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The Effect of Gasification by Air (623 K) or CO_2 (1098 K) in the Development of Microporosity in Activated Carbons

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The adsorption of nitrogen, benzene, n-butane, iso-butane, 2,2-dimethylbutane and iso-octane has been carried out in two series of activated carbons, one prepared by activation of carbonized olive stones in CO_2 at 1098 K and another by reacting activated carbon (of the same origin) in air at 623 K. Carbons of the former series have narrower microporosity which is gradually developed upon activation, whereas air produces a more considerable widening of the microporosity. Carbons with low burn-off exhibit a molecular sieving effect toward iso-octane (minimum dimension, 0.59 nm). For carbons with medium burn-off, in which molecular sieving is not exhibited (34–52% burn-off), the characteristic curve is coincident for all adsorbates, but for larger burn-off the N_2 data do not fit the characteristic curve. In the case of the latter carbons, with wide and heterogeneous microporosity, only the micropore volume deduced from the higher relative pressure branch of the Dubinin–Radushkevich plot or characteristic curve for N_2 at 77 K (usually in the relative pressure range 0.05–0.25) is coincident with that obtained from the hydrocarbons.

The use of an activated carbon in a given process is conditioned by its adsorptive properties, which are basically a function of the porous structure. Therefore, the tailoring of the porosity of activated carbons for use in different types of applications is an aim of many research laboratories. CO_2 is a convenient activating agent, especially on the laboratory scale, and as such has been described in previous works[1, 2] as producing activated carbons with a wide range of adsorptive properties. However, activated carbons may be used or recycled in contact with air at moderate temperatures and these conditions may gradually modify their porous structure.

According to these considerations it is of interest to study the evolution of the porous structure of a series of carbons prepared by activation in CO_2 as a function of burn-off and to compare it with the evolution observed in another series of activated carbons with similar burn-off but obtained by reaction in air at 623 K.

The two series of activated carbons cover a wide range of burn-off, including samples with a very narrow microporosity (showing a molecular sieving effect) and superactivated carbons (with a wide micropore size distribution). Consequently, the carbons of the two series offer the possibility of a complete analysis of the Dubinin–Radushkevich (DR) equation applied to the adsorption of different hydrocarbons, showing the possible limitations and their relationship with the evolution in the size of the microporosity.

Experimental

The two series of carbons have been described in detail previously[3, 4] and have been prepared from olive stones carbonized in nitrogen for 2 h at 1123 K. The carbonized material was activated in a flow of carbon dioxide at 1098 K for different periods of time to yield six activated carbons (series D) with burn-off ranging from 8 to 80%. Another

Table 1. Overall burn-off percentage and nomenclature of samples

CO_2 series		air series		
			burn-off (%)	
nomenclature	burn-off (%)	nomenclature	in air	global
D-8	8	B-0	—	32
D-19	19	B-5	5	36
D-34	34	B-31	31	53
D-52	52	B-52	52	67
D-70	70	B-71	71	80
D-80	80			

activated carbon prepared similarly (with a 32% burn-off) was reacted with dry air at 623 K to yield four carbons (series B) with overall (CO_2 plus air) burn-off similar to carbons of series D, as detailed in table 1. However, to maintain the same nomenclature used in previous papers, the percentage burn-off for series B will be referred only to air gasification.

The adsorption of hydrocarbons (benzene, n-butane, iso-butane, 2,2-dimethylbutane and iso-octane) was carried out at 298 K in a grease-free gravimetric system using silica spring balances and a Baratron (MKS) pressure transducer; the adsorbates were all of a minimum 99% purity and where possible were further purified by the freeze–thaw technique. Equilibrium time was short for most of the samples and a minimum of 1 h was allowed for each experimental point; however, for carbons D-8 and D-19 the time required for equilibrium was longer, especially for the largest molecules (*ca.* 4 days for each experimental point in the case of iso-octane). The physical parameters for all hydrocarbons have been given previously;[5] the minimum dimensions (nm) used were: N_2 (0.30), benzene (0.37), n-butane (0.43), iso-butane (0.51), 2,2-dimethylbutane (0.56) and iso-octane (0.59).

