

An overview of methods for the characterization of activated carbons

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Abstract The adsorption of N_2 (77 K), CO_2 (273 K) and the preadsorption of n-nonane have been used to characterize two series of activated carbons covering a very wide range of micropore size distribution. The results show that the α method applied to the nitrogen isotherms provides the total micropore volume whereas the n-nonane preadsorption or the DR method applied to the CO_2 isotherms can yield the volume of narrow micropores. In this way the distinction between narrow and wide micropores in activated carbons can be achieved using a rather simple experimental procedure.

1. INTRODUCTION

Activated carbons are adsorbents with a well developed and accessible internal pore structure; in general terms, at least 90% of the total surface area corresponds to the micropores but both the meso and the macropores play a very important role in the adsorption process. Because of this porous structure, the adsorption isotherm of, say, N_2 at 77 K in a conventional activated carbon is of type I, having a very steep initial branch followed by a more or less gradual approach to the plateau at higher relative pressures. For a type I adsorption isotherm the micropore volume can be evaluated by means of the Dubinin-Radushkevich (DR) equation or by the use of α -plots (ref. 1). There are however some applications of activated carbons in which the presence of a wide distribution of micropores or even a relatively large fraction of mesopores is needed. In these cases the N_2 adsorption isotherms may be far from the conventional type I, the evaluation of the microporosity becoming then more difficult (ref. 2). This paper presents the analysis of the porous structure (essentially the microporosity) of activated carbons with a wide range of pore size distribution and, consequently, with a wide range of isotherm shape. For such analysis, several approaches will be used.

2. EXPERIMENTAL

The two series of activated carbons presented here were prepared in the laboratory from lignocellulosic materials using different experimental procedures. The adsorption isotherms of N_2 (77 K) and CO_2 (273 K) were determined in a conventional gravimetric system using silica spring balances; in some cases the adsorption of N_2 (77 K) has been measured in an Omnisorp - 100 Analyzer. The preadsorption of n-nonane has been carried out in a slightly modified gravimetric system following the procedure already published (ref. 3).

3. RESULTS AND DISCUSSION

3.1 Adsorption of N_2 (77 K)

A.- Adsorption isotherms

Fig. 1a shows the nitrogen adsorption isotherms for one series of activated carbons with increasing degree of burn-off (included in the nomenclature). The basic character of all these isotherms is type I but the shape progressively changes with burn-off. At low burn-off the very steep initial branch is followed by an almost horizontal plateau; once the micropores (which must be narrow and rather uniform in size) have been filled with the adsorbate the amount adsorbed remains almost constant for higher relative pressures. As burn-off increases there is an opening of the knee of the isotherm with a

