the precursors and, to some extent, on the carbonization and the activation processes. We have recently shown [1] that the development of the micropore volumes and widths during physical activation leads basically to three patterns. The most favorable development, characterized by the possibility of obtaining relatively large micropore volumes, corresponds essentially to materials of vegetable origin carbonized under standard conditions, as well as polyarylamide carbon fibers and some resins. The larger micropore volume W_o arises from the presence of an initial volume $W_o(0)$ developed during the carbonization stage and the removal of disorganized carbon in the early stages of burn-off (up to 20%). This leads to a volume of ~0.20–0.25 cm^3/g which then increases linearly with the average micropore width L_o, as activation proceeds. The corresponding gradient, $\Delta L_o/\Delta W_o$, is close to 2.6 $nm/cm^3\ g^{-1}$ on average.

In the case of cokes, semi-cokes and pyrolyzed tyres, on the other hand, one observes practically no initial volume and the resulting carbons have a smaller micropore volume, although the gradient $\Delta L_o/\Delta W_o$ is somewhat higher (4 $nm/cm^3\ g^{-1}$).

In the present study we show that in the case of petroleum pitches the latter situation corresponds to the insufficient removal of low molecular weight compounds during thermal soaking at 400°C. A better removal of these compounds modifies the precursor and leads to a more favourable structural condition for the subsequent activation.

2. Experimental

2.1. Materials

Two different raw petroleum (P) and coal tar (H) pitches have been selected to be used as precursors for the production of activated carbons. Pitch compositions will be discussed in terms of α-, β- and γ-resins, corresponding to the quinoline-insoluble fraction (QI), to the quinoline-soluble but toluene-insoluble fraction (TI-QS) and to the

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*Corresponding author. Tel.: +33-4-6866-2110; fax: +33-4-6866-2141.
E-mail address: guillot@univ-perp.fr (A. Guillot).

Table 1
Characterization of initial pitches based on petroleum (P) and coal tar (H) pitches and on centrifugated coal tar pitch (HC)

Material	Composition (wt.%)						
	QI (α-resins)	TI-QS (β-resins)	TS (γ-resins)	KS (K)[a]	C/H	O ($\%_{wt}$)	S ($\%_{wt}$)
P	<0.1	4	96	393	1.34	0.30	2.73
H	11	17	72	383	1.67	1.58	0.56
HC	1.9	13.5	84.6	365	1.50	1.45	0.48

[a] KS, Kraemer–Sarnov softening point (data given by pitch suppliers).

toluene-soluble fraction (TS), respectively. Their characteristics are summarized in Table 1. Another pitch, HC, derived from H by centrifugation has also been considered. As shown in the same table, this operation leads to an efficient primary QI removal, but at the same time part of its associated β-resins were also removed.

2.2. Heat treatments and fractionation

Standard heat treatments were applied to the pitches, using a conventional stirred tank reactor described previously [2]. Temperature and residence time conditions were selected carefully, in order to increase the β-resin content without developing mesophase spheres. Two different heat treatments were applied and their influence on the precursor of activated carbons was investigated. Separate batches of 500 g of pitches P, H and HC were used, the first being heated at 2°C min^{-1} up to 400°C and soaked for 5 h. This produced sample series P-M400, H-M400 and HC-M400. Another group was obtained by heating the pitches at the same rate to 470°C, but without soaking at this temperature. This led to series P-M470, H-M470 and HC-M470. In all cases, rapid cooling to room temperature was applied. In this study, the pitch evolution during heat treatment was mainly investigated through the various mechanisms of γ-resin removal (see Section 4). The chemical characteristics of heat-treated pitches from both groups are given in Table 2.

The solids were ground and sieved to 100 μm and subjected to fractionation in toluene at 298 K, in order to reduce their γ-resin contents. This operation was carried out according to an established procedure, 1 g of pitch being mixed with 125 g of toluene. The resulting materials correspond to series P-, H- and HC-M400E and -M470E (E = toluene extracted) which contain essentially quinoline-soluble β-resins. After filtration and drying, the residual solubilities in toluene and in quinoline were determined, to provide an accurate resin characterization. The chemical characteristics of this series are given in Table 3.

2.3. Activated carbon preparation

Batches of 5 g of extracted pitches were first oxidized for 1 h at 280°C in a stream of air (0.5 l min^{-1}) and subsequently heated to 900°C at a rate of 2°C min^{-1}. At this temperature, the carbonized materials were gasified with carbon dioxide (0.5 l min^{-1}) for periods up to 17 h. This led to activated carbons with degrees of burn-off between 12 and 60%. As discussed below, only the toluene extracted pitches (series E) gave significant results.

2.4. Characterization of the activated carbons

The samples were characterized by combined adsorption and immersion techniques described in detail elsewhere [3]. The data were analyzed within the framework of Dubinin's theory [3,4] and its extension to immersion calorimetry [3–8]. The relevant equations used in this study are based on the Dubinin–Radushkevich equation,

$$N_a = N_{ao}\exp[-(A/\beta E_o)^2] \quad (1)$$

Table 2
Chemical characterization of thermally treated pitches

Material	Composition (wt.%)			γ-resins removal		
	QI (α-resins)	TI-QS (β-resins)	TS (γ-resins)	$\Delta\gamma$ (%)	$\Delta\gamma_d$ (%)	$\Delta\gamma_p$ (%)
P-M400	4	20	76	21.8	9.7	90.3
P-M470	6.5	22	71.5	30.8	27	73
H-M400	15	25.5	59.5	20.1	22.9	77.1
H-M470	17.3	21.8	60.9	19.4	33.9	66.1
HC-M400	5.1	25.3	69.6	17.7	17.7	82.3
HC-M470	4	23.7	72.3	19.6	30.2	69.8

Table 3
Chemical characterization of toluene-extracted pitches

Material	Composition (wt.%)					
	QI (α-resins)	TI-QS (β-resins)	TS (γ-resins)	C/H	O ($\%_{wt}$)	S ($\%_{wt}$)
P-M400E	19	67	12	1.58	1.70	1.90
P-M470E	13	71	16	1.48	1.48	1.69
H-M400E	32.7	51.6	15.7	1.99	1.99	0.25
H-M470E	34.7	54.4	10.9	1.98	1.98	0.27
HC-M400E	14.1	69.8	16.1	1.91	2.11	0.30
HC-M470E	13.5	72.1	14.4	1.90	1.72	0.31

where $A = RT \ln (p_s/p)$; N_a is the amount (usually given in mol/g) adsorbed at relative pressure p/p_s and temperature T, and N_{ao} is the limiting amount filling the micropores. In the absence of molecular sieve effects, $N_{ao}V_m$ corresponds to the micropore volume W_o of the solid, V_m being the molar volume of the condensed adsorbate. It has been shown [3] that E_o, the characteristic energy of the solid, is an inverse function of the average micropore width L_o

$$L_o \text{ (nm)} = 10.8/(E_o - 11.4) \quad (E_o \text{ in kJ/mol}). \tag{2}$$

This expression provides reliable data in the domain $0.4 < L < 1.7$–1.8 nm, or $E_o > 17$–18 kJ/mol, and it follows, that the surface area of ideally slit-shaped micropores is given by

$$S_{mi} \text{ (m}^2\text{/g)} = 2000\, W_o \text{ (cm}^3\text{/g)}/L_o \text{ (nm)}. \tag{3}$$

Finally, as a thermodynamic consequence of Eq. (1), one obtains an expression for the enthalpy of immersion of an activated carbon into the corresponding liquid

$$\Delta h_i \text{ (J/g)} = -\beta E_o W_o (1 + \alpha T)(\pi)^{1/2}/2V_m + h_i S_e \tag{4}$$

where α is the thermal expansion coefficient of the liquid and $h_i S_e$ represents the wetting of the external (non-microporous) surface S_e of the carbon. S_e can be obtained by a variety of techniques [3,4]. Eq. (4) can be used either to cross-check the adsorption data obtained from Eq. (1), or to detect molecular-sieve effects, by using liquids with variable molecular dimensions (0.35 to 1.5 nm) [3–8].

The main results for the carbons obtained from the toluene-extracted pitches (series E) are given in Table 4. Nitrogen adsorption isotherms were determined at 77 K on samples of 0.6 g, following outgassing at 473 K for 24 h and under a residual vacuum of less than 1×10^{-4} Pa. With the help of Eqs. (1)–(3), the adsorption data led to the volume of the micropores W_o, their average width L_o and their real surface area S_{mi}. Immersion calorimetry into liquids such as CH_2Cl_2 and C_6H_6 at 293 K, confirms the adsorption data obtained from Eq. (4). More information was also obtained by using liquid probes of different molecular sizes.

3. Results

3.1. Heat-treated and fractionated pitches

The composition of the residual pitches of series (P-, H-, HC-) M400 and M470 are given in Table 2. It appears that both temperature treatments lead to similar α-, β- and γ-resin contents. All samples are characterized by a low α-resin content and the mesophase development is below 6%, taking into account the initial QI content. The simultaneous increase in mesogens (β-resins) and the loss of the light γ-resins indicates that the transformation experienced by the pitches during the heat treatments at 400°C and at 470°C is due essentially to the distillation of low molecular weight species and to the polymerization of reactive species [2,9,10].

The characteristics of the fractionated pitches obtained after toluene extraction (series E) are given in Table 3. All fractionated pitches are mostly toluene-insoluble with parts

Table 4
Characteristics of the carbons obtained by activating different pitch-based precursors with CO_2 at 900°C

Precursor	P-M400E			P-M470E			HC-M400E			HC-M470E			H-M400E			H-M470E		
Burn-off (%)	12	37	61	16	39	58	12	37	52	11	27	55	13	39	52	16	37	53
W_o (cm^3 g^{-1})	0.06	0.12	0.17	0.18	0.36	0.44	0.12	0.31	0.39	0.15	0.24	0.49	0.16	0.35	0.41	0.18	0.33	0.48
E_o (kJ mol^{-1})	26.4	23.3	20.8	32.6	23.5	20.9	33.9	24.9	21.0	33.4	30.3	20.5	34.4	25.4	22.3	33.0	24.1	19.1
L_o (nm)	0.7	0.9	1.2	0.5	0.9	1.1	0.5	0.8	1.1	0.5	0.6	1.2	0.5	0.8	1.0	0.5	0.9	1.4
S_{mi}(m^2 g^{-1})	149	313	470	491	939	1168	325	804	1030	6.9	17.3	27.2	13.3	22.6	48.2	17.5	34.1	63.3
S_e (m^2 g^{-1})	6.8	15.2	36.5	15.6	31.0	44.2	2.1	6.4	17.5	393	644	1303	435	927	1109	484	883	1212

of residual γ-resins in the range of 11 to 16 wt.%. Optical microscopy observations [11] of such fractionated pitches reveal four different types of microtextures: (i) coal tar pitches primary QI, (ii) Brooks and Taylor spheres, (iii) anisotropic particles representing the bulk of the extracted powders and (iv) isotropic matter surrounding the anisotropic particles. Textures (ii) and (iii) were present in all samples, but isotropic matter was observed only in sample P-M400E.

3.2. Activation

The activation of series (P-, H-, HC-) M400 and M470 was not successful and we concentrated our investigations on the activation of the toluene-extracted materials (series E). Fig. 1 shows the evolution of the burn-off as a function of time. The action of CO_2 at 900°C is regular, but one observes two distinct patterns, corresponding to the coal-based materials (series H and HC) and to the petroleum-based materials (series P). The burn-off rates, under the same conditions, are, respectively, 6.8 and 3.6% per hour. It appears clearly that this property depends essentially on the origin of the pitch and not on the subsequent thermal and extraction treatments.

The relatively low gasification rate of petroleum-based and extracted pitches has already been reported [12] for P-M400E and it has been ascribed to isotropic γ-resins of type (iv). On the other hand, P-M470E shows the same gasification rate as P-M400E but with an anisotropic texture close to coal-derived samples (mostly of type (iii) with no type (iv)). This suggests that differences in reactivity during gasification, as well as the resulting microporosity, should not only be related to their composition derived from the solubilities of the pitch precursors into various solvents, but also to their aromaticity. The relation between the heat treatment of the raw pitch, the aromatic character of the precursor and the microporosity resulting from activation process will be reported later.

3.3. Micropore volume

As shown in Fig. 2, the evolution of the micropore volume W_o with the degree of burn-off is linear, but for the activation of sample P-M400E, the gradient $\Delta W_o/\Delta$burn-off (1.3×10^{-3} cm^3/g %) is much lower than for the other materials (6.3×10^{-3} cm^3/g % for HC-M400E and 8.0×10^{-3} cm^3/g % for the other carbons). These gradients can be compared with those observed under similar activation conditions for cokes and pyrolyzed tyres ($2–3\times10^{-3}$ cm^3/g %) and for materials of vegetable origin ($6–9\times10^{-3}$ cm^3/g %) [1].

As opposed to the reactivity shown in Fig. 1, the poorer performance in the development of the micropore volume results from the combination of two factors, namely the origin of the pitch (petroleum-based) and the heat treatment (400°C). The latter factor is essential, since the carbons based on P-M470E belong to the group with the highest micropore volumes. The positive effect of the heat treatment at 470°C on the development of microporosity has already been reported [12] and it can be explained by

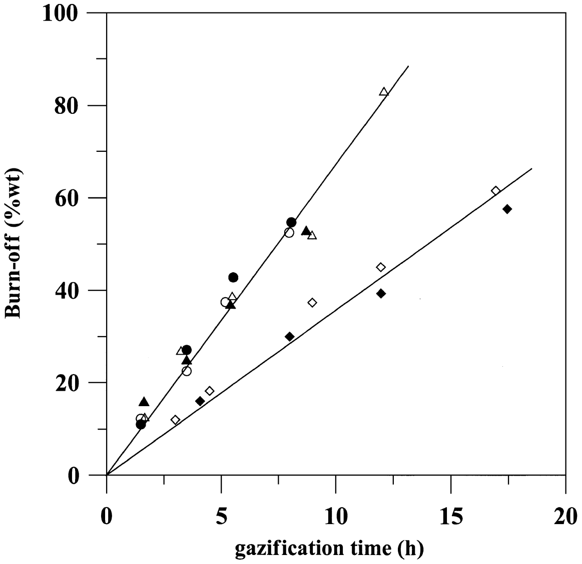

Fig. 1. Variation of the burn-off, as a function of time, for pitch based precursors activated with CO_2 at 900°C. (◇) P-M400, (○) HC-M400, (△) H-M400, (♦) P-M470, (●) HC-M470, (▲) H-M470.

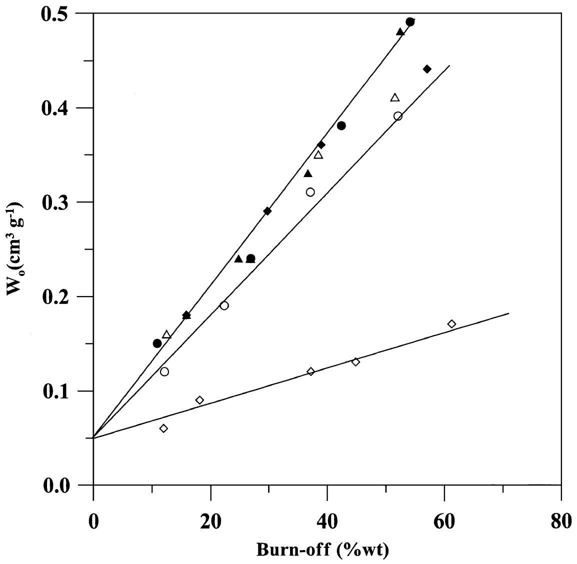

Fig. 2. Variation of the micropore volume W_o, with the degree of burn-off, for pitch-based precursors activated with CO_2 at 900°C. (◇) P-M400, (○) HC-M400, (△) H-M400, (♦) P-M470, (●) HC-M470, (▲) H-M470.

the fact that species of low molecular weight have not been removed prior to carbonization and activation.

It is also interesting to note that the linear sections shown in Fig. 2 extrapolate to an initial value $W_o(0)$ of 0.05 cm^3/g. It reflects a feature common to all pitch-based chars of series E. A similar pattern has been reported for a number of activated carbons [13–16]. For example, Stoeckli and Ballerini [16] obtained initial volumes $W_o(0)$ close to 0.1 cm^3/g for activated wood chars and for pyrolyzed tyres. The pattern revealed by Fig. 2 is therefore common to a variety of carbonaceous materials, but with specific gradients and initial volumes $W_o(0)$, depending on their origin.

3.4. Pore sizes

Fig. 3 shows the evolution of the average pore size L_o, calculated by Eq. (2), as a function of the degree of burn-off. As expected, L_o increases, but it appears that the series based on P-M400E form a separate class, with relatively high initial values. The value extrapolated to zero burn-off, $L_o(0)$ is near 0.9 nm. All other samples start from lower values and $L_o(0)$ is close to 0.5 nm. The comparison of Figs. 3 and 2 confirms the existence of two distinct patterns, one corresponding to the P-M400 series and the other to the rest of the precursors, whatever their origin and the treatments. In the latter group, one may distinguish some specificity for burn-offs between 30 and 60%, series H-M400 having the smallest pores.

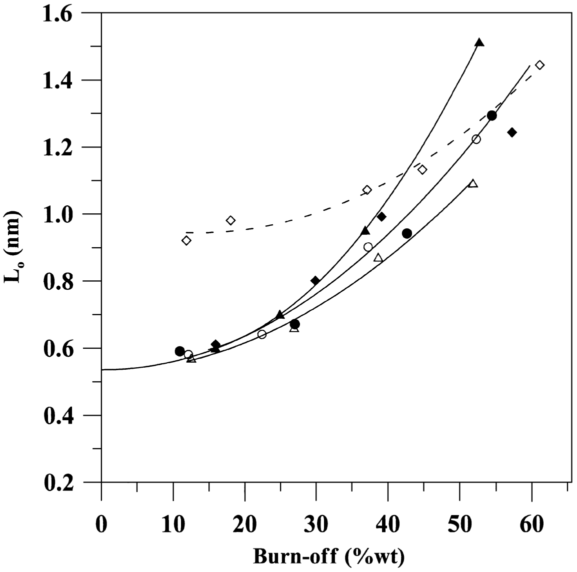

Fig. 3. Variation of the average micropore width L_o, with the degree of burn-off, for pitch-based precursors activated with CO_2 at 900°C. (◇) P-M400, (○) HC-M400, (△) H-M400, (♦) P-M470, (●) HC-M470, (▲) H-M470.

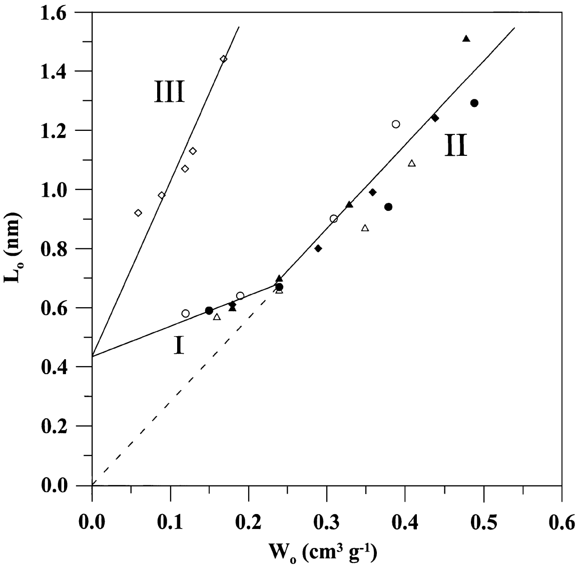

Fig. 4. Variation of the average micropore width L_o with W_o for pitch-based precursors activated with CO_2 at 900°C. (◇) P-M400, (○) HC-M400, (△) H-M400, (♦) P-M470, (●) HC-M470, (▲) H-M470. The lines are taken from Ref. [1] based on various carbons not shown here for the sake of clarity.

3.5. Pore size as a function of the micropore volume

The combination of the data shown in Figs. 2 and 3 (see also Table 4) leads to Fig. 4, which shows the correlation between L_o and W_o for the different activated carbon series. As expected, the carbons based on P-M400E form a separate class and the patterns revealed by Fig. 4 will be discussed in detail below.

4. Discussion

Fig. 4 summarizes some fundamental properties of active carbons prepared from heat treated and toluene-extracted pitches, in the light of our recent work on the evolution of micropore width and volumes during physical activation [1]. It had been shown, that three distinct patterns can be identified, depending on the precursor.

In the present case, it appears that the activated carbons based on pitches P, H and HC belong, with one exception (series based on P-M400E), to the same class as materials from vegetable origin. They follow regime I at low degree of burn-off and regime II at medium and high degrees of burn-off. The transition between the two occurs for a micropore volume W_o of 0.20–0.25 cm^3/g and a pore-width around 0.6 nm. As revealed by a number of studies, this corresponds to a burn-off between 30 and 40%. The volume of 0.20–0.25 cm^3/g corresponds to the initial hidden volume $W_o(0)$ of ~0.1 cm^3/g and disorganized material removed in the early stages of activation (regime I). From this point, L_o and W_o increase linearly and in the present case the gradient $\Delta L_o/\Delta W_o = 2.9$ nm/cm^3 g^{-1} is similar to that found for the different carbons (2.6 nm/cm^3 g^{-1}).

Below 0.20–0.25 cm^3/g, one observes regime I, which may be due either to the fact that the size of the molecular probes is limited (0.30 to 0.35 nm for the smallest probes [3]) or to the early stage of a development of microporosity leading eventually to true molecular sieve carbons [17,18]. The limiting value of $L_o(0)$ around 0.4 nm, seen in Fig. 4, is also in agreement with the data reported earlier [1].

As mentioned above (Section 3.3), the gradient ΔW_o/Δburn-off (activability) of the pitch-based precursors leading to regime II is around $6–8\times10^{-3}$ cm^3/g and percent of burn-off and therefore similar to that of the other carbonaceous materials ($6–8\times10^{-3}$ cm^3/g and percent). This suggests that all the carbonized materials following regime II have similar structures.

As shown in Fig. 4, the activation series based on sample P-M400E does not conform to this pattern and follows regime III. This corresponds also to the activation of acetylene cokes [19], of Spanish anthracite [20] and of pyrolyzed tyres [16], with a gradient $\Delta L_o/\Delta W_o$ similar to that of regime II. Regime III produces micropores with relatively modest volume, due to the absence of a significant initial volume.

The activability of carbon P-M400E (1.3×10^{-3} cm^3/g and percent burn-off) is similar to that of the cokes and the tyre residues ($2–3\times10^{-3}$ cm^3/g %), which confirms that it belongs to the class of carbons described by section III. The fundamental difference between sample P-M400E and the other pitch-based samples resides in the heat treatment (400°C) and in the origin of the pitch (petroleum pitch). This is suggested by the fact that the carbons derived from P-M470E belong, like all other carbons, to the same class represented by section II in Fig. 4. One may therefore conclude that carbon P-M400E possesses specific structural properties leading to section III, but which are destroyed by the heat treatment to 470°C. This will be examined in more detail below.

Greinke has shown in Ref. [10] that the disappearance of γ-resins during isothermal heat treatment is the result of both distillation of low molecular weight species and polymerization of reactive toluene soluble molecules. In a recent study [2], both processes of γ-resin removal were quantified using the mass balance equation

$$\Delta\gamma = \Delta\gamma_p + \Delta\gamma_d \tag{5}$$

in which it is assumed that the total loss of γ-resins during heat treatment $\Delta\gamma$ is the addition of the removal of low molecular weight species by distillation $\Delta\gamma_d$, and by polymerization $\Delta\gamma_p$. In this study, $\Delta\gamma_d$ was quantified by the overall pitch weight loss during the heat soaking treatment and $\Delta\gamma$ was calculated from the evolution of chemical composition given in Table 2. The loss of γ-resins due to polymerization was obtained by difference. In the present case, the corresponding data, expressed in weight percentage, are given in Table 2.

As expected, pitch evolution differs depending on the composition of the raw pitch and on the heat treatment applied, but in all cases $\Delta\gamma$ increases with the temperature of the treatment (in the present case, $\Delta\gamma$ represents 20 to 30% in weight). However, as seen in Table 2, in the case of sample P-M400, the loss of light molecular weight species, $\Delta\gamma_d$, is unusually low (only 9.7% against 17 to 30% for all other samples). Since these species are known to inhibit the development of pores during activation [12], their higher proportion in the carbon may explain the pattern followed by sample P-M400E, in spite of the toluene extraction stage.

Inspection of Table 1 also shows that with respect to pitches H and HC, the petroleum-based pitch P has a higher content of γ-resins (96% as opposed to 72 and 85% for the others). It is therefore plausible that their removal during soaking requires a longer time and/or a higher temperature. The latter is clearly illustrated by the activation series based on P-M470E.

5. Conclusions

The present study, based on pitches, confirms our recent observation, according to which the physical activation of most carbonaceous materials leads to microporous solids which follow three basic patterns. It appears that the materials leading eventually to regime III (see Fig. 4) can be, at least

1. well-organized carbons such as cokes and semi-cokes, and
2. precursors containing an important fraction of low-molecular weight species (for example petroleum-based pitch P, or pyrolyzed tyres [16]).

In the first case, physical activation will almost invariably follow regime III and there is little hope for improving the micropore volume W_o. On the other hand, in the case of materials containing light molecular weight compounds, their extraction or oxidation may induce changes leading to regimes I and eventually II, with an appreciable gain in micropore volume. The extension of regime I beyond micropore volumes W_o of 0.20–0.25 cm^3/g and leading to interesting molecular sieve carbons, remains to be investigated. Results will be published in due course.

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