The results obtained with the hydrocarbons will be compared with those obtained for the same carbons but using other adsorptives.[3, 6]

Results and Discussion

The reaction of an activated carbon with air at 623 K or CO_2 at 1098 K leads to changes in the porous structure which largely depend on the reactant gas. The development of the adsorptive capacity and its evolution as a function of burn-off are significantly different for both gases:[3–6] it increases continuously in series D for increasing burn-off, but there is a decrease in series B after 31% burn-off in air. In general terms, carbons of series D have a larger adsorptive capacity than the equivalent (comparable burn-off) of series B.

A method of comparing the evolution of porosity in the two series would be to calculate the percentages of pore volume filled at four well defined relative pressures (0.02, 0.1, 0.3 and 0.95) in respect to the amount adsorbed at saturation ($P/P_0 = 1$); such percentages have been plotted as histograms in fig. 1 for carbons of both series, the adsorbate being benzene. It is clearly shown that carbons of series D are much more microporous than those of series B, the differences increasing with burn-off; in fact, carbons of series D have a minimum of 65% of the pore volume filled at $P/P_0 = 0.02$ (this is a very large percentage considering that it is referred to the total volume at saturation), whereas in series B this minimum is 38%. The different sequence in both

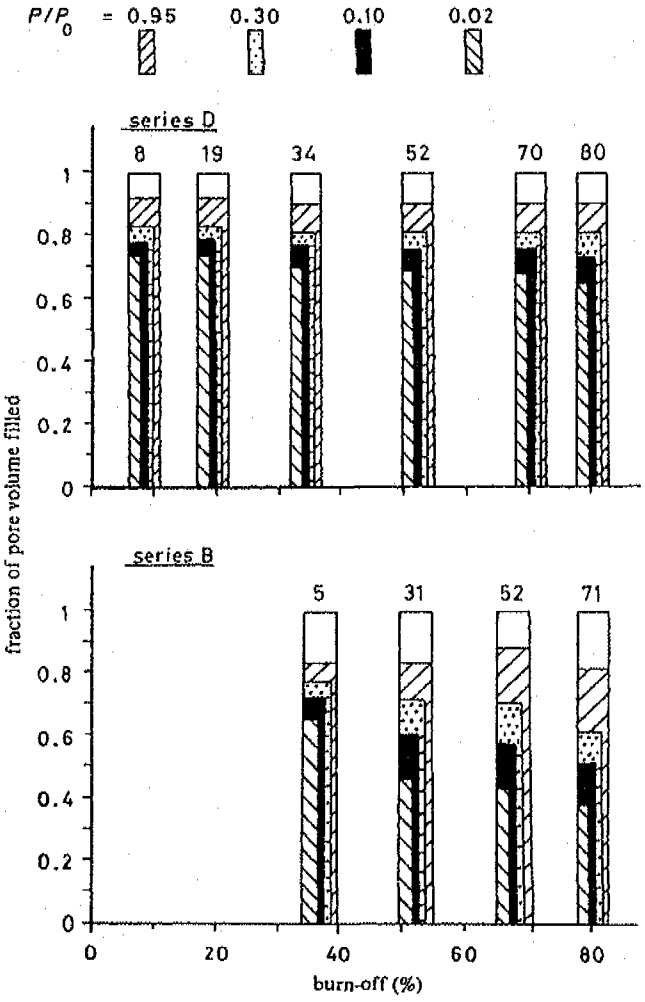

Fig. 1. Fraction of pore volume filled with benzene at different relative pressures with respect to saturation (see table 1 for details of samples).

series indicates that air produces a more important destruction of the micro- and meso-porosity leading to a more considerable change in the pore size distribution.

The reaction in CO_2 (series D) produces an almost uniform evolution in the contribution of the different types of porosity for increasing activation, although the more important changes take place below $P/P_0 = 0.3$ (in other words, meso- and macro-porosity, with *ca.* 20% of the total porosity, remain almost constant throughout the series). A more noticeable decrease upon gasification is observed in the narrow microporosity which is filled below $P/P_0 = 0.02$.