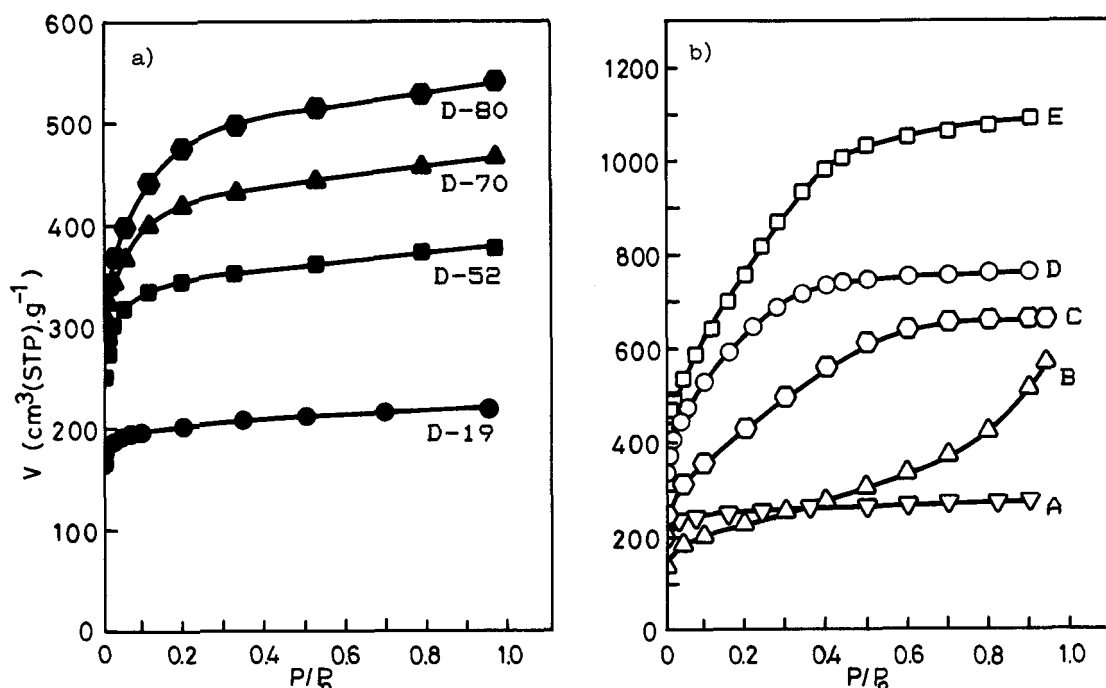


Fig. 1.- Nitrogen adsorption isotherms on: a) some carbons of Series D and b) some activated carbons.

more gradual approach to the plateau, which becomes less well-defined. Increasing activation then results in a widening of the microporosity with increasing contribution from wide micropores (ref. 4). Fig. 1 b includes, as typical examples, the nitrogen adsorption isotherms for some selected activated carbons prepared from lignocellulosic materials and using different activation procedures in order to have a wide range of pore size distribution. The direct observation of the isotherms can provide a qualitative information about the approximate pore structure of the carbons. Thus, carbon A exhibits a type I isotherm as found in carbons with low burn-off and having predominantly narrow and uniform microporosity, with a very low value of external surface area. On the other hand, carbon B exhibits a type II isotherm with an apparent contribution from microporosity. The other three adsorption isotherms have shapes which can be considered as lying between these two extremes. Carbon C exhibits a steep initial branch which is followed by a very open and almost straight knee approaching a relatively well-defined plateau at $P/P_0 \approx 0.7$. Carbon D has a more rounded knee and the well-defined plateau starts at $P/P_0 \approx 0.5$. Finally, carbon E is more similar to carbon C but the isotherm shows an ill-defined plateau.

The analysis of these adsorption isotherms will be centered on the microporosity and the external surface area, these being the two fundamental parameters defining an activated carbon. As it is well known, the additional characterization of the meso and macroporosity can be achieved by the analysis of the adsorption-desorption isotherms or by mercury porosimetry (ref. 1).

B.- Dubinin-Radushkevich plots

Dubinin and coworkers (ref. 5) developed the micropore volume theory, based on the Polanyi concept of characteristic curve, to describe the adsorption on micropores. The characteristic curve could be expressed as

$$V/V_0 = \exp[-(A/E)^2] \quad (1)$$

where V is the amount of gas adsorbed at P/P_0 and V_0 is the volume needed to fill the micropores. A is the affinity, or differential free energy of adsorption

$$A = RT \ln(P/P_0) \quad (2)$$

and E is the characteristic free energy of adsorption. By combining equations (1) and (2) the well-known Dubinin-Radushkevich (DR) equation can be obtained:

$$V/V_0 = \exp[-B(T/\beta)^n \log^2(P_0/P)] \tag{3}$$

where B is the structural constant and β is a similarity coefficient. Equation (3) may be written for plotting as

$$\log V = \log V_0 - D \log^2(P_0/P) \tag{4}$$

where $D = B(T/\beta)^n$.

A more general expression was developed by Dubinin and Astakhov (ref. 6)

$$V/V_0 = \exp[-(A/E)^n] \tag{5}$$

which is applicable to a wider range of microporous carbons.

