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EFFECT OF STEAM AND CARBON DIOXIDE ACTIVATION IN THE MICROPORE SIZE DISTRIBUTION OF ACTIVATED CARBON

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Abstract—This work presents the different effects of steam and carbon dioxide activation of a char in both the development of microporosity and the micropore size distribution using immersion microcalorimetry of liquids with different molecular size (benzene, 2,2 dimethylbutane, iso-octane and α -pinene). The study has been carried out with three series of carbons, two of them prepared by steam activation and the third one by carbon dioxide activation, covering a wide range of burn-off (8–70%). The experimental results show that carbon dioxide activation mainly causes the creation of microporosity. However, steam activation widens the microporosity as from the early stages of the activation process, the resulting activated carbons exhibiting a lower micropore volume. The different porous structures produced by both activating agents is related to the oxygen surface groups in the carbon, as measured by temperature programmed desorption (TPD). Activation by carbon dioxide creates not only a larger number of groups evolving as CO but also these groups are thermally more stable than those produced by steam activation. Copyright © 1996 Elsevier Science Ltd

Key Words—Activated carbon, CO₂ activation, steam activation, microporosity, immersion microcalorimetry.

1. INTRODUCTION

Physical activation of lignocellulosic chars with steam or carbon dioxide is a conventional manufacturing process of activated carbon [1]. Since the molecular size and reactivity of both activating agents with the char is different [2,3], one could expect some differences in the porosity developed. This has been shown in a previous paper [4] when analyzing the evolution of porosity in a series of activated carbons prepared from a common precursor, olive stones. The analysis of creation or destruction of porosity upon activation (measured by adsorption of N₂ at 77 K and CO₂ at 273 K, and mercury porosimetry) showed that the largest increases in porosity are produced in the early stages of the activation process, being caused by the opening of constrictions in the char porosity and the development of new interconnecting pores. Burn-off increases the widening of existing micropores, and external burning of the particle outweighs the creation of new porosity, resulting in a net destruction of porosity, especially above 40–50% burn-off.

Although the above behavior is, in general terms, common to both activating agents, the way in which microporosity is developed differs from one to another. In the early stages of the process, up to about 20% burn-off, carbon dioxide develops narrow micropores (which can be measured by adsorption of CO₂ at 273 K), whereas steam widens the initial microporosity from the beginning of the reaction, the final result being a carbon with lower micropore

volume. The widening of microporosity is especially noticeable at high burn-offs, at which the activated carbons prepared with steam exhibit larger meso and macropore volumes than those prepared with carbon dioxide.

The objective of this work is to make a more in-depth analysis of the different effects caused by activation with carbon dioxide and steam of a common char in the development of microporosity. For this reason the micropore size distribution of the resulting activated carbons has been determined by immersion microcalorimetry of liquids with different molecular dimensions. This technique, widely used to characterize the surface properties of solids [5,6], yields results similar to physical adsorption of vapors, but is simpler and faster [7]. The type and amount of oxygen surface groups (evolved as CO and CO₂ in TPD experiments) of the activated carbons prepared with steam and carbon dioxide have also been analyzed as a function of burn-off.

2. EXPERIMENTAL

The three series of activated carbons were prepared from a common char, prepared by the carbonization of olive stones (nitrogen flow of 80 ml min⁻¹; 850°C; heating rate, 5°C min⁻¹; residence time 2 hours). A common horizontal furnace was used for the different activation processes, defined as follows:

- Series D: a flow of CO₂ (80 ml min⁻¹) at 825°C. Burn-off range: 8–70%;
- Series W: a flow of pure water vapor

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- (100 ml min⁻¹) at 800°C. Burn-off range: 10–71%;
- Series H: a flow of pure water vapor (100 ml min⁻¹) at 750°C. Burn-off range: 8–74%.

The activation temperature of series H was selected to reach the same gasification rate as in series D (about 0.01 h⁻¹); the rate was around 0.021 h⁻¹ for series W. Further experimental details can be found in reference [4]. The nomenclature of all activated carbons includes the letter for the series and the burn-off reached.