The reaction in air (series B) leads to a different evolution of the pore size distribution. Although carbon B-5 exhibits a relatively similar histogram to that of carbon D-34 (as expected because its low air burn-off), the differences are very marked for higher burn-off. There is a considerable decrease in the contribution of the microporosity (especially that of narrow microporosity) and a subsequent increase in the contribution of meso- and macro-porosity (it was almost constant in series D). Consequently, the reaction in air

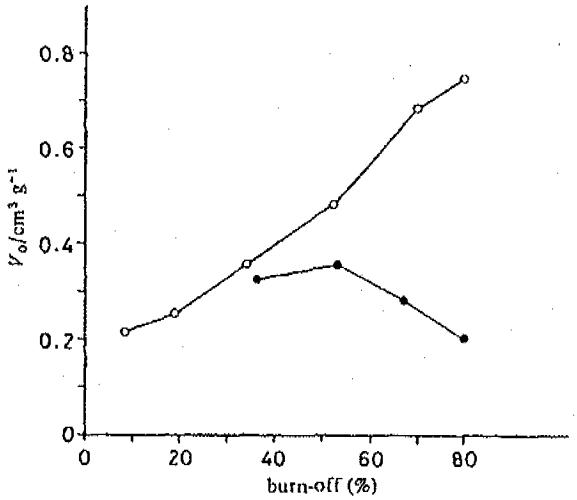

Fig. 2. Micropore volumes (cm^3 g^{-1}) from benzene adsorption as a function of the overall percentage burn-off: ○, D series; ●, B series.

produces, basically, a considerable widening of the microporosity, so that for the larger burn-off only 38% of the pore volume is filled below $P/P_0 = 0.02$.

A more quantitative analysis of the adsorption isotherms has been undertaken using the micropore volume filling theory of Dubinin;[7] in this way the micropore volume, V_0, of the different carbons has been calculated from the adsorption data for all adsorbates used. Those corresponding to benzene (taken as a typical example) have been plotted in fig. 2 as a function of the overall burn-off. The behaviour of both series is, again, completely different, with a continuous increase in V_0 through series D and a decrease after 53% burn-off (B-31) in series B. Consequently, the micropore volumes of carbons D-34 and B-5 are similar, but they are different for the rest of the carbons, the difference increasing with increasing burn-off as a consequence of the widening (and even destruction) of part of the microporosity, produced by the reaction with air. The same sequence was found for all other hydrocarbons used in this work.

The micropore volumes deduced from all carbons and adsorbates have been plotted in fig. 3 as a function of the minimum dimension of the adsorbate molecule. In this way, fig. 3 can be taken as the micropore size distribution of the carbons.

The reaction in CO_2 (series D) produces a development of microporosity which increases with burn-off [fig. 3(*a*)]. The micropore volume of carbon D-8 is relatively low and decreases with increasing size of the adsorbate, showing a clear molecular sieving toward 2,2-dimethylbutane and, especially, iso-octane (minimum dimension, 0.59 nm). Carbon D-8 has a very narrow microporosity, probably because the low burn-off has not eliminated all the constrictions present in the carbonized material.[1] The inaccessibility of 2,2-dimethylbutane and iso-octane as compared to smaller molecules such as N_2 or benzene and the long time required for adsorption equilibrium confirm the narrow size of the micropores. As the burn-off increases up to 19% (D-19) there is an increase in micropore volume, basically due to the creation of new micropores by the complete elimination of constrictions, although iso-octane is not yet completely accessible to them (see fig. 3). For carbons D-34 to D-80 the microporosity is now equally accessible to all adsorbates, leading to an almost constant value of micropore volume. However, for carbons with large burn-off [as shown in fig. 3(*a*)] the micropore volume measured by N_2 at 77 K is given by two different values, one well below that of the hydrocarbons.