The DR plots of Fig. 2 were constructed in the usual way, i.e., as $\log V$

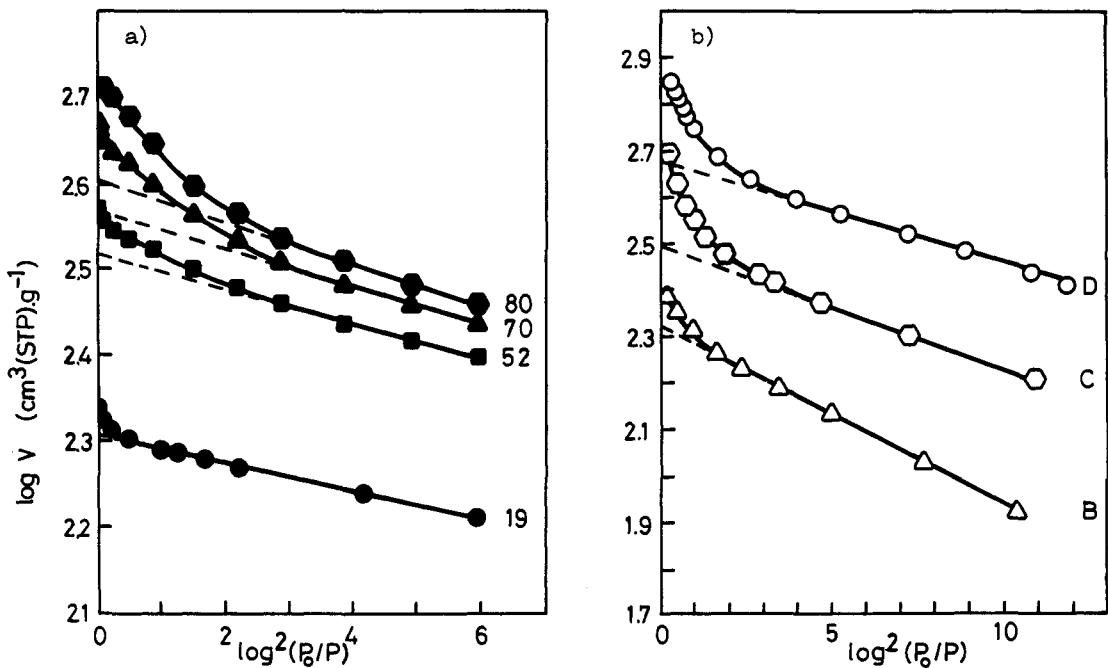


Fig. 2.- DR plots for: a) some carbons of Series D and b) some activated carbons.

TABLE 1. Micropore volume (cm^3g^{-1}) and external surface area (m^2g^{-1}) of activated carbons.

Sample	N_2 (77K)		CO_2 (273K)	n-nonane preadsorption		S_{ext}
	DR	α	DR	V_{NP}	V_{NP}	
D-19	0.31	0.31	0.30	0.31	0.24	24
D-52	0.50	0.53	0.41	0.51	0.41	41
D-70	0.57	0.64	0.48	0.52	0.47	58
D-80	0.62	0.76	0.51	0.52	0.50	56
A	0.39	0.39	0.36	0.38	0.31	39
B	0.32	0.08	0.09	--	--	577
C	0.49	1.01	0.27	0.20	0.25	10
D	0.75	1.12	0.48	0.46	0.51	34
E	0.92	1.61	0.51	0.49	0.52	53

against $\log^2(P_0/P)$, from the nitrogen isotherms of Fig. 1. The range of linearity of the DR plots of Fig. 2a is larger for the carbon with low burn-off and decreases for increasing burn-off, the plots exhibiting a clear upward deviation. The back extrapolation of the linear DR plots are converted into the micropore volume (see Table 1) by assuming that the pores have been filled with liquid nitrogen (density 0.808 g cm^{-3}). The DR plots of Fig. 2b show a similar behaviour but now the upward deviation starts at even lower values of P/P_0 for carbons having nitrogen isotherm with a very open knee (gradual approach to the plateau).

The values of micropore volume (Table 1) deduced from the DR plots of Fig. 2 seem to be too low for some carbons (especially C, D and E, with an important contribution from wide microporosity) in respect to what could be expected from the direct observation of the nitrogen isotherms. The use of the Dubinin-Astahkov equation increases the range of linearity of the plots when the value of the exponent n of equation (5) is lower than 2 (the value for the DR equation) and yields larger values than the DR plots. However, the linear portions of the plots are not as well defined (they have lower correlation coefficients) and there are more uncertainties in the extrapolation. This effect is more noticeable the larger the contribution of wide microporosity.

