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Activated Carbons from Eucalyptus Wood. Influence of the Carbonization Temperature

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ABSTRACT

CO_2 activation of eucalyptus wood chars obtained at 400, 600, and 800°C has been studied. The carbonization stage develops an incipient microporosity. The micropore volume and width increase with increasing temperature. Partial gasification of these chars with CO_2 allows one to obtain activated carbons which show differences in micropore size distribution depending on the temperature at which the starting char was obtained. No significant effect on mesoporosity development was noticed whereas lower macropore volumes were obtained with activated carbons resulting from the char prepared at the highest temperature (800°C).

Key Words. Char; Activated carbon; Physical activation; Porous structure; Gas adsorption

INTRODUCTION

Exploitation of wood is a very significant activity in the Uruguayan economy, with eucalyptus the most relevant species. The development of potential applications for the residues coming from wood processing

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and forest maintenance is of great importance. One of these potential applications is the use of these residues as raw material for activated carbon production.

Activated carbons are porous solids with a high surface area obtained from carbonaceous precursors through catalytic pyrolysis (chemical activation) or carbonization followed by partial gasification with steam, CO_2, or combustion gases (physical activation). They are widely used as adsorbents in a number of processes such as air purification, recovery of gasoline from natural gas, refining of sugar, gold recovery, water and wastewater treatment, etc. (1).

Preparation of activated carbons from different lignocellulosic precursors has been reported in the literature. Rodríguez-Reinoso presented an extended report on the characterization of activated carbons prepared by CO_2 activation of almond shells and olive stones (2). That author and Linares-Solano published an interesting chapter where they compared CO_2, air, and steam activation of different lignocellulosic precursors (3). Both references include extensive bibliographies. The book of Bansal et al. provides updated information on the manufacture of activated carbons including data on the contribution of different raw materials (1). With regard to wood, López-González et al. studied the preparation of activated carbons from olive wood (4), and Blasco et al. investigated chemical activation of holm oak wood with $ZnCl_2$ and H_3PO_4 (5). In previous works we reported our results on CO_2 activation of kraft lignin (6, 7), and in a more recent paper we studied the preparation of activated carbons from eucalyptus wood using steam, CO_2, and CO_2–O_2 mixtures as activating agents (8). In this paper we study the development of porosity occurring upon CO_2 activation of three chars obtained from eucalyptus wood at different charring temperatures in order to learn about the influence of the carbonization stage on the porous structure of further activated carbons.

The applications of activated carbons are intimately related to their porous structures. For gas cleaning and air purification processes a microporous carbon with a moderate surface area is in general quite acceptable, while activated carbons for wastewater treatment require a more developed meso- and macroporosity with a higher surface area. Although carbon molecular sieves can also be prepared, the most common activation procedures lead to final products which have a relatively wide distribution of pore sizes. According to the IUPAC classification (9), pores up to 2 nm in width are called micropores, in the range of 2–50 nm are found the mesopores, and pores above this width are macropores. The relative contributions of micro-, meso-, and macroporosity in a particular activated carbon depend on the starting material, the activation procedure, and the degree of activation.

The characterization of the porous structure of activated carbons is accomplished through gas adsorption, using N_2 and CO_2 as the most frequent adsorptives. N_2 adsorption isotherms are carried out most commonly at 77 K, and in the case of CO_2 273 K and 298 K are the most frequently used temperatures. Applications of the BET equation to the 77 K N_2 adsorption isotherm allows the BET surface area to be obtained, which is also known as the apparent surface area. From the N_2 adsorption isotherm, values of the micropore volume can be obtained through the t (10) and α_s (11) methods. These values are associated with the total microporosity, whereas the volume of narrow micropores can be determined from application of the Dubunin–Radushkevich equation to the N_2 and CO_2 isotherms. The term "narrow micropore" is used to identify the lower-sized micropores where adsorption takes place by a primary filling mechanism as the result of enhancement of the adsorption energy (12). Distribution of the micropore size can be obtained by the Horvath–Kawazoe method (13) or assessed in a semiquantitative approach through adsorption with adsorptives of different dimensions like *n*-butane, benzene, cyclohexane, and isooctane, among others (2, 4). Mercury porosimetry allows the macropore and mesopore volumes to be obtained, although in the case of mesoporosity this technique does not cover the whole range and has to be combined with the N_2 adsorption isotherm. The Washburn equation applied to the mercury intrusion curves provides the pore size distribution within the porosity range covered by this technique (macro- and part of mesoporosity). The mesopore size distribution can be obtained from the Barrett et al. (14) or the Pierce (15) methods, whether applied to the desorption or the adsorption branches of the N_2 isotherm (10). A comprehensive description of the methods used for the characterization of porous solids can be found in Refs. 1, 3, 10, and 16.