The enthalpy of immersion at 30°C for the activated carbons and the carbon black used as reference (V3G) were determined in a Tian-Calvet differential microcalorimeter (Setaram, C80D). The sample (about 0.15 g) was placed into a glass bulb with a brittle end and outgassed at 250°C and 10⁻⁵ torr for 4 hours. Then, the bulb was sealed and placed in the interior of the microcalorimeter cell containing 7 ml of the liquid. Once the thermal equilibrium was reached in the calorimeter block, the brittle end was broken and the liquid allowed to enter into the bulb and wet the carbon sample, the heat flow evolution being monitored as a function of time. Thermal effects related to the fracture of the brittle end and the evaporation of the liquid to fill the empty volume of the bulb with the vapor at the corresponding vapor pressure were calibrated by using empty bulbs of different volume. The liquids used to determine the heats of immersion, benzene (C₆H₆), 2,2 dimethylbutane (2,2-DMB), iso-octane and α -pinene, were of a minimum 99% purity. The properties of these liquids have already been described [1,7]; the minimum dimensions (nm) used were: benzene (0.37), 2,2-dimethylbutane (0.56), iso-octane (0.59) [8] and α -pinene (0.70) [5].

The volume of micropores has been calculated using the equation proposed by Stoeckli and Kraehenbuehl [9] which relates the micropore filling theory of Dubinin [10] with the enthalpy of immersion:

$$-\Delta H_i \text{ (J g}^{-1}\text{)} = \frac{[\beta E_0 W_0 (1 + \alpha T) \pi^{1/2}]}{[2 V_m]} - h_i S_{ext} \quad (1)$$

In this equation α and V_m are the thermal coefficient of expansion and the molar volume of the liquid, respectively, and $-h_i$ is the specific enthalpy of wetting (J m⁻²) of the external surface area. The application of this equation requires the knowledge of the characteristic adsorption energy E_0 and the external surface area S_{ext} of the carbon. The former has been calculated from the adsorption isotherms of CO₂ at 273 K, whereas the external surface area has been calculated by application of the α_s -method [11] to the adsorption isotherms of N₂ at 77 K, using as standard isotherm the one corresponding to a non-porous carbon of the same chemical nature [12].

The oxygen surface groups of the carbons has been analyzed by TPD. 0.15 g of the carbon were placed

into a vertical quartz reactor and heat treated at 10°C min⁻¹ from room temperature up to 1050°C under a flow of helium, and the gases evolved were analyzed in a quadrupole mass spectrometer (Balzers, MSC 200) connected to the reactor. The amounts of CO and CO₂ evolved during the heat treatment were obtained by integration of the desorption profiles. Both CaC₂O₄·H₂O and known mixtures of both gases were used as references for the calibration of the spectrometer.

3. RESULTS AND DISCUSSION

3.1 Micropore size distribution

Table 1 includes the results of the enthalpy of immersion for the three series of activated carbons and the carbon black used as reference, and shows that the values are a function of both the carbon and the liquid used. For a given series, the enthalpy of immersion for benzene (the liquid with the smallest dimensions) increases with burn-off as expected, since there is a continuous increase in the volume of micropores. If carbons with similar burn-off are compared, the sequence of enthalpy of immersions is D > W > H, thus indicating that the microporosity developed by carbon dioxide activation is higher than in the two series activated with steam. The same sequence is found for the rest of the liquids, provided the burn-off reached is larger than 30%, but not for lower burn-offs. Since the enthalpy of immersion is also a function of the liquid (for instance, the difference in enthalpy is up to 10% for the non porous carbon V3G), the comparison of the three series will be based on the volume of micropores accessible to the liquid deduced from the enthalpy values given in Table 1.

Figure 1 includes the micropore size distributions — expressed as volume of micropores versus the minimum dimension [8] of the molecules — for the three series of activated carbons. The values of micropore volume deduced from the adsorption of N₂ at 77 K has also been included. For a given series,

Table 1. Experimental enthalpies of immersion (J g⁻¹) of activated carbons and V3G

Carbon	Benzene	2,2-DMB	iso-octane	α -pinene
V3G	7.1	6.6	6.8	7.3
D-8	85.8	12.5	7.2	7.6
D-19	104.3	57.7	50.7	25.4
D-34	126.9	102.0	101.6	101.6
D-52	159.6	126.9	136.1	147.8
D-70	176.7	144.5	160.0	202
W-10	82.1	16.8	12.7	8.1
W-23	105.2	81.1	81.3	59.7
W-41	137.3	109.2	120.4	143.3
W-58	145.7	122.3	134.1	156.2
W-71	162.0	133.8	146.7	195.1
H-8	81	12.9	6.1	5.5
H-22	109.9	94.9	91.7	77.2
H-37	119.1	99.9	104.0	104.3
H-52	130.0	107.6	120.6	122.7
H-74	134.3	110.1	122.3	135.4

