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ON THE ACTIVATION OF ASTURIAN ANTHRACITE FOLLOWING VARIOUS PRETREATMENTS

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Abstract—An Asturian anthracite has been subjected to different pretreatments and subsequently activated by steam at 850°C to a total burn-off of 55 percent. The physical properties (micropore sizes and distributions, external surface areas, etc.) of the solids are compared with those of the carbon obtained by direct activation. Although the yield is generally low, it appears that better results are obtained by activation following preoxidation in air at 270°C for 3 days. In the case of pretreatments with a mixture of nitrogen, air, and water vapor at 450°C, the subsequent activation is less efficient. The micropore volumes and the pore size distributions are similar to those observed for soft precursors, but at a much lower degree of burn-off.

Key Words—Anthracite, activation, pretreatment, microporosity.

1. INTRODUCTION

Activated carbons are materials with large adsorption capacities from the gas phase and solution, as a result of their well-developed porous structures and the chemical nature of their surfaces. The characteristics of these carbons are affected by the type of raw material and the manufacturing conditions[1]. By choosing the starting material correctly, the preliminary treatments, and the activation conditions, the volume and size of the pore system can be controlled and adapted to a given application[2].

Many carbonaceous materials are used for the manufacture of activated carbons (for example, agricultural byproducts, petroleum coke, etc.), but coals, mainly low-rank coals, are one of the most important sources for the production of these carbons[1]. However, the use of anthracites as starting materials is not very common. These materials present a higher degree of orientation of the carbonaceous lamellaes than the low-rank coals[3]. As a result, the diameter and the accessibility of the pores of the anthracites decrease, and their physical activation is difficult.

As reported by different authors, the porosity of activated carbons is strongly influenced by their initial treatment. Thus, it was observed that coal preoxidation with air at temperatures between 100 and 270°C produces a marked increase in the pore volume of both chars and active carbons obtained from coals with plastic properties[4,5]. On the other hand, as shown previously[6], at 450°C a mixture of air and water vapor in a stream of nitrogen induces the development of a significant external surface area, and of some microporosity in an acetylene coke. Both low-temperature treatments also create favorable conditions for activation by steam around 800°C.

As described below, these pretreatments were applied to a typical Asturian anthracite, prior to steam activation. The resulting active carbons were subjected to a full characterization by adsorption and immersion techniques developed in this laboratory[2,7–9]. This provides a good insight into the effect of the pretreatment on the development of microporosity at a final weight loss of 55%, relative to the dry and ash-free starting material.

2. EXPERIMENTAL

2.1 *Raw material*

In this study, an anthracite from the Asturian Basin (North of Spain), Coto Minero Narcea, has been used as starting material. The chemical composition of raw coal was: ash, 4.0%(d.b.); V.M., 5.1%(daf); C, 91.6%(daf); H, 2.1%(daf); N, 0.9%(daf); S, 1.2%(daf); O(diff.), 4.2%(daf). Its density in helium is found to be 1.54 g/cm^3, which is relatively low and indicates the presence of closed porosity. The raw material was crushed and sieved, to obtain particles sizes between 1 and 1.5 mm, and subjected to three different treatments.

2.2 *Sample preparation*

2.2.1 *Direct activation.* The anthracite (3 g) was treated at 850°C with a stream of nitrogen (flow rate of 2.5 l/min) saturated with water vapor provided by a bath at 70°C ($p = 233.7$ mmHg). The equipment is described in detail elsewhere[9]. One obtains sample CM-A.

2.2.2 *Coal preoxidation followed by steam activation.* Approximately 20 g of anthracite was placed in a square tray, with a bed height of 3 mm. The sample was heated to 270°C, for 3 days, in an oven with forced-air convection. In a second stage, the oxidized solid was activated by steam to a burn-off of 55% (sample CMOP-A).

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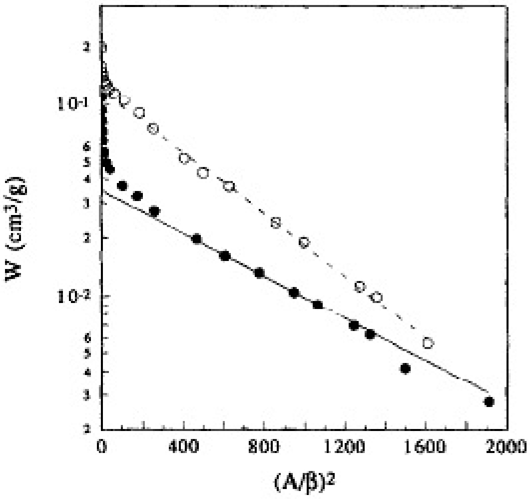

Fig. 1. D-R plot for the adsorption of CH_2Cl_2 vapour at 293 K by samples CM20 (●) and CM20-A (○).