The results of fig. 3(*a*) for the micropore volumes measured by adsorption of N_2 at

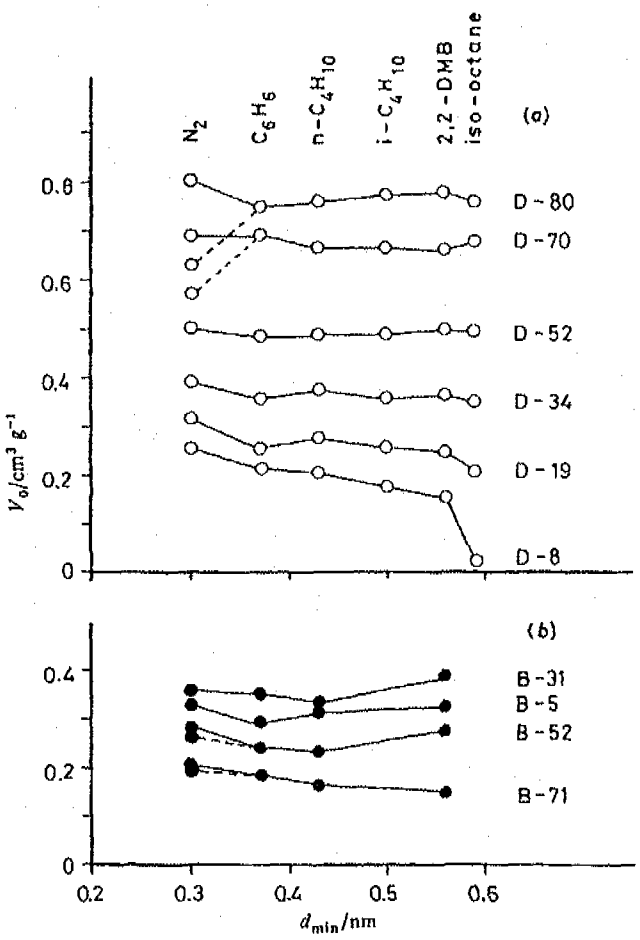

Fig. 3. Micropore volume *vs.* minimum dimension of the adsorbates: ○, D series; ●, B series.

77 K in carbons D-70 and D-80 could be explained in terms of the corresponding DR plots. The DR plots for three typical carbons of series D (D-8, D-34 and D-80) have been plotted in fig. 4 for both N_2 (77 K) and benzene (298 K); the experimental points included in the DR plots correspond to the usual pressure range covered by conventional adsorption systems, from *ca.* 1 Torr (1 Torr ≈ 133.3 Pa) to the saturation pressure of the adsorbate at the temperature of adsorption. The benzene and N_2 DR plots for D-8 and D-34 exhibit a well defined straight line for $\log^2(P_0/P) > 0.5$ (*i.e.* $P/P_0 < 0.2$) and extrapolation would supply one well defined micropore volume, with little uncertainty. However, the DR plots for D-80 are very different for both adsorbates; thus, the extrapolation is unambiguous in the case of benzene, whereas there would be two possible values of micropore volume in the case of N_2, since two different straight lines can be drawn. The two straight lines may be related to the filling of micropores with different size, the first one [for $\log^2(P_0/P) > 3$] corresponding to narrow micropores and the second [at higher relative pressures up to $\log^2(P_0/P) \approx 0.5$] corresponding to wider micropores (supermicropores) in which the filling mechanism is different as deduced from the sudden change in slope of the DR plot. The same type of behaviour is observed in carbon D-70. It could be argued that if the relative pressure range covered by benzene is lower [$\log^2(P_0/P) > 3$] there would also be two straight lines (as in the case of N_2) for

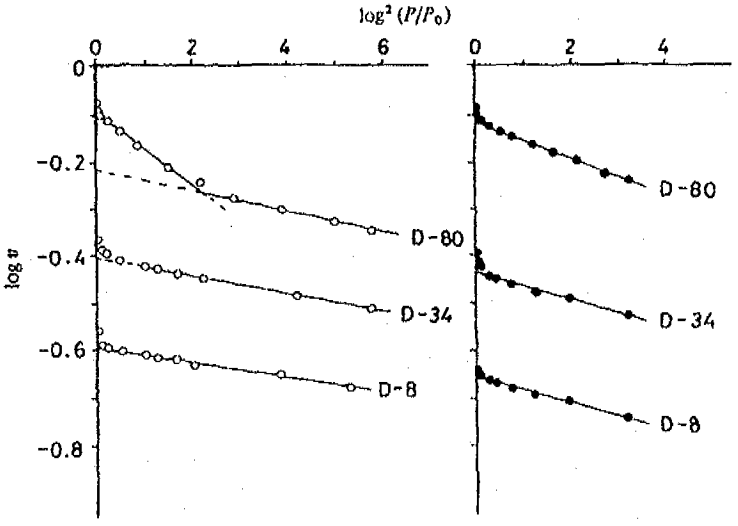

Fig. 4. DR plots for nitrogen (77 K) (○) and benzene (298 K) (●) for some activated carbons.