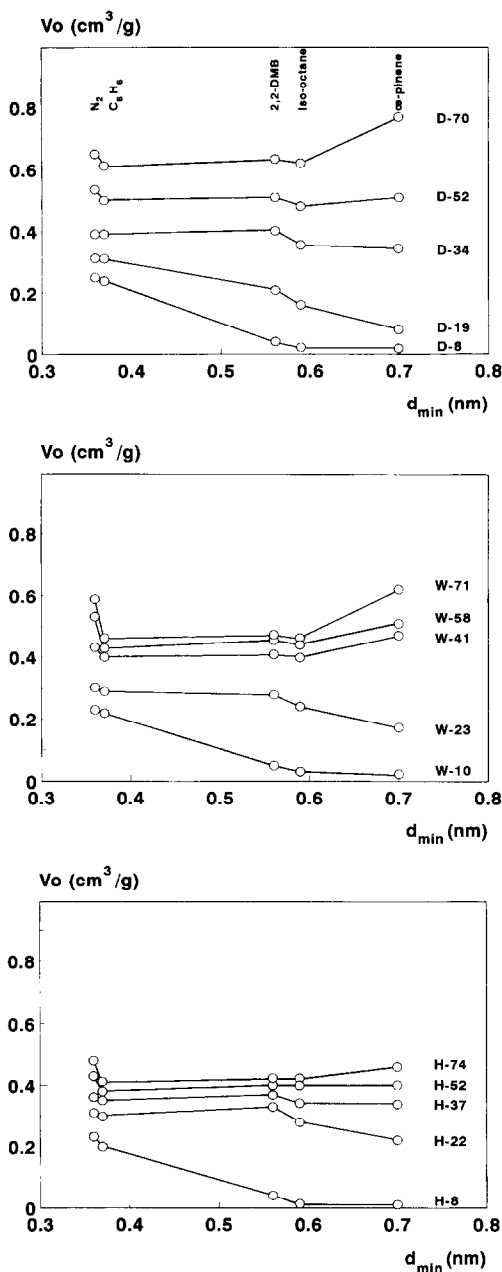


Fig. 1. Micropore size distribution deduced from physical adsorption (N_2) and immersion calorimetry (benzene, 2,2 dimethylbutane, iso-octane, and α -pinene) for series D, W and H.

for instance series D, there is an increase in the volume of micropores with increasing activation. However, such increase is gradual for small molecules such as nitrogen and benzene but not for larger molecules such as iso-octane and α -pinene, for which there is a fast increase in the first stages of activation. Since at low burn-off the order of volume accessible to the liquids is benzene > 2,2 dimethylbutane > iso-octane > α -pinene, which corresponds well with the increase in minimum molecular dimension and molecular volume, one can deduce that carbons with low burn-off (D-8, and to a lower extent, D-19) exhibit

some molecular sieving character for around 0.5–0.6 nm, which disappears at larger burn-offs.

The above comments apply to carbons of series W and H (Fig. 1b and Fig. 1c), although two main differences must be emphasized:

- The larger widening of microporosity produced by steam in respect to carbon dioxide for carbons with 19–23% burn-off. Thus, while some differences among the pore volume accessible to benzene and 2,2 dimethylbutane are still appreciable in carbon D-19 (activated with carbon dioxide), such differences are not seen in carbons H-22 and W-23 (activated with steam).
- The increase in micropore volume with burn-off above 40% for carbons activated in steam (series W and H) is less than for the series D, which was activated in carbon dioxide. This different microporosity development is characteristic of the activating agent and independent of the activation temperature, since the behavior of series W and H is similar.

In order to analyze the creation or destruction of pores during activation it is convenient to use the results expressed per unit mass of the starting char. Figure 2(a) includes the micropore volumes deduced from the immersion of benzene and Fig. 2(b) the volumes of meso and macropores deduced from mercury porosimetry, V_{Hg} [4]. Only in the early stages of the process is there a net development of micropores (in part, as a result of destruction of the molecular sieving effect shown by the char), the widening of micropores and external burning of the particle becoming more important at burn-offs larger than 40% for series D and W, and larger than 20% for series H. The difference in burn-off at which the maximum micropore volume is produced when steam is used as activating agent (series H and W) has been described previously [4] and was attributed to the fact that the inhibiting effect of hydrogen (produced in the $C-H_2O$ reaction) is less effective with increasing temperature [13], thus favoring the internal burning of the particle rather than external burning. On the other hand, there is a larger creation of microporosity when activation is carried out with carbon dioxide rather than steam, thus confirming the results obtained previously by adsorption of N_2 at 77 K and CO_2 at 273 K [4].

Figure 2(b) shows that the maximum development of large size porosity takes place for all series at burn-offs similar to those shown in Fig. 2(a). This means that: (i) at low burn-offs the development of microporosity is accompanied by the development of meso and macroporosity, and (ii) at high burn-offs the external burning of the particles makes all pore volumes decrease, especially V_{Hg} for series D, since for series W and H the loss of mesoporosity and macroporosity is partly compensated by the widening of micropores. It is important to note the relationship between Figs. 2(a) and (b), since up to about 40%

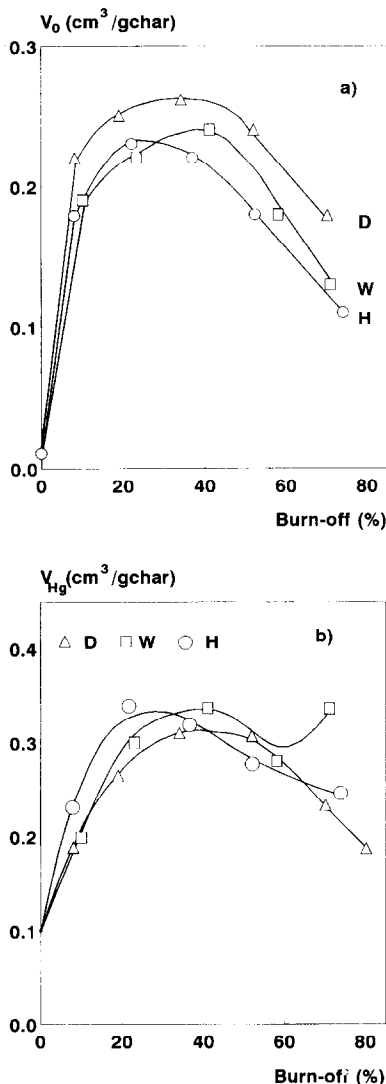


Fig. 2. Evolution of pore volume (per gram of char) as a function of burn-off. (a) Micropores from benzene immersion; (b) meso and macropores from mercury porosimetry.

burn-off, series D exhibits larger values of micropore volume than series W and H, and above 40% burn-off series W and H exhibit larger values of V_{Hg} than series D, thus showing the larger widening of microporosity produced by steam.

The explanation of the different porous structure of activated carbons produced by the two activating agents on the same char is not simple. Considering the porous structure of the char, which as shown above is constituted by narrow microporosity and constrictions caused by the solid tars produced during pyrolysis of the precursor (olive stones), one could expect that the smallest molecule — water — could have a more favorable access to the entrance of the micropores. Additionally, the effective diffusivity of water vapor through the porous network of the particle is larger than that of carbon dioxide. In other words, for a common char with a given porosity, one would expect a larger development of microporosity

for water vapor, as suggested by Wigmans [3]. However, as shown in this and previous works [4] the experimental results show the opposite effect.

Since the gasification rate is relatively low in the three series, it is possible that the nature and amount of oxygen surface groups generated by each activating agent play an important role in the development of porosity. In order to measure these surface groups, TPD experiments were carried out with all activated carbons.

3.2 Oxygen surface groups

When a carbon is heat treated under a flow of inert gas, the oxygen surface groups decompose at different temperatures, originating CO and CO_2 . The relationship between the products evolved and the type of functional groups (carbonyl, carboxylic, phenolic, etc.) has been discussed by Barton *et al.* [14] and Tremblay *et al.* [15].

Figure 3 includes the CO and CO_2 profiles for three comparable carbons of series D, W and H. As expected in activated carbons, the groups decomposing to CO appear at higher temperatures than those decomposing to CO_2 . The analysis of the CO_2 profiles does not show any relationship between burn-off of the carbon and the temperature and height of the peaks; also there are not significant differences among the series activated with carbon dioxide and steam. Since the activation temperature is much higher than the temperature for the decomposition to CO_2 , these groups might possibly be due to the chemisorption of oxygen after activation and not to the formation during the reaction of the carbon with the activating agents. The CO profiles show only one peak at a temperature (T_{max}) independent of burn-off. Burn-off only affects the peak height and, consequently, the concentration of surface groups. It is important to note that T_{max} (885°C) is identical for series W and H, and somewhat lower than in series D (920°C). Taking into account that the activation temperature with steam is different in the two series, one can deduce that under the experimental conditions used the type of oxygen surface groups is characteristic of

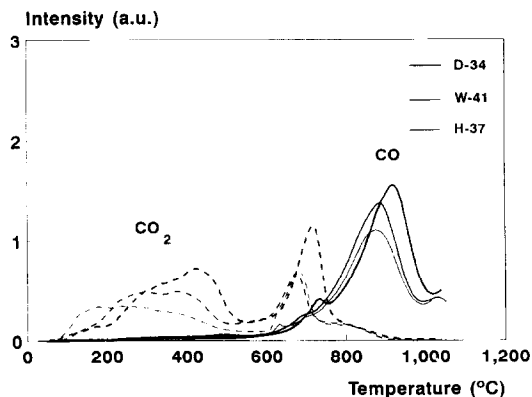


Fig. 3. CO and CO_2 profiles for some activated carbons.

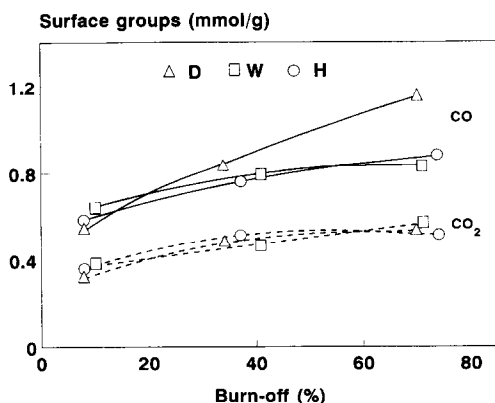


Fig. 4. Evolution of CO and CO₂ surface groups as a function of burn-off.

the activating agent, those produced when the agent is carbon dioxide being more stable.

Figure 4 includes plots of the amounts of CO and CO₂ for carbons with low, medium and high burn-off of the three series. These values are relatively low, as is typical in carbons prepared at high temperature [16], and they increase with increasing degree of activation [17]. However, there is an important difference in the evolution of CO and CO₂: whereas the amount of the latter slightly increases with burn-off for all series, the amount of CO evolved is higher and is also a function of the activating agent, as already noted in the temperature of the peaks shown in Fig. 3. On the other hand, the increase in the amounts of CO evolved with burn-off above 40% for carbons activated in steam (series W and H), is less than for the series D. This behavior is similar to that described above for the evolution of microporosity: higher volume of micropores and faster increase in this volume when activation was carried out with carbon dioxide.

The similarity in behavior for the evolution of microporosity and oxygen surface groups should be expected since in microporous carbons, most of the surface is formed by the walls of the micropores and consequently, the larger the volume of micropores the greater will be the number of active sites for reaction, and the larger the amount of surface groups.

The fact that the microporosity and the amount of oxygen surface groups only increase slightly in the series activated with steam — even though a considerable amount of carbon atoms are being removed — must mean that activation is producing a change from micro- to meso- and macropores by removal of carbon atoms mainly from the entrance of the micropores. When activation is carried out with carbon dioxide, the microporosity and the amount of oxygen surface groups also increase in a parallel way, although more active sites are created during activation. In this case, the reaction is more localized in the interior of the micropores, and the amount of surface groups formed will be larger than when

activating with steam, since a larger micropore volume means a larger surface area available for creation of active sites.

4. CONCLUSIONS

Carbon dioxide and steam develop the microporosity initially present in the char, but with different effects. Activated carbons prepared by carbon dioxide activation exhibit a larger micropore volume and a narrower micropore size distribution than those prepared by steam activation. For carbons with low burn-off (<10%), there is a molecular sieving effect for 0.5–0.6 nm, but for carbons with around 20% burn-off the molecular sieving is much lower for carbons prepared by steam activation. In any case, micropore widening is the predominant effect of activation with steam even as from the early stages of the process. The larger development of narrow microporosity produced by carbon dioxide and the widening produced by steam are paralleled by the evolution of oxygen surface groups decomposing in TPD experiments as CO.

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