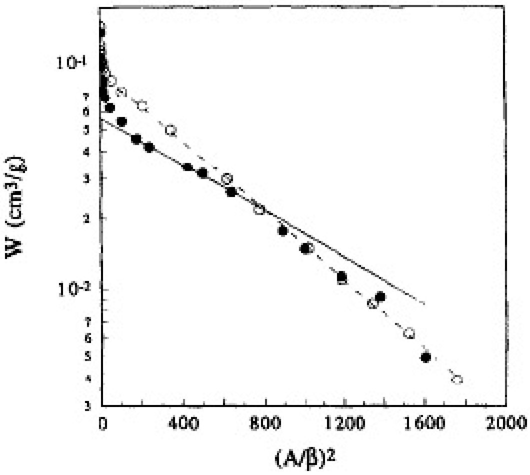

Fig. 2. D-R plot for the adsorption of CH_2Cl_2 vapour at 293 K by samples CM43 (●) and CM43-A (○). Note the downward deviation in the case of CM43.

2.2.3 *Low-temperature pretreatment followed by steam activation.* The anthracite (12 g) was treated at 450°C with a mixture of nitrogen (2.25 l/min) and air (0.25 l/min) containing water vapor produced at 70°C. We obtained samples CM20 and CM43, corresponding to weight losses of 20% and 43%. In a second stage, these solids were activated by steam, as in (2.2.1), the final degree of burn-off being 55% with respect to the original material. The resulting active carbons are CM20-A and CM43-A. We also examined an acetylene coke used in a previous study (low-temperature treatment followed by steam activation[6]), with a total mass-loss of 42%. This provided an interesting clue as to the influence of the precursor itself.

2.3 *Sample characterization*

The microporosity of the samples was characterized by the adsorption of CH_2Cl_2 vapors at 293 K and by immersion calorimetry into dichloromethane, benzene, carbon tetrachloride, tetrabutylurea, and tri-2,4-xylylphosphate at the same temperature. Information about the hydrophilic/hydrophobic character of the carbon surface was obtained from immersion in water.

The adsorption isotherms were analyzed by applying the Dubinin-Radushkevich equation (D-R)[2,10]. Classical D-R plots, shown in Figs. 1 and 2, lead to parameters W_0, the volume of the micropores and E_0, the characteristic energy. As shown elsewhere[8], the average micropore width L can be calculated from the characteristic energy E_0 (in kJ/mol) by the expression

$$L\ (\text{nm}) = 10.8/(E_0 - 11.4) \qquad (1)$$

The surface of the micropore walls was calculated as described in a previous paper[8].

As shown elsewhere[2,11], the enthalpy of immersion of a porous carbon into an organic liquid, whose vapor follows the Dubinin-Radushkevich equation, is given by

$$\Delta h_i\ (\text{J/g}) = -\beta E_0 W_0 \pi^{1/2}(1 + \alpha T)/2V_m + h_i S_e, \qquad (2)$$

where α and V_m are the thermal expansion coefficient and the molar volume of the liquid filling the micropore system, β is the affinity coefficient of the liquid, h_i represents the specific enthalpy of immersion of the open surface (Table 1), and S_e is the external surface area. For a liquid having a critical dimension L_c and acting as a molecular probe, the micropore volume $W(L_c)$ filled by it can be calculated using the expression

Table 1. Characteristics of the liquids at 293 K[2]

Liquid	L_c (nm)	α [10^{-3}] (K^{-1})	V_m (cm^3/mol)	β	$-h_i$ (J/m^2)
Dichloromethane	0.33	1.34	64.02	0.66	0.152
Benzene	0.41	1.24	88.91	1.00	0.114
Carbon tetrachloride	0.63	1.22	96.50	1.05	0.115
Tetrabutylurea	0.93	0.85	283.34	3.50	0.118
Tri-2,4-xylylphosphate	1.50	0.66	360.04	4.05	0.160

Table 2. Main characteristics of the samples obtained from Coto Minero Narcea anthracite

Sample	CM20	CM43	CM20-A	CM43-A	CM-A	CMOP-A
Burn-off (%)	20	43	55	55	55	55
W_0 (cm^3/g)	0.035	0.056	0.12	0.091	0.15	0.18
E_0 (kJ/mol)	28.0	29.1	23.2	23.8	23.6	23.4
L (nm)	0.65	0.61	0.92	0.87	0.88	0.90
S_{mi} (m^2/g)	108	184	261	209	341	400
S_{ext} (m^2/g)	39	41	31	5	60	90
S_{tot} (m^2/g)	147	225	292	214	401	490
$-\Delta h_i$ (CH_2Cl_2) (J/g)	13.5	22.3	32.8	28.3	51.9	59.4
$-\Delta h_i$ (C_6H_6) (J/g)	10.7	17.9	33.2	20.4	47.0	50.9
$-\Delta h_i$ (CCl_4) (J/g)	4.9	6.8	22.7	16.4	38.7	46.4
$-\Delta h_i$ (tetrabutylurea) (J/g)	4.6	7.1	23.4	13.9	39.6	43.2
$-\Delta h_i$ (trixylylphosphate) (J/g)	4.3	3.9	11.5	8.2	18.3	26.4
$-\Delta h_i$ (H_2O) (J/g)	10.0	19.9	11.4	9.3	16.2	18.6
$-h_i$ (H_2O) (J/m^2)	0.068	0.088	0.039	0.043	0.040	0.038

$$W(L_c) = -\frac{[\Delta h_i(\exp) - h_i S_e] \cdot 2V_m}{\beta E_0(1 + \alpha T)\sqrt{\pi}} \qquad (3)$$

E_0 is the characteristic energy obtained from the reference isotherm of a small adsorbate (in the present case, CH_2Cl_2) and L_c is the smallest micropore width accessible to the molecules of the liquid. Since E_0 itself is a function of the average micropore width, a correction should be applied to E_0 as L_c increases. However, it does not modify significantly the histograms derived from eqn (3).

The external (or non-microporous) surface area of the carbons, S_e, can be obtained either from eqn (2), provided that the term $h_i S_e$ is not too small, or by different mathematical treatments of the isotherm (decomposition[2,12] and/or the use of comparison plots based on non-porous carbons[13,14]).

3. RESULTS AND DISCUSSION

Table 2 provides an overall view of the data obtained for the various samples, with the exception of the starting material. The latter shows no open porosity, as suggested by its low enthalpy of immersion in CH_2Cl_2 and water. On the other hand, the low helium density (1.54 g/cm^3) indicates the presence of internal porosity.

As illustrated by Figs. 1 and 2, the D-R equation is followed over a wide range of relative pressures, with the exception of sample CM43. In this case, the downward deviation at low pressures probably reflects molecular sieve effects, the average micropore size being the smallest for the carbons under investigation (0.61 nm).

From the enthalpies of immersion in various organic liquids, it is possible to derive the micropore volumes $W_0(L_c)$ filled by the molecules with critical dimension L_c. Therefore, as illustrated by Fig. 3 for sample CMOP-A, $W_0(L_c)$ represents the volume of the pores with entrances wider than L_c. The data for $W_0(L_c)$ leads to the micropore distribution shown in Figs. 4–9 (histograms of $\Delta W_0/\Delta L_c$ versus L). As illustrated below, this type of representation is more convenient to compare carbons of a given series and their evolution, than the representation of $W_0(L_c)$ versus L.

As mentioned in the introduction, $W_0(L_c)$ is calculated from eqn (3) by using $E_0(CH_2Cl_2)$, and a correction must be applied to take into account the

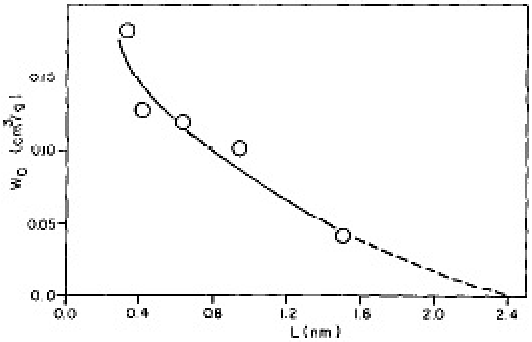

Fig. 3. The micropore volume W_0 of sample CMOP-A filled by liquids with different critical dimensions.

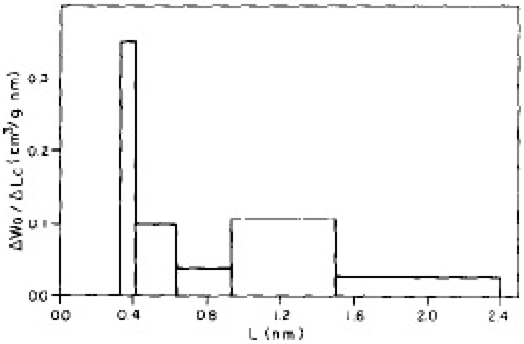

Fig. 4. The micropore distribution in carbon CM-A obtained from molecular-sieve experiments.

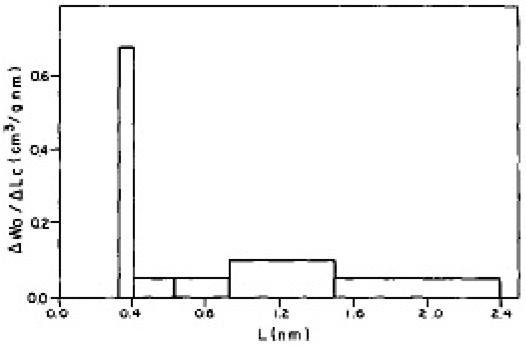

Fig. 5. The micropore distribution in carbon CMOP-A.

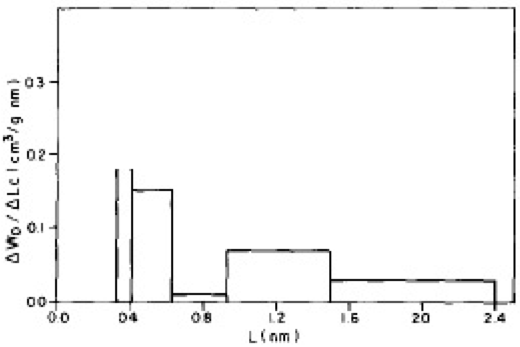

Fig. 7. The micropore distribution in carbon CM20-A.

fact that E_0 varies with the average micropore width L. However, as discussed elsewhere[15], this correction does not change the histogram significantly.

Our experiments show that the direct activation of the Asturian anthracite by steam to a burn-off of 55% (sample CM-A) has limited success. The micropore volume of 0.15 cm³/g and the profile of the pore size distribution (Fig. 4) correspond to those observed for other precursors at an early stage of activation (15% to 25% burn-off)[9,11]. The enthalpy of immersion in benzene (47.0 J/g) is also small, as it represents one fifth of the value observed by Stoeckli and Ballerini[9] for "soft" precursors activated to 50%–60% burn-off, and for which the micropore volume W_0 is around 0.40–0.50 cm³/g. The initial part of the distribution (0.35–0.55 nm) probably reflects the original microporosity, but it does not exclude this sample containing constrictions at the entrance of wider pores. As shown elsewhere[9,11], the smaller porosity tends to disappear as the degree of burn-off increases. At the same time, the carbons become heterogeneous and the average micropore width increases.

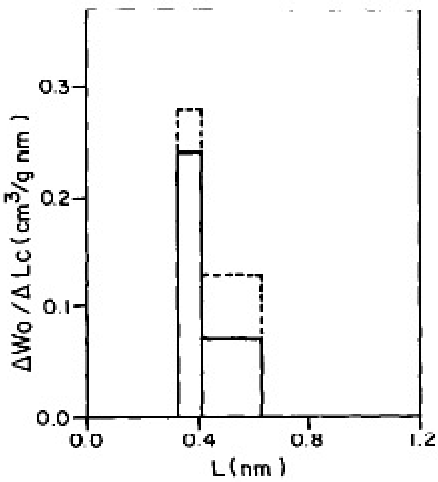

Fig. 6. The micropore distribution in carbons CM20 (——) and CM43 (– – –).

This result indicates that the internal porosity of the precursor, suggested by its low density (1.54 g/cm³), corresponds more to macro- and mesopores, than to potential micropores. The micropores of the precursor are inaccessible to the gaseous reactant, which results in development of the meso- and macroporous structure only during activation. This may explain, partly at least, the relatively important external surface, $S_e = 60$ m²/g, with respect to the internal surface area, $S_{mi} = 341$ m²/g. An initial section of the H_2O adsorption isotherm shows a Langmuir type, which indicates the presence of oxygen complexes in sample CMOP-A.

The influence of the pretreatments of the original anthracite on the final product is shown by the comparison of samples CM20-A, CM43-A, and CMOP-A with CM-A. Their common feature is the average micropore width L, around 0.9 nm, and the specific enthalpy of immersion in water, $\Delta h_i(H_2O)/S_{tot}$, which is close to 0.040 J/m².

It appears that preoxidation of the starting material in air at 270°C improves the yield of the subsequent activation by steam to a burn-off of 55% (sample CMOP-A), although it remains low. With respect to CM-A, the micropore volume W_0 and the external surface area of sample CMOP-A are respectively 20% and 30% higher. The comparison of Figs. 4 and

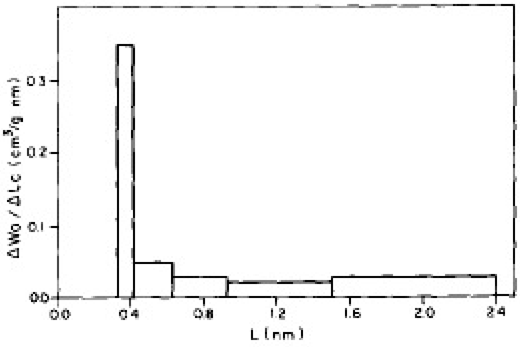

Fig. 8. The micropore distribution in carbon CM43-A.

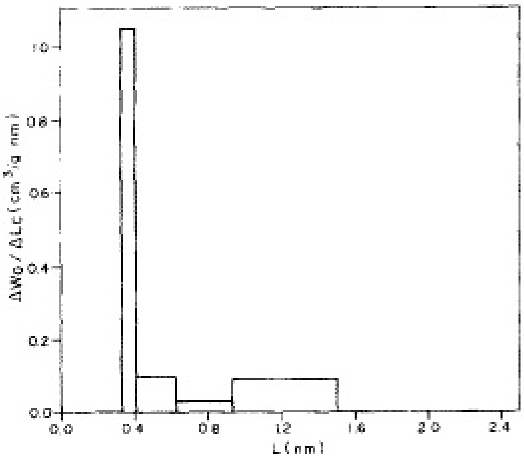

Fig. 9. The micropore distribution in an acetylene coke pretreated and subsequently activated by steam to a 42% burn-off.

5 shows that the volume of the smallest micropore ($L < 0.4$ nm) is larger, whereas the porosity in the range of 0.4 to 0.6 nm is reduced. This probably reflects the effect of the pretreatment on the anthracite, the two carbons having the same degree of burn-off. It is well known that air pretreatment of bituminous coals destroys their thermoplasticity[5], and thereby increases the volume and the accessibility of the pores of the carbonized materials. However, the advantage of air pretreatment in anthracite activation is not related to reduction of the coal plasticity. It is believed that a selective reactivity increase of the edge atoms of the microcrystallites by formation of oxygenated groups is achieved, which enhances the removal of the pore constrictions. In the case of low temperature treatment by air, nitrogen, and water, applied successfully to acetylene coke[6], the results are less encouraging for the present anthracite. The pretreatment itself produces some degree of microporosity and an external surface area (as shown in Fig. 6, samples CM20 and CM43 have a narrow microporosity, in the range of 0.35 to 0.6–0.7 nm). It is also found that the specific enthalpies of immersion in water are relatively high (0.068 and 0.088 J/m^2), which indicates the presence of oxygen complexes. As shown in Table 2, this pretreatment has an adverse effect on subsequent activation by steam to a total burn-off of 55%. The resulting micropore volumes and external surface areas of samples CM20-A and CM43-A are smaller than those of CM-A and CMOP-A, and they decrease with the extent of the pretreatment. The micropore distributions, shown in Figs. 7 vs 4 and 8 vs 5, are similar to that of sample CMOP-A, but the total micropore volumes, W_0, are smaller.

It is interesting to point out that in the case of the acetylene coke described earlier[6], the same pretreatment to a 10% weight loss, followed by activation with steam to a total burn-off of only 42%, produces better results than for the Asturian coal (sample CM20-A). One obtains $W_0 = 0.17$ cm^3/g, $E_0 = 21.3$ kJ/mol or $L = 1.10$ nm, $S_e = 101$ m^2/g, and $h_i(H_2O) = 0.043$ J/m^2. The corresponding micropore distribution, shown in Fig. 9, is similar to that observed for the anthracite (samples CM20 and CM43, shown in Fig. 6).

The present study shows that in the case of the Asturian anthracite "Coto Minero Narcea," pretreatment in air at 270°C produces a slightly better active carbon than direct activation by steam. However, the yield is generally low and the properties of the resulting carbons correspond to those of soft precursors at much smaller degrees of burn-off.

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