D-70 and D-80. Although this could probably be expected, it is important to insist that the experimental points used are referred to the usual range covered by conventional adsorption systems used in most of laboratories. Furthermore, the characteristic curves discussed below will reinforce the validity of the plots of fig. 4.

The evolution of the microporosity in carbons of series B (reacted in air) is rather different. Since the starting material is an activated carbon with 32% burn-off, the molecular sieve effect is not seen even in carbon B-5 [see fig. 3(*b*)] and the micropore volume does not change much from one adsorbate to another since, as shown in fig. 1, the widening of the narrow micropores is the predominant effect of gasification. Again two values of micropore volume deduced from the adsorption of N_2 at 77 K are found for the two carbons with larger burn-off (B-52 and B-71).

The above results for micropore volume have been deduced from the micropore-filling theory of Dubinin. This theory is based on the earlier Polanyi theory of adsorption[8] for which the adsorption potential A is defined by the expression:

$$A = RT \ln (P_0/P). \tag{1}$$

The adsorption potential A decreases with distance from the surface and when $A = 0$ the volume V enclosed by an equipotential surface will be V_0, the total adsorption space, *i.e.* the volume of micropores. The plot of V as a function A is called the characteristic curve.[7,9] After analysing characteristic curves for a wide range of microporous carbons Dubinin and Radushkevich[10] proposed the equation:

$$\frac{V}{V_0} = \exp\left[-K\left(\frac{A}{\beta}\right)^2\right] \tag{2}$$

where β is a scaling factor to bring the characteristic curves for different adsorbates into coincidence with the curve for benzene (taken as standard, with $\beta = 1$) and K is a constant characteristic of the microporous structure. By combining eqn (1) and (2) one arrives at the DR equation:

$$\frac{V}{V_0} = \exp\left[-K\left(\frac{RT}{\beta}\right)^2 (\ln P_0/P)^2\right]. \tag{3}$$

According to Dubinin's theory, the characteristic curve can indicate the way in which the adsorption space is being filled by the different adsorbates and, consequently, can

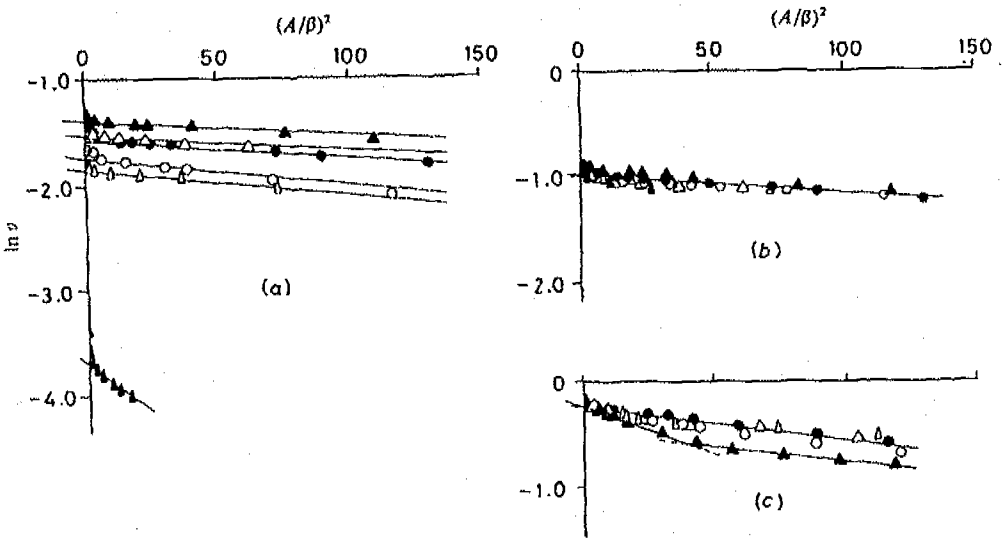

Fig. 5. Characteristic curves for carbons: (*a*) D-8, (*b*) D-34 and (*c*) D-80. ▲, N_2 (77 K); △, benzene (298 K); ●, n-butane (273 K); ○, iso-butane (273 K); ∆, 2,2 DMB (298 K); ▲, iso-octane (298 K).

provide a fuller understanding of the microporous structure of the carbons of series B and D. Fig. 5 includes, as a typical example, the characteristic curves for carbons D-8, D-34 and D-80. The β values used for the different adsorbates were: 0.33 (N_2), 1 (benzene), 0.87 (n-butane), 0.93 (iso-butane), 0.89 (2,2-dimethylbutane) and 1.71 (iso-octane). The density of the adsorbed phase has been taken as 0.808 for N_2, 0.867 for benzene, 0.600 for n-butane, 0.582 for iso-butane, 0.644 for 2,2-dimethylbutane and 0.688 for iso-octane, all in g cm^{-3}.[11, 12]

In the case of carbon D-8 [fig. 5(*a*)] all characteristic curves are different as a consequence of the molecular-sieving effect exhibited by the narrow microporosity and the curves are ordered according to the minimum dimension of the adsorbates. On the other hand, the slopes of the characteristic curves increase slightly, in general terms, with increasing dimension of the adsorbate and in the case of iso-octane the slope is very large, indicating that is accessible to only a small amount of micropores of dimensions larger than 0.59 nm.

The characteristic curves for carbon D-34 [fig. 5(*b*)] are practically coincident for all adsorbates and consequently the limiting space for adsorption (micropore volume) is the same for all of them, as expected from Dubinin's theory. Some similar results have been described recently for carbons with narrow (but accessible) and uniform microporosity using dynamic methods.[13] It is to be noted that the slope of the common characteristic curve for D-34 is very similar to that of N_2 for D-8, indicating that the reaction in CO_2 has eliminated the constrictions rendering the micropores equally accessible to all adsorbates, the micropore size distribution remaining almost unchanged.

The characteristic curves of the different hydrocarbons for D-80 [fig. 5(*c*)] are almost coincident and different from that of N_2 for which two well defined straight lines are found above and below $(A/\beta)^2 \approx 50$ (kJ mol^{-1})^2, corresponding to the two branches found in the DR plots (see fig. 4). The branch at larger $(A/\beta)^2$ is parallel to that of the hydrocarbons and its extrapolation would lead to a lower micropore volume; however, for lower $(A/\beta)^2$ the slope is larger and the micropore volume deduced from its extrapolation is practically coincident with that given by the different hydrocarbons (as shown also by fig. 3). In any case, the slopes for D-80 are larger than for D-34, indicating

that the microporosity is wider and more widely distributed in the former as a consequence of the large burn-off. Similar behaviour is found for D-70 and this is the reason why there are uncertainties in the extrapolation of the N_2 DR plots to obtain the micropore volume in these two carbons.

The characteristic curves for D-70 and D-80 show that although N_2 and benzene cover a similar range of $(A/\beta)^2$, benzene does not exhibit two different branches as N_2 does; this confirms the assumption used above when comparing the DR plots for both adsorbates given in fig. 4 for carbon D-80 for which only one branch for benzene is found under the experimental conditions used here.

The characteristic curves of carbons of series B (reacted in air) show similar behaviour as a function of overall burn-off. Thus, the characteristic curves for B-5 are very similar to those of D-34 and even have similar slopes, and those of B-52 and B-71 are qualitatively comparable with D-70 and D-80, although the former have much larger slopes because of their wider micropore size distribution shown in fig. 1.

These results show that when N_2 is used as adsorbate in the characterization of highly activated carbons, those with a wide micropore size distribution, care must be taken with the range of relative pressure chosen to calculate the micropore volume. In order to obtain the same micropore volume as with the hydrocarbons the higher relative pressure branch (usually in the relative pressure range 0.05–0.25) must be taken. On the other hand, these results found for series D confirm the complexity of the analysis of the microporosity of this type of activated carbons indicated by other authors.[14]

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