In so-called physical activation, the devolatilized product resulting from a previous pyrolytic decomposition, namely the char, is gasified with steam, CO_2, or combustion gases to the required extent expressed as burn-off, a term which indicates the weight loss undergone in this stage relative to the initial char weight. The carbonization stage is important in developing the starting porous structure for further activation. As indicated before, in this work we studied the preparation of activated carbons from chars obtained from eucalyptus wood at three carbonization temperatures in order to learn about the influence of the carbonization stage.

EXPERIMENTAL

The raw material in this work was *Eucalyptus grandis* wood, used as powdered sawdust with a particle size of 0.5–0.8 mm. The sawdust was obtained from single logs of 12-year-old trees. A typical analysis of the raw material gave 14% fixed carbon, 85.7% volatile matter, and 0.3% ash content, all on a dry basis (d.b.). The ultimate analysis, dry ash-free (d.a.f.), gave 47.2% C, 6% H, 0.1% N, and 46.7% O (by difference).

The chars and activated carbons were prepared in a conventional horizontal electrically heated tube furnace. The chars were prepared under continuous N_2 flow at 100 mL (STP)/min. Three different carbonization temperatures were used, 400, 600, and 800°C, with a holding time of 2 hours and a 10°C/min heating rate to reach the operating temperature. The activation experiments were carried out at 800°C with CO_2 at a 200-mL (STP)/min flow rate. The activation temperatures were reached at a 10°C/min heating rate under a N_2 atmosphere. Once a run was completed, the furnace was cooled under N_2 flow.

The porous structures of the chars and activated carbons were evaluated by 77 K N_2 adsorption–desorption, 273 K CO_2 adsorption, and mercury porosimetry. A Quantachrome Autosorb-1 model was used to obtain the N_2 and CO_2 isotherms, and a Carlo Erba 4000 porosimeter for mercury porosimetry. The mesopore volume was obtained by combining mercury porosimetry and the N_2 adsorption isotherms. The former allows mesopore volumes larger than 3.7 nm diameter to be obtained. To complete the whole range of mesoporosity, we added the adsorbed volume derived from the N_2 isotherm up to the relative pressure corresponding to a pore diameter of 3.7 nm minus the micropore volume deduced from the *t*-method. With regard to micropore volume, we obtained three values, two from the Dubinin–Radushkevich equation applied to CO_2 and N_2 adsorption and one from the *t* method applied to the N_2 isotherm.

RESULTS AND DISCUSSION

Carbonization

Table 1 shows the yield values in the carbonization step and the proximate and ultimate analyses of the resulting chars. These are identified by the corresponding carbonization temperature followed by a C. As can be seen, devolatilization is still quite incomplete at 400°C. A substantial amount of volatilizable matter and a relatively high percentage of oxygen remain in the solid. In the 400–600°C range a significant volatile loss is observed, giving rise to a highly carbonized product.

The porous structures of the resulting chars are presented in Table 2, where for the sake of comparison we have included that of the starting wood. Wood and the 400C and 600C chars gave negligible adsorption values with N_2, which in the case of the chars may be attributed essentially to equilibrium problems. Adsorption of N_2 at 77 K in very narrow micro-

TABLE 1
Yield Values and Analysis of the Chars

	400C	600C	800C
Carbonization yield (%, d.b.)[a]	31	25	23
Proximate analysis (%, d.b.):[a]			
Fixed carbon	68.9	88.2	89.4
Volatile	30.1	10.4	8.7
Ash	1.0	1.4	1.9
Ultimate analysis (%, d.a.f.):[b]			
C	76.7	89.2	90.3
H	3.7	2.0	2.1
N	≈0.1	≈0.1	≈0.1
O (by difference)	19.5	8.5	7.5

[a] Dry basis.
[b] Dry ash-free.

pores needs very long equilibration times. With CO_2 at a substantially high temperature (273 K), adsorption becomes much faster and measurable values are obtained, indicating an incipient development of microporosity. The 800C char shows a more developed microporosity but is still within a relatively narrow micropore size range as suggested by the higher value of micropore volume obtained with CO_2 with respect to that derived from N_2 adsorption. In spite of the fact that with CO_2 at 273 K and a final pressure of 1 atm we only cover the relative pressure range up to 0.03 whereas the complete range is covered in the case of N_2 at 77 K, higher adsorption values were obtained with CO_2. This indicates that the microporosity of the 800C still remains within a low size range.

TABLE 2
Characterization of the Porous Structure of the Chars

	Wood	400C	600C	800C
BET surface area (m^2/g)	—	—	—	490
Micropore volume (DR, CO_2, cm^2/g)	—	0.13	0.19	0.26
Micropore volume (DR, N_2, cm^3/g)	—	—	—	0.21
Micropore volume (*t* method, N_2, cm^3/g)	—	—	—	0.21
Mesopore volume (cm^3/g)	0.03	0.03	0.03	0.05
Macropore volume (cm^3/g)	0.41	0.87	1.01	0.92

Carbonization does not seem to improve the mesoporosity of the chars with respect to that of the initial wood, whereas a substantial increase of macroporosity is observed.

As a general conclusion, carbonization creates a more significant and widely distributed incipient microporosity with increasing temperature, although the microporosity remains within a narrow-sized micropore range even at 800°C. A significant development of macroporosity is obtained upon carbonization.

Activation

In order to examine the evolution of the porous structure of the three chars upon activation, in each case we chose an activated carbon corresponding to a relatively low burn-off level (25–30%) and another obtained at a higher burn-off (in the vicinity of 50%). We identify each activated carbon by using the nomenclature of the starting char followed by the burn-off value as a percentage (for example, 600C26 indicates the activated carbon obtained at 26% burn-off from the 600°C char).

During the time necessary to reach the activation temperature (800°C), the chars undergo a weight loss which is much more significant in the case of the 400C char due to its substantially higher volatile matter content. The weight loss during the heating step preceding CO_2 gasification was 8% for the 800C char, 13% for the 600C, and 32.6% for the 400C as determined in blank experiments in which the chars were heated at 10°C/min under N_2 atmosphere until the 800°C activation temperature was reached. Then, in the activation runs the burn-off values were calculated by taking the weight at the end of the heating stage as the initial char weight.

Figure 1 shows the extent of burn-off versus activation time. As can be seen, a higher carbonization temperature leads to a less reactive char. This is a well-known effect which has been widely reported in the literature for many other carbon precursors (17, 18).

Combining the definitions of burn-off and reactivity:

$$\text{Burn-off:} \qquad X = \frac{w_0 - w}{w_0}$$

$$\text{Reactivity:} \qquad r = -\frac{1}{w}\frac{dw}{dt}$$

the following expression can be easily deduced:

$$r = \frac{1}{1 - X}\frac{dX}{dt}$$

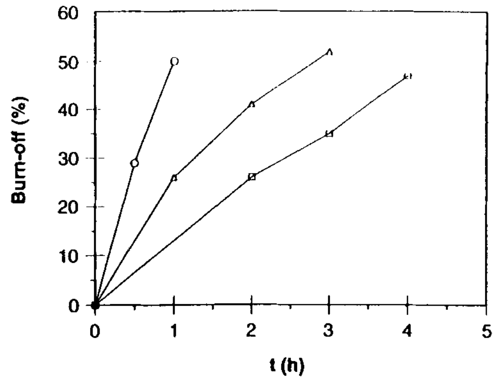

FIG. 1 Burn-off versus time for CO_2 activation at 800°C of different chars: 400C (○), 600C (△), and 800C (□).

where w represents the solid weight remaining at time t and w_0 is the initial char weight.

By using this expression, values of the apparent reactivity can be deduced from Fig. 1. These values always fall below the corresponding values of intrinsic reactivity obtained from TG experiments under kinetic control conditions reported in a previous work (19). Thus, in our experimental system, activation takes place under mass-transfer limitations which favor the development of meso- and macroporosity.

Figure 2 shows the 77 K N_2 adsorption–desorption isotherms of selected activated carbons obtained by CO_2-partial gasification of the 400, 600, and 800°C chars (Figs. 2a, 2b, and 2c, respectively). In the three cases, as expected, the micropore volume increases with increasing burn-off, as indicated by the amount of nitrogen adsorbed at low relative pressure. Increasing the burn-off produces more mesoporosity as revealed by the steeper slope of the curves within the intermediate to high relative pressures range. Hysteresis loops are observed in all the cases as the result of capillary condensation in the mesopores; this hysteresis becomes more pronounced at increasing burn-off.