In view of these results, the use of a different approach to analyse the nitrogen isotherms seems to be indicated (ref. 2,7).

C.- α plots

The α method (ref. 8) is another empirical approach for the determination of the microporosity. The application of the method requires a standard isotherm of the adsorptive (nitrogen in this case) on a non-porous reference material with a similar surface structure to the carbon under investigation. The amount adsorbed is plotted against the reduced standard adsorption α (placing $\alpha = 1$ at $P/P_0 = 0.4$).

The α plots for the activated carbons were constructed taking as standard the adsorption data of an olive stone carbon in which the micropores had been closed by heat treatment (ref. 9). The α plots of Figs. 3a and 3b exhibit a wide range of shapes as expected from the different shape of the nitrogen adsorption isotherms. The micropore volume (Table 1) deduced by back extrapolation of the linear portion of the α plots is in agreement with the value deduced from the DR plots only in the case of carbons with narrow microporo-

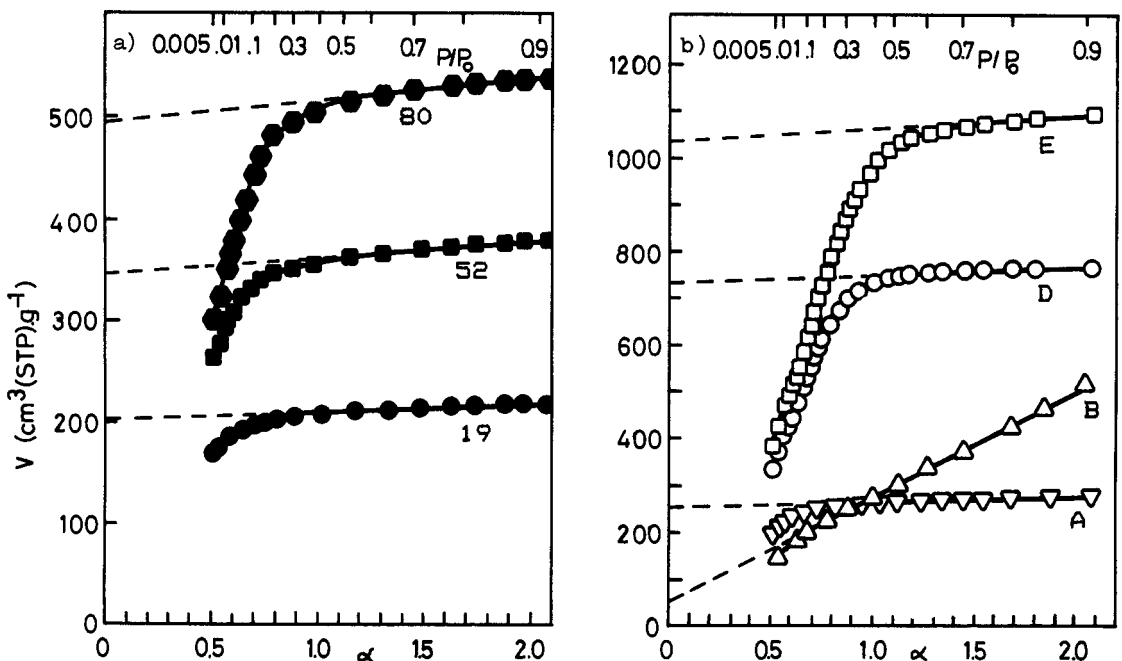


Fig. 3.- α plots for: a) some carbons of Series D and b) some activated carbons.

sity (low degree of activation) as described in previous works (ref. 2, 10, 11). In all other carbons of both series the α method gives larger values and for carbons C and D are about twice the DR value.

Recent work (ref. 7, 12) has shown that when the adsorption of several hydrocarbons was carried out in activated carbons such as those of series D, the DR plots (provided no molecular sieving to the hydrocarbons could take place) gave values of micropore volume which were very near those of the α plots for nitrogen and larger than those of DR plots for nitrogen. Only in cases in which a 0.05-0.3 relative pressure range straight portion could be defined in the nitrogen DR plots the extrapolated values would be in fairly good agreement with the results obtained with hydrocarbons and the α method applied to the nitrogen isotherms.

One may conclude then that the α plots for the nitrogen isotherms provide the total micropore volume of these carbons, including both narrow and wide micropores, whereas the DR plots for nitrogen normally yield too low values when wide micropores are present in the carbon. As stated above, the use of the Dubinin-Astakhov equation increases the range of linearity of the plots and yield values larger than the DR plots (and nearer to those of the α plots). However, the interpretation of the results is not straightforward.

The α plots can also be used to calculate the external surface area from the slope of the linear portion at high values of relative pressure (ref. 1). Table 1 includes the values for all carbons and it shows that the external surface area is very low in all carbons of series D, as expected from the shape of the isotherms. For all other carbons, the external surface area increases from 10 m²/g in carbon C to 577 m²g⁻¹ in carbon B.

3.2 Adsorption of CO₂ (273 K)

The adsorption of CO₂ at 273 K, because the low relative pressure range covered (up to P/P₀ ≈ 0.03), can be used to determine the volume due to only the narrow micropores, as shown in previous works (ref. 4, 7). The CO₂ DR plots are more linear than the corresponding N₂ DR plots and the extrapolation to calculate the micropore volume is less ambiguous for carbons with large burn-off. The DR plots for the CO₂ adsorption isotherms of the carbons described in this work yield the micropore volumes listed in Table 1. Again, only in the case of activated carbons with narrow microporosity the CO₂ values are in agreement with the nitrogen DR and α results. In all other cases the CO₂ values are smaller, and for carbons with an important contribution of wide micropores (e.g. C, D, E) the CO₂ value can be lower than 50% of the value obtained from the α plots. This is not surprising since both adsorptives at the temperatures used define different portions of the characteristic curve (ref. 7) and the extrapolation of the CO₂ data in highly activated carbons always yields lower values of micropore volume. The only exception to this general behaviour is carbon B. This carbon exhibits a type II nitrogen adsorption isotherm, with an apparent contribution from microporosity. The results of Table 1 indicate that the micropore volume given by the α plot is coincident with that obtained from the adsorption of CO₂. This means that a small fraction of the amount adsorbed (see Fig. 1b) is contained within narrow micropores. However, the DR plot for N₂ (77 K) gives a micropore volume larger than both the α plot or the CO₂ adsorption. This is probably due to a very important contribution of adsorption in the mesoporosity being taken into account in the DR plot, leading to a too large value of micropore volume.

3.3 Preadsorption of n-nonane

The preadsorption of n-nonane was introduced by Gregg and Langford (ref. 13) as a relatively direct method to evaluate the microporosity of carbon black since n-nonane would be strongly retained in narrow pores after outgassing at room temperature, leaving the rest of the surface available for nitrogen adsorption. The vertical separation of the nitrogen isotherms before and after the n-nonane preadsorption should give the micropore volume. This technique has been applied in the last few years to activated carbons (ref. 2, 14, 15) but the results were not always satisfactory.

The n-nonane preadsorption has been carried out on the carbons described here using the following experimental procedure: the carbons were outgassed overnight at 573K and the N₂ isotherm at 77 K determined. After outgassing the carbons again under the same experimental conditions, they were exposed to n-nonane vapour for 30 min. at 77 K, left in contact for 3 h. at room tempera-

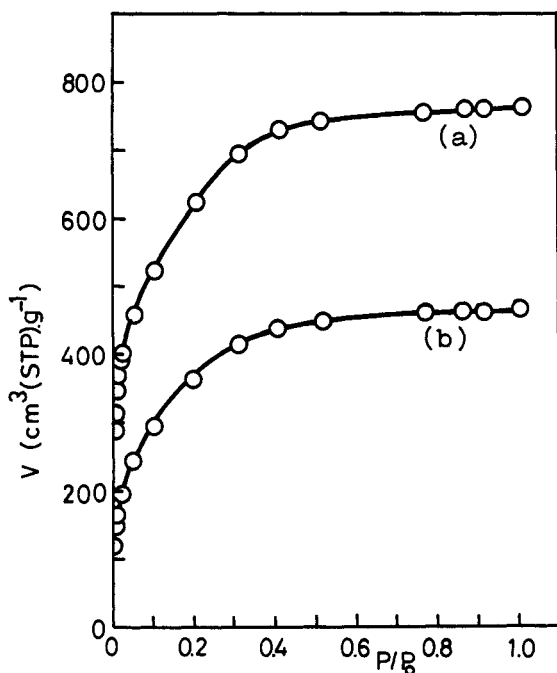


Fig. 4.- N_2 (77K) adsorption isotherms on carbon D: before (a) and after (b) n-nonane preadsorption.

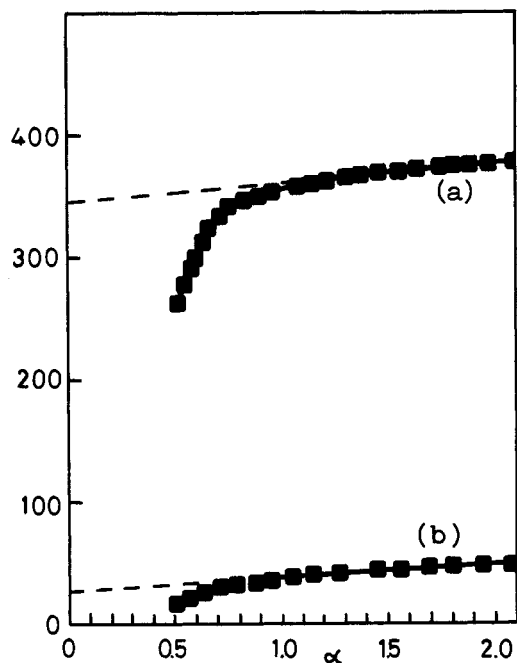


Fig. 5.- α plots for carbon D-52 before (a) and after (b) n-nonane preadsorption.

ture and later outgassed at 298 K overnight prior to the redetermination of the nitrogen (77 K) isotherm. One typical example of the application of this technique to carbon D is shown in Fig. 4. The values of micropore volume (V_{NP}) are included in Table 1; this table also includes the volume of n-nonane (V_{nnp}) retained by the carbons after outgassing at 298 K, calculated by using a density for n-nonane of 0.717 gcm⁻³ at 298 K.

The results for carbons of series D merit a detailed discussion. It was shown previously (ref. 3, 17) that for carbons with low burn-off the V_{NP} values are exactly coincident with the values obtained from the DR plots for N_2 at 77 K and CO_2 at 273 K; in these carbons the narrow micropores are completely blocked by the preadsorbed n-nonane; this is in agreement with results found for carbons having only very narrow pores of width < 0.7 nm (ref. 7). On the other hand, the V_{NP} value for these carbons (for instance carbon D-19 in Table 1) is usually lower than V_{NP} because n-nonane does not completely fill the narrow micropores but effectively blocks them. As burn-off increases and there is a widening of the microporosity there is a change in the situation, as shown by the results of Table 1 for carbons D-19, D-52, D-70 and D-80. For D-19, the V_{NP} value is still lower than V_{NP} and $V(CO_2)$ because the carbon has predominantly narrow microporosity. However, V_{NP} for carbon D-52 is larger than V_{NP} which is coincident with $V(CO_2)$; the difference is smaller for D-70 and the three values are in very good agreement for carbon D-80. To a first approximation, the data for carbon D-52 would indicate that n-nonane is filling the narrow micropores but blocking the entrance of nitrogen to wider micropores so that the nitrogen isotherm on the carbon with n-nonane preadsorbed stands lower than it should, giving a too high value of V_{NP} . This is so because V_{NP} is exactly coincident with V_{CO_2} and this means that both values are giving the volume of the narrow micropores only. As burn-off proceeds up to D-70 the degree of interconnectivity between the pores decreases and now V_{NP} is more similar (although still larger) to V_{NP} and $V(CO_2)$. For a very large burn-off (carbon D-80) the pore texture is more open, with a very low degree of interconnectivity, and the three values - V_{NP} , V_{NP} and $V(CO_2)$ - are practically coincident.

A further test of this idea can be obtained from the analysis of the isotherms using the α plots. The α plot of the original isotherm would give the total micropore volume, V_{α} , the α plots of the isotherm after nonane preadsorption (see Fig. 5 for the case of carbon D-52 taken as example) would give the volume of the wide micropores ($V_{\alpha(NP)}$) and, of course, the α plot

TABLE 2.- Micropore volume (cm^3g^{-1}) from α -plots before (V_{α}) and after ($V_{\alpha(\text{NP})}$) n-nonane preadsorption and residual isotherm ($V_{\alpha(\text{res})}$).

Sample	V_{α}	$V_{\alpha(\text{NP})}$	$V_{\alpha(\text{res})}$
D-19	0.31	0.01	0.30
D-52	0.53	0.05	0.48
D-70	0.64	0.14	0.50
D-80	0.76	0.25	0.51

TABLE 3. Volume (cm^3g^{-1}) of narrow (V_n) and wide (V_w) micropores of carbons.

Sample	V_0	V_n	V_w
D-19	0.31	0.30	0.01
D-52	0.53	0.41	0.12
D-70	0.64	0.48	0.16
D-80	0.76	0.51	0.25
A	0.39	0.36	0.03
B	0.08	0.09	-
C	1.01	0.27	0.74
D	1.12	0.48	0.64
E	1.61	0.51	1.10

for the residual isotherm (the isotherm obtained by subtracting the isotherms before and after n-nonane preadsorption) would give the volume of the narrow micropores ($V_{\alpha(\text{res})}$). The three sets of values can be found in Table 2. The values of V_{α} are larger than $V(\text{CO}_2)$, V_{NP} and V_{NP} for carbons D-52, D-70 and D-80. However, whereas the difference is large, as expected, for D-70 and D-80, it is very small for D-52; this in turn leads to a too high value of $V_{\alpha(\text{res})}$ obtained from the residual isotherm for carbon D-52 and a too low value of $V_{\alpha(\text{NP})}$ obtained from the α plots of the preadsorbed sample. For carbon D-80, $V_{\alpha(\text{res})}$ is coincident with $V(\text{CO}_2)$ and V_{NP} and then $V_{\alpha(\text{NP})}$ is the value to be expected and coincident with the value deduced by subtracting $V(\text{CO}_2)$ from the micropore volume deduced from the α plot. The case for D-70 lies between D-52 and D-80, the differences being smaller than for D-52.

Consequently, these results confirm that during the process of slow and controlled activation of carbonised lignocellulosic materials such as olive stones and almond shells (ref. 3) there is a stage at about 50-60% burn-off in which a noticeable degree of pore interconnectivity takes place. This means, in turn, that the use of n-nonane preadsorption should be used with care in this type of carbons. Something similar has been observed by Carrott et al. (ref. 18) when studying carbons prepared from charcoal cloth having a wide distribution of micropores. On the other hand, our results confirm the validity of using the volume of n-nonane retained after preadsorption to obtain the volume of narrow micropores (ref. 3) independently of the interconnectivity of the pore system. However, this is true only if the n-nonane can fill the micropores; this is not the case for carbons with very low burn-off in which the micropores may be blocked but not filled. Because of this, the use of CO_2 at 273K is to be preferred to calculate the volume of narrow micropores (up to two molecular dimensions, i.e. about 0.7 nm).

The above results confirm previous work (ref. 2, 17) in the sense that the α method applied to the nitrogen isotherms may provide the total micropore volume V_0 ($=V_{\alpha}$) whereas the adsorption of CO_2 at 273 K or the n-nonane preadsorption (provided no problems related to the interconnectivity of the pore structure exist) can yield the volume of narrow micropores. If this is so, one can then easily deduce the volume of narrow (V_n) and wide (V_w) micropores of an activated carbon. V_0 is given by the α plot, V_n by the adsorption of CO_2 at 273K and V_w is deduced by subtracting V_n from V_0 . The results of Table 3 indicate that carbon D-19 has almost exclusively narrow micropores as it could be deduced from the shape of the isotherm; as activation proceeds, there is a widