

## Chars and Activated Carbons Prepared from Asturian Apple Pulp

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**ABSTRACT:** Asturian apple pulp was carbonised under nitrogen at 400°C and 750°C and subsequently activated with CO<sub>2</sub> at 750°C. The resulting active carbon exhibited properties in line with those expected from precursors of vegetable origin, with the carbonisation stage appearing to have only a limited influence on the final porosity. In the case of carbonisation at 400°C, the initial micropore system of the char was accessible to dichloromethane, CO<sub>2</sub> and water, but presented a strong gate effect at ca. 0.35–0.40 nm. The pore volume,  $W_0$ , was equal to 0.13 cm<sup>3</sup>/g and the average pore width 0.70 nm. The pore size distribution was obtained from CO<sub>2</sub> adsorption at 0°C, using isotherms derived from computer modelling. With the char prepared at 750°C, the initial porosity was only accessible to water and its presence was confirmed by extrapolation of  $W_0$  for the activated carbons.

## INTRODUCTION

Activated carbons can be prepared from a variety of precursors, among which materials of vegetable origin are a traditional source. Besides coconut as a precursor, detailed studies have also been published on almond shells (Marcilla *et al.* 2000), palm shell (Wan Mohd 2000) and apricot stones (Gergova and Eser 1996), as well as on less popular precursors.

Following carbonisation and physical activation by steam or carbon dioxide, the materials obtained exhibit different micropore volumes and surface areas. It appears, however, that the resulting microporosity follows certain patterns which limit the degree of freedom. For example, it is well known that in the case of cellulosic precursors the micropore volumes  $W_0$  can reach values of 0.6–0.7 cm<sup>3</sup>/g at high degrees of burn-off, but at the same time the average micropore size  $L_0$  increases regularly from 0.4–0.5 nm to ca. 1.5–2 nm (Stoeckli *et al.* 1999).

Stoeckli *et al.* (1999) have shown recently that the evolution of the average micropore width  $L_0$  with the micropore volume  $W_0$  follows three distinct patterns characterised by their gradients  $\Delta L_0/\Delta W_0$  and the presence or absence of an initial micropore volume developed during carbonisation. Activated carbons based essentially on cellulosic precursors (wood and fruits) and on semi-anthracites, activated with steam or CO<sub>2</sub>, correspond to a behaviour classified as type II. This is characterised by a regular increase in  $L_0$  and  $W_0$  [ca. 2.6 nm/(cm<sup>3</sup> g)] beyond 0.20–0.25 cm<sup>3</sup>/g, which corresponds to a burn-off of ca. 30%. This volume corresponds, in part, to the presence of a microporous volume of 0.10–0.15 cm<sup>3</sup>/g in the char as suggested by extrapolation of the micropore volume  $W_0$  as a function of the degree of burn-off.

As shown below, carbonisation of Asturian apple pulp followed by physical activation by carbon dioxide followed the general pattern observed for cellulosic precursors (type II), and hence no

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surprises were to be expected. However, a closer study showed that the carbonisation stage can influence the outcome to some extent, as suggested by different authors (Dubinin and Zaverina 1961; Mackay and Roberts 1982; Alvarez *et al.* 1994; Byrne and Nagle 1997; Warhurst *et al.* 1997; Rodriguez-Reinoso and Solano 1998). It was therefore of interest to investigate the preparation of the char and its properties. In the present case, following carbonisation at low temperature (ca. 400°C), it appeared that the original microporosity of the char could be examined directly by using small probe molecules such as CH<sub>2</sub>Cl<sub>2</sub> or CO<sub>2</sub>. This original microporosity had an average width, L<sub>0</sub>, close to 0.7 nm, but was only accessible to small molecules such as CH<sub>2</sub>Cl<sub>2</sub> and CO<sub>2</sub>, with benzene and CCl<sub>4</sub> being excluded by a 'gate' effect of ca. 0.4–0.5 nm at the entrance of the pore system. On the other hand, if carbonisation was effected at a higher temperature (750°C), the system was no longer accessible and the micropore system obtained by subsequent physical activation by CO<sub>2</sub> at 750°C was somewhat different at similar degrees of burn-off. This therefore demonstrates the existence of limits for the optimisation of activated carbons prepared from a typical precursor of vegetable origin following classical carbonisation and physical activation steps.

## THEORETICAL

The characterisation of the chars and of the activated carbons derived from them has been carried out within the framework of Dubinin's theory as described in detail elsewhere (Dubinin 1989; Stoeckli 1995). The relevant expression used in the present study was the Dubinin–Radushkevich (DR) equation:

$$N_a = N_{a0} \exp[-(A/E)^2] \quad (1)$$

where  $A = RT \ln(P_s/P)$ ;  $N_a$  is the amount (usually expressed in mol/g) adsorbed at a relative pressure of  $P/P_s$  and temperature  $T$ , and  $N_{a0}$  is the limiting amount filling the micropores. The volume of the micropores is given by  $W_0 = N_{a0} V_m$ , where  $V_m$  is the volume of the condensed adsorbate. The quantity  $E$  is the characteristic energy of the system which depends on the solid and on the adsorbate. The effect of the adsorbate can be expressed by a factor  $\beta$ , called the affinity coefficient, such that  $E = \beta E_0$ , the reference being benzene by convention and hence  $\beta(C_6H_6) = 1$ . The affinity coefficients for the other adsorbates used in the present study were  $\beta(CH_2Cl_2) = 0.66$ ,  $\beta(CO_2) = 0.35$ ,  $\beta(CCl_4) = 1.05$  and  $\beta(\text{trixylyl phosphate}) = 4.05$ . It appears that  $E_0$  is an inverse function of the average micropore width  $L_0$  (Stoeckli 1995):

$$L_0 \text{ (nm)} = 10.8/(E_0 - 11.4 \text{ kJ/mol}) \quad (2)$$

This expression provides reliable data in the domain  $0.4 < L_0 < 1.7\text{--}1.8$  nm, or  $E_0 > 16\text{--}17$  kJ/mol.

As a thermodynamic consequence of equation (1), one obtains an expression for the enthalpy of immersion of an activated carbon into the corresponding liquid:

$$\Delta H \text{ (J/g)} = -\beta E_0 W_0 (1 + \alpha T) (\pi)^{1/2} / 2V_m + h_1 S_c \quad (3)$$

where  $\alpha$  is the thermal expansion coefficient of the liquid and  $h_1 S_c$  represents the wetting of the external (non-microporous) surface,  $S_c$ , of the carbon. The last term is usually only a fraction of the total enthalpy of immersion. Equation (3) can be used in connection with liquids of variable molecular dimensions (0.4–1.5 nm) to detect molecular sieve effects in carbons. The references are liquids such as dichloromethane or CS<sub>2</sub> with critical diameters of 0.33 nm and 0.35 nm, respectively.

As described elsewhere (Stoeckli 1995), the micropore size distribution:

$$f(L) = 2W_0 L^{(3v-1)} a^v \exp[-aL^3]/\Gamma(v) \quad (4)$$

can be derived from a modified Dubinin equation, i.e.

$$N_a/N_{a0} = [a/(a + (A/\beta K_0)^3)]^v \quad (5)$$

In these expressions,  $a$  and  $v$  are adjustable parameters and  $K_0 = E_0 L_0$ . This approach is based mainly on the selective adsorption of liquids with molecular dimensions between 0.4 nm and 1.5 nm which has been shown recently to be in good agreement with molecular simulations based either on  $N_2$  ( $-196^\circ\text{C}$ ) (Carrott *et al.* 1998) and  $\text{CO}_2$  ( $0^\circ\text{C}$ ) (Stoeckli *et al.* 2000). The latter is used in the present study for the characterisation of microporosity and in connection with the reference isotherm recently proposed by Guillot and Stoeckli (2001).

## EXPERIMENTAL

### Precursors and char preparation

Batches of dry Asturian apple pulp (30 g) were used in a horizontal quartz reactor. Pyrolysis was carried out under nitrogen (100 ml/min) by heating up to  $400^\circ\text{C}$  (sample C-400) or  $750^\circ\text{C}$  (sample C-750) at a rate of  $15^\circ\text{C}/\text{min}$ , with the samples being maintained at the maximum temperature for 1 h. Cooling to room temperature was also effected under nitrogen. The proximate and ultimate analyses of the chars are given in Table 1, which also shows the weight losses obtained from pyrolysis and from thermogravimetry (TG) under similar conditions.

Char C-400 was subjected to oxidation in air for 3 d at  $270^\circ\text{C}$  to produce sample C-400-ox. This technique has been described previously by Alvarez *et al.* (1994) and by Centeno and Stoeckli (1995).

### Activation

Activated carbons were prepared by reaction with  $\text{CO}_2$  at  $750^\circ\text{C}$  [ca. 160 ml (STP)/min] to weight losses of ca. 40% or 70%, respectively. The corresponding samples are listed as AC-400-36, AC-400-63, AC-400-66, AC-400-72, AC-750-41 and AC-750-72 respectively below, the last number giving the exact degree of burn-off.

### Characterisation techniques

The chars and the activated carbons were characterised by immersion calorimetry at  $20^\circ\text{C}$  into various liquids, using a calorimeter of the Tian-Calvet type as described elsewhere (Bansal *et al.* 1988). In the present study, samples of 0.100–0.150 g weight were outgassed at  $300^\circ\text{C}$  for 12 h

TABLE 1. Characteristics of C-400 and C-750 Chars

Char	Carbonisation yield (%)	TG yield (%) at		Elemental analysis (w/w%)			Ash ( $900^\circ\text{C}$ ) (w/w%)
		$10^\circ\text{C}/\text{min}$	$20^\circ\text{C}/\text{min}$	C	H	O	
C-400	30	31	45	80.3	3.7	12.28	3.8
C-750	25	10	15	86.7	1.3	7.6	4.4

under a dynamic vacuum of  $10^{-3}$  Pa. In the case of immersion into water, however, the outgassing temperature was reduced to 110–120°C, in order to avoid the destruction of oxygen-containing surface complexes.

Adsorption isotherms of  $\text{CH}_2\text{Cl}_2$  and/or  $\text{C}_6\text{H}_6$  were determined at 20°C on selected samples, using standard gravimetric equipment. Sample C-400 was also characterised by  $\text{CO}_2$  adsorption at 0°C and pressures up to 0.35 MPa through the use of high-pressure equipment as described by Guillot *et al.* (2000).

The adsorption isotherms were also compared with standard isotherms obtained by Hugi-Cleary and Stoeckli (2000) on non-porous carbon blacks Hoechst ( $\text{CH}_2\text{Cl}_2$  and  $\text{C}_6\text{H}_6$  at 20°C) and by Guillot and Stoeckli (2001) on Vulcan-3G ( $\text{CO}_2$  at 0°C) in order to determine the external (non-microporous) surface area,  $S_e$ , and to cross-check the micropore volume.

## RESULTS AND DISCUSSION

### Chars

Chars C-400 and C-750, prepared respectively at 400°C or 750°C, corresponded to yields of 25–30% and to C, H and O contents as listed in Table 1. It appears that char C-750 contained more carbon and less oxygen than C-400.

The values of the enthalpies of immersion of chars C-400, C-400-ox and C-750 into various liquids, including water, are listed in Table 2. With C-400, immersion into  $\text{CH}_2\text{Cl}_2$  with a critical diameter close to 0.35 nm produced an unusually high enthalpy (–70 J/g), suggesting that this adsorptive fills a micropore system virtually inaccessible to benzene (0.42 nm),  $\text{CCl}_4$  (0.63 nm) and larger molecules. Consequently, the adsorption isotherms of  $\text{CH}_2\text{Cl}_2$  (20°C) and  $\text{CO}_2$  (0°C) were determined on char C-400.

The DR plot for dichloromethane adsorbed at 20°C led to a micropore volume  $W_0 = 0.13 \text{ cm}^3/\text{g}$  and a characteristic energy,  $E_0$ , of 26.7 kJ/mol (Table 3). From equation (2), this corresponds to an average micropore width  $L_0 = 0.70 \text{ nm}$ . The low enthalpies of immersion into benzene and larger molecules suggest the presence of a gate effect at the entrance of the pores. It is reasonable to postulate that water, with a critical diameter of ca. 0.30 nm, also filled this micropore system.

A comparison of the adsorption isotherms of  $\text{CH}_2\text{Cl}_2$  on C-400 and on carbon black Hoechst (Figure 1) led to a micropore volume of  $0.13 \text{ cm}^3/\text{g}$  and an external surface area,  $S_e$ , of  $12 \text{ m}^2/\text{g}$ . Using the data for  $E_0$ ,  $W_0$  and  $S_e$  given in Table 3, equation (2) leads to an enthalpy of immersion  $\Delta_i H(\text{CH}_2\text{Cl}_2)$  of –50.1 J/g. This is smaller than the experimental value of –70 J/g and no explanation can be offered at this stage for the difference.

TABLE 2. Enthalpies of Immersion of Chars and Activated Carbons into Different Liquids at 20°C<sup>a</sup>

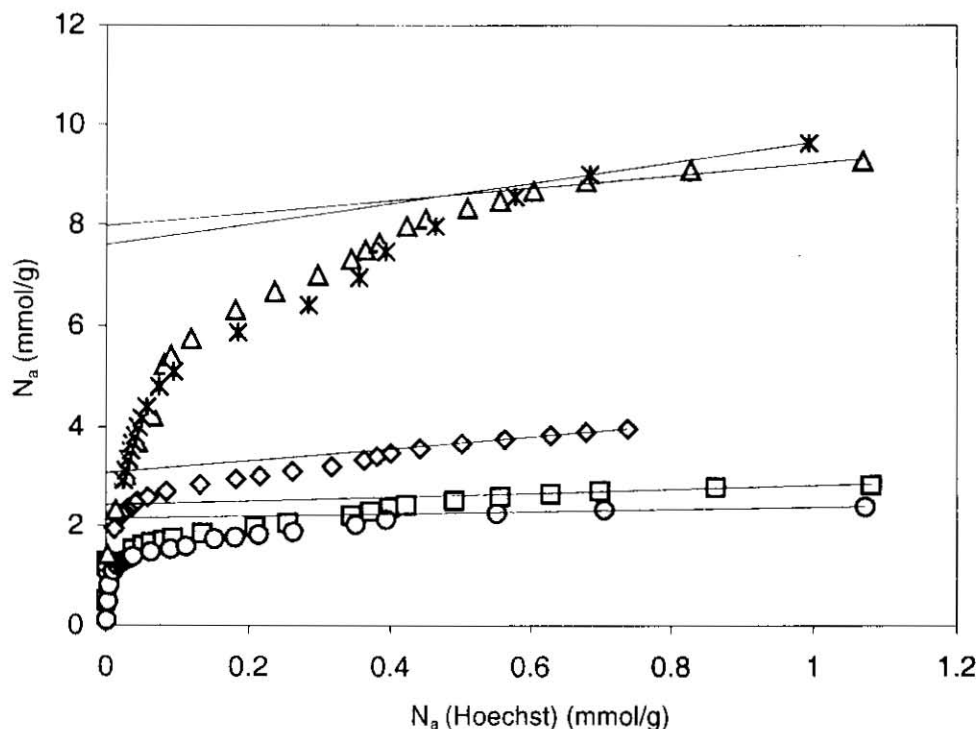
Carbon	$-\Delta_i H(\text{H}_2\text{O})$ (0.30 nm) <sup>c</sup>	$-\Delta_i H(\text{CH}_2\text{Cl}_2)$ (0.33 nm) <sup>c</sup>	$-\Delta_i H(\text{C}_6\text{H}_6)$ (0.42 nm) <sup>c</sup>	$-\Delta_i H(\text{CCl}_4)$ (0.63 nm) <sup>c</sup>	$-\Delta_i H(\text{TXP})^b$ (1.50 nm) <sup>c</sup>
C-400	30.0	70.0	10	6.4	13.9
C-400-ox	58.9	15.0	17.3	7.4	16.0
C-750	31.2	9.2	9	2	15.7
AC-750-72	119.7	158.5 (152) <sup>c</sup>	141.0 (145.3) <sup>c</sup>	120.5 (140.5) <sup>c</sup>	133.4 (133) <sup>c</sup>

<sup>a</sup>All values quoted in J/g. <sup>b</sup>TXP = tri-2,4-xylyl phosphate. <sup>c</sup>All values in brackets calculated from equation (3).

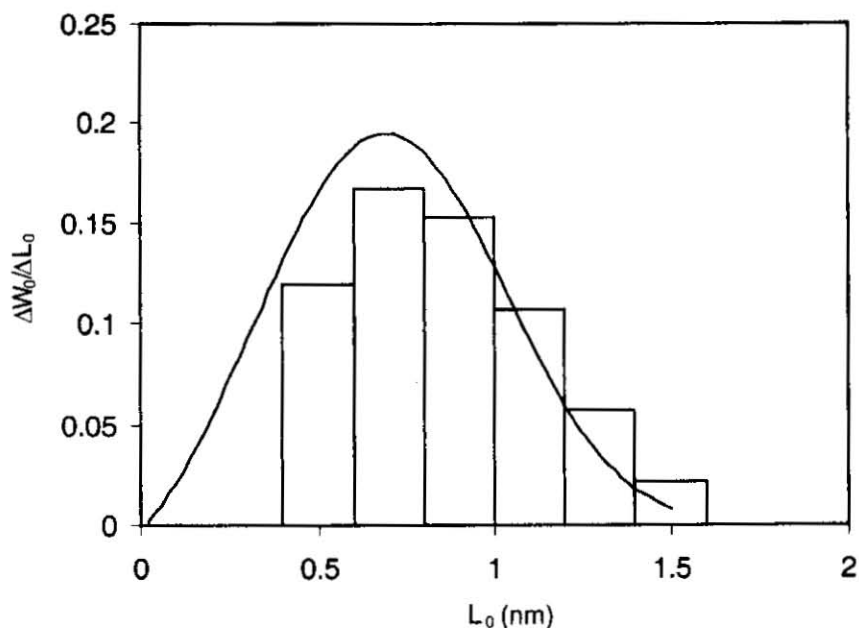
**TABLE 3.** Structural Properties of Char C-400 and of the Activated Carbons of the Series AC-400 and AC-750 as Derived from the Adsorption Isotherms for  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$  and  $\text{CO}_2$

Carbon	Adsorbate	$W_0(\text{DR})$ ( $\text{cm}^3/\text{g}$ )	$W_0(\text{C-black})$ ( $\text{cm}^3/\text{g}$ )	$E_0$ ( $\text{kJ/mol}$ )	$L$ ( $\text{nm}$ )	$S_e$ ( $\text{m}^2/\text{g}$ )
C-400	$\text{CH}_2\text{Cl}_2$ (20°C)	0.130	0.13	26.7	0.70	12
	$\text{CO}_2$ (0°C)	0.117	0.12	28.4	0.63	41
AC-400-36	$\text{C}_6\text{H}_6$ (20°C)	0.282	0.28	25.8	0.75	34
AC-400-66	$\text{CH}_2\text{Cl}_2$ (20°C)	0.487	0.49	18.0	1.64	133
AC-750-41	$\text{CH}_2\text{Cl}_2$ (20°C)	0.233	0.22	24.3	0.83	62
AC-750-72	$\text{CH}_2\text{Cl}_2$ (20°C)	0.540	0.48	18.3	1.50	96

The  $\text{CO}_2$  isotherm at 0°C led to a micropore volume  $W_0 = 0.117 \text{ cm}^3/\text{g}$  and  $E_0 = 28.4 \text{ kJ/mol}$ , corresponding to an average width  $L_0 = 0.63 \text{ nm}$ . This is in good agreement with the value of  $0.70 \text{ nm}$  suggested by  $\text{CH}_2\text{Cl}_2$ . Comparison of the  $\text{CO}_2$  isotherm with the reference for Vulcan-3G led to a micropore volume of  $0.11 \text{ cm}^3/\text{g}$  and an external (non-porous) surface  $S_e = 41 \text{ m}^2/\text{g}$ . Although this value was somewhat larger than that obtained for  $\text{CH}_2\text{Cl}_2$ , it was used to correct the experimental isotherm for adsorption outside the micropores before analysing it in terms of model isotherms



**Figure 1.** The  $\text{CH}_2\text{Cl}_2$  isotherms at 20°C on char C-400 (○) and activated carbons AC-400-36 (◇), AC-400-66 (\*), AC-750-41 (△) and AC-750-72 (□) and the  $\text{C}_6\text{H}_6$  isotherm at 20°C on AC-400-36 (□). The reference employed was carbon black Hoechst.



**Figure 2.** Pore-size distribution in char C-400, as suggested by the  $\text{CO}_2$  isotherm at  $0^\circ\text{C}$  analysed with the model isotherm based on Monte Carlo simulations.

obtained from computer simulations (Stoekli *et al.* 2000). The latter approach leads to the pore-size distribution shown in Figure 2 (histogram), in good agreement with the distribution corresponding to equation (5) (continuous curve) and based on the  $\text{CH}_2\text{Cl}_2$  isotherm.

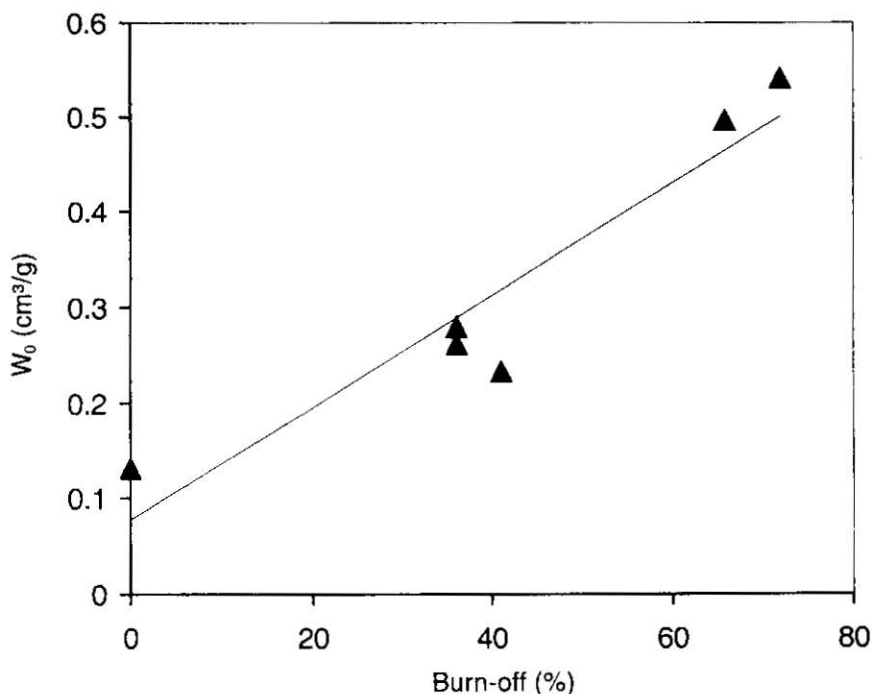
For the chars C-400-ox and C-750, the enthalpies of immersion into  $\text{CH}_2\text{Cl}_2$  were much lower than for C-400, indicating that this molecule was largely excluded from the internal micropore system. On the other hand, the enthalpies of immersion of the three chars into water suggest that their micropore systems were still accessible to this molecule. The higher value obtained for C-400-ox reflects the increase in surface oxygen following treatment in air.

### Activated carbons

Activated carbons AC-400-36, AC-400-66, AC-750-41 and AC-750-72 were analysed by  $\text{CH}_2\text{Cl}_2$  or  $\text{C}_6\text{H}_6$  adsorption at  $20^\circ\text{C}$  (Table 3) and by immersion calorimetry into various liquids. As an example, the table lists the experimental and calculated values for the enthalpies of immersion of carbon C-750-72, the sample with the highest degree of activation.

Comparison plots based on the non-porous reference Hoechst (Figure 1) provide information on the external surface areas,  $S_e$ , and confirm the values of the micropore volumes obtained from the DR plots.

As shown in Figure 3, the plot of the micropore volumes,  $W_0$ , of the different carbons versus the degree of burn-off extrapolated to the original volume of ca.  $0.13 \text{ cm}^3/\text{g}$ , as observed directly for char C-400. A linear increase of  $W_0$  with the degree of burn-off has been reported in the past (Stoekli and Ballerinin 1991; Stoekli and Huguenin 1994), but in most cases the limiting value  $W_0(0)$  was only obtained by extrapolation to zero burn-off.



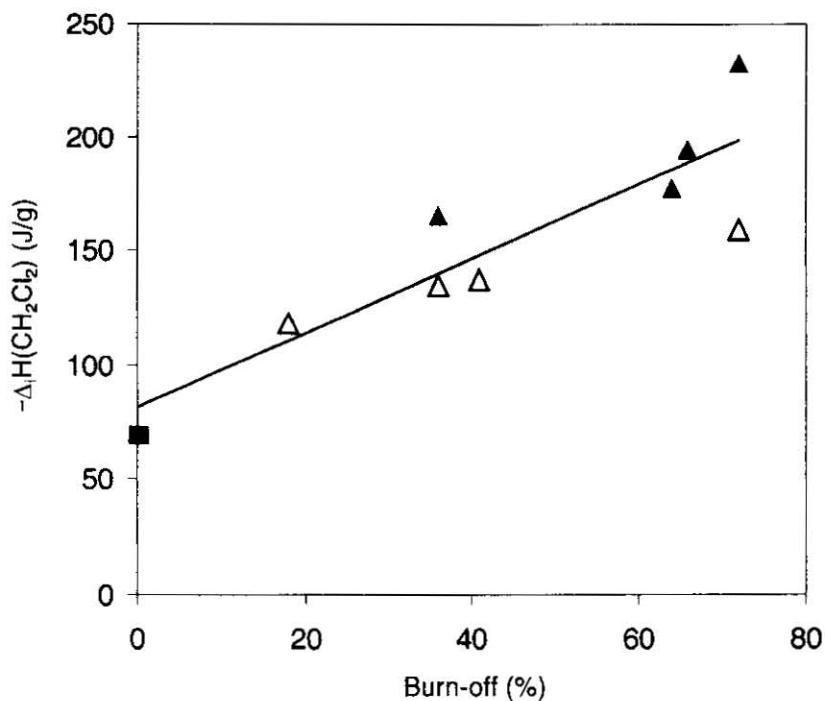
**Figure 3.** Variation of the micropore volume,  $W_0$ , with burn-off for char C-400 and active carbons of series AC-400 and AC-750.

As seen in Figure 4, the enthalpies of immersion of the activated carbons into  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_6\text{H}_6$  at  $20^\circ\text{C}$  showed a regular increase with the degree of burn-off. The data in this figure include intermediate values which were not investigated by adsorption techniques. It appears from the figure that series C-400 and C-750 behaved in a similar fashion.

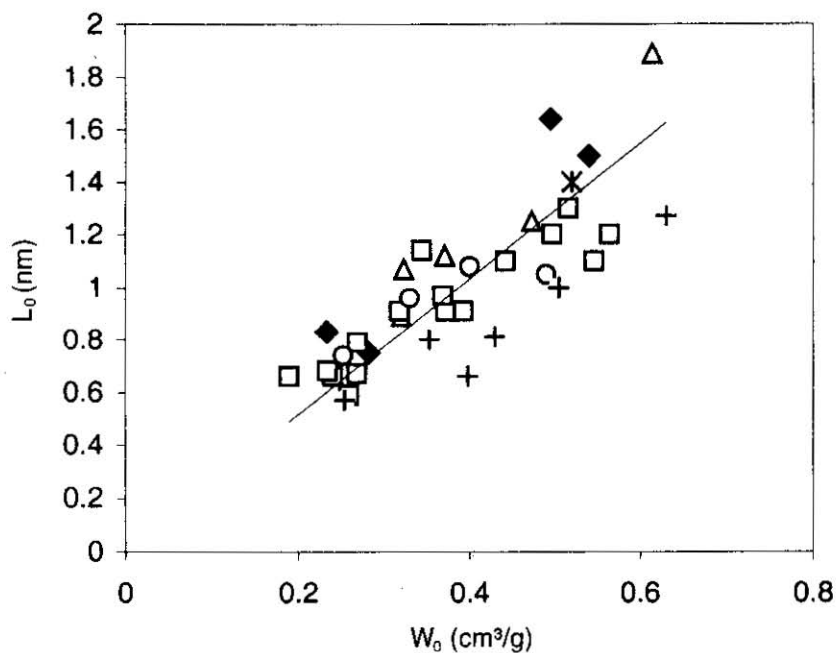
For the carbons obtained in the present study, one observes relatively high enthalpies of immersion into water, i.e.  $-70$ ,  $-119$ ,  $-104$  and  $-120$  J/g for activated carbons AC-400-36, AC-400-72, AC-750-41 and AC-750-72. This corresponds to ratios of  $\Delta_i H(\text{H}_2\text{O})/\Delta_i H(\text{C}_6\text{H}_6)$  between 0.46 and 0.75, as opposed to values between 0.25 and 0.35 for carbons with low ash contents and ca. 1–2 mmol surface oxygen/g (Stoeckli and Lavanchy 2000; López-Ramón *et al.* 1999). The apparent hydrophilic character of these carbons probably reflects the effect of the ash content, which increased from 4% in the chars to 10% in the case of carbon AC-750-72.

As shown in Figure 5, the activated carbons produced from Asturian apple pulp fall in line with the general behaviour reported earlier by Stoeckli *et al.* (1999). In the present case, the plot shows only materials of vegetable origin (wood, olive stones, peat, etc.) subjected to physical activation. The gradient  $\Delta L_0/\Delta W_0 = 2.6$  nm/(cm<sup>3</sup>/g) is practically the same as reported earlier when precursors of other origins were included.

It appears that, in the case of the Asturian apple pulp, the carbonisation stage had only a small influence on the final activated carbon as far as the correlation between  $L_0$  and  $W_0$  was concerned. On the other hand, the graph shows that within the pattern observed for the materials of vegetable origin, the precursors themselves may fall into slightly different families. However, it appears that no great surprises are to be expected from materials of vegetable origin when subjected to physical



**Figure 4.** Variation of the enthalpy of immersion of char C-400 (■) and of the activated carbons of series AC-400 (▲) and AC-750 (Δ) into  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .



**Figure 5.** Variation of the average micropore width  $L_0$  with  $W_0$  for carbons of series AC-400 and AC-750 (◆), from plum stones (Δ), peat (□), banana (\*), olives (○) and soft wood (+).

activation by steam or CO<sub>2</sub>. Under these circumstances, only the cost of the precursor may finally decide on its use.

## ACKNOWLEDGEMENTS

The authors wish to thank Dr. A. Guillot (CNRS-IMP, Université de Perpignan, France) for the determination of CO<sub>2</sub> isotherms at high pressures, and Mr. A. Slasli for assistance with computer modelling.

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