Figure 3 shows the porosity distribution of the activated carbons. The most important difference is the lower total pore volume of the 800C series as the result of a lower macropore volume. The lower intrinsic reactivity of carbons derived from the 800C char leads to a less pronounced effect of diffusional limitations in the gasification process, which gives rise to a

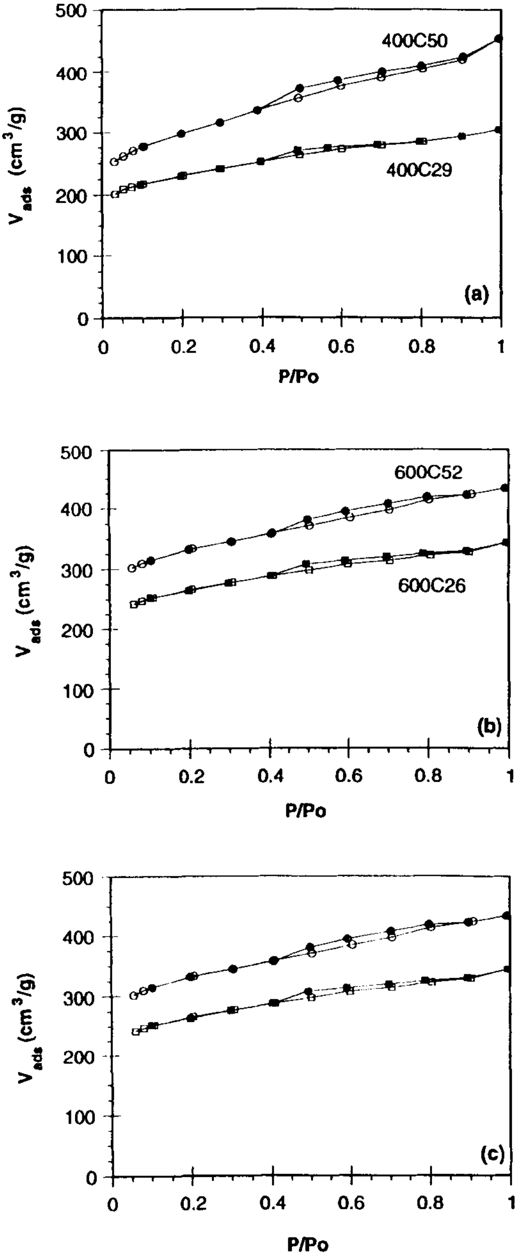

FIG. 2 N_2 adsorption–desorption isotherms of selected CO_2-activated carbons. Open symbols indicate adsorption and closed symbols indicate desorption.

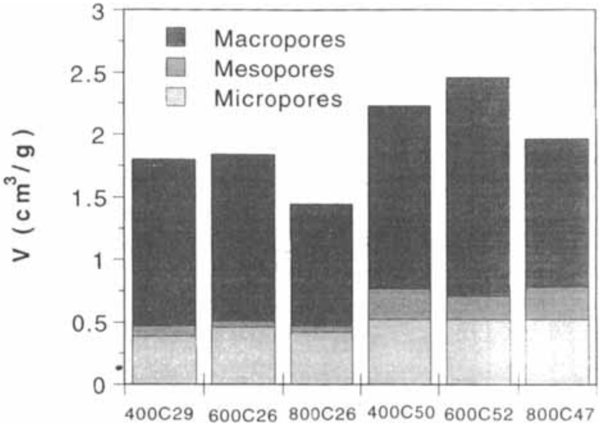

FIG. 3 Distribution of porosity in selected CO_2-activated carbons.

porous structure where the relative contribution of macroporosity is lower and that of microporosity is higher.

With regard to the microporosity, although essentially similar values of total micropore volume are observed in the three carbon series at comparable burn-off levels, the corresponding size distributions show some important differences, as can be seen in Fig. 4. The activated carbons obtained from the lower temperature char (400°C) exhibit a micropore distribution centered toward higher size values than the two other series resulting from the 600 and 800°C chars. As indicated before, the carbons from the 400C series are more reactive. Thus, internal diffusion limitations are more significant in the gasification process and development of microporosity occurs mainly through widening of the more accessible parts of existing micropores rather than the creation of new ones or opening of the internal network through the removal of constrictions.

Table 3 reports the BET surface area. It can be seen that carbons of the 400C series show somewhat lower values consistent with the aforementioned wider micropore size of these carbons. At comparable burn-off levels the activated carbons reported in this work show BET surface area values fairly close to the ones obtained from other lignocellulosic raw materials like olive stone and almond shells (3), and superior to those obtained from some other wood species like olive (4). When compared in terms of porosity distribution, the activated carbons obtained from eucalyptus wood have a more developed mesoporous structure and a substan-

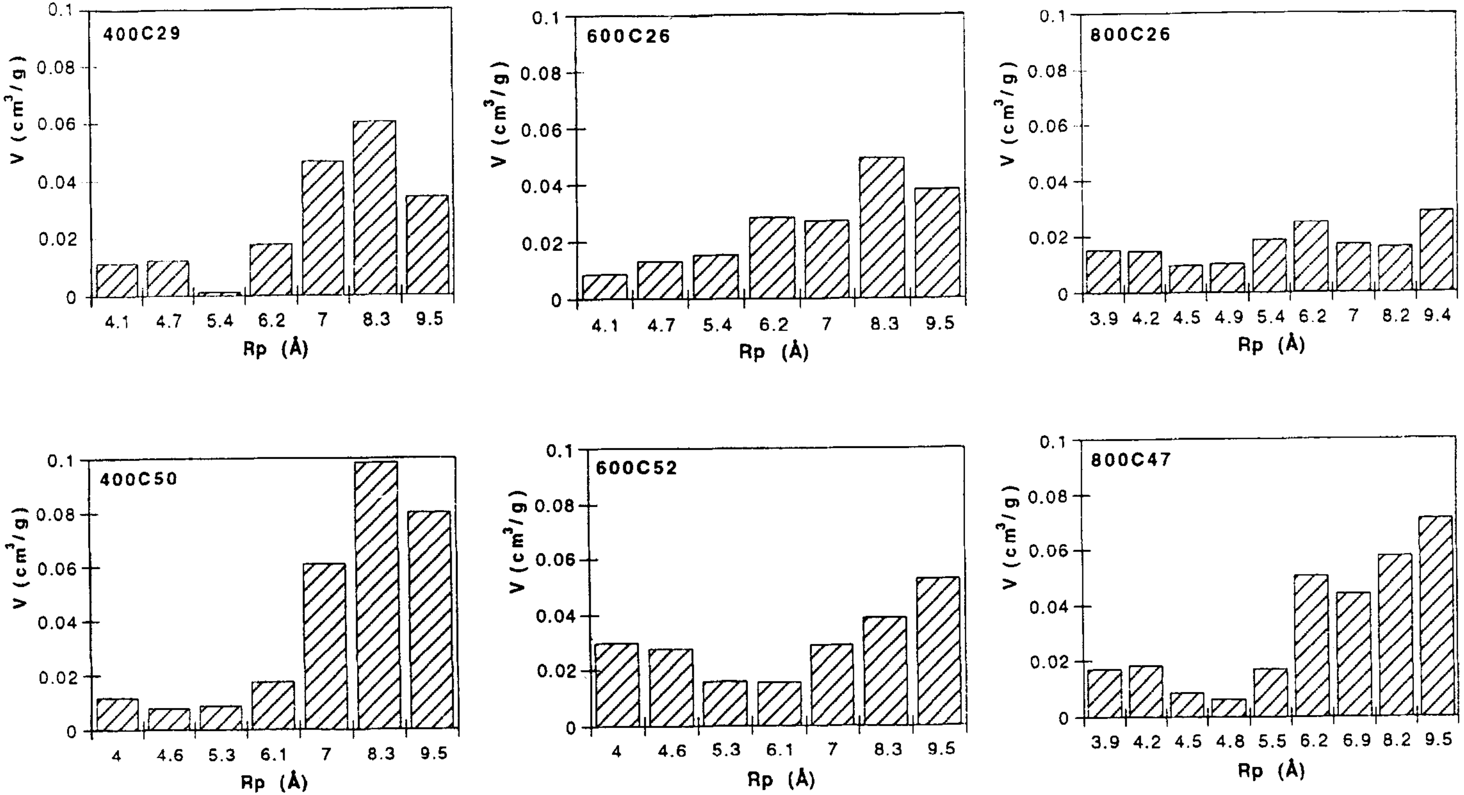

FIG. 4 Micropore size distribution of CO_2-activated carbons.

TABLE 3
Values of the BET Surface Area of CO_2-Activated Carbons

Activated carbon	BET surface area (m^2/g)
400C29	840
600C26	960
800C26	970
400C50	1090
600C52	1250
800C47	1190

tially higher macroporosity, both interesting features for liquid-phase applications like water and wastewater treatment.

CONCLUSION

The temperature of carbonization of eucalyptus wood within the range investigated (400–800°C) shows some effect on the subsequent development of porosity upon CO_2 gasification. Differences in micropore size distribution have been noticed, with the lower carbonization temperature giving rise to wider micropores in the resulting activated carbons. The development of mesoporosity does not seem to be particularly affected by the temperature of the carbonization step, whereas significantly lower values of total macropore volume are found for activated carbons obtained from the highest temperature char (800°C). These differences in porous structure do not seem to be highly relevant from a practical point of view, although they may have some effects in liquid-phase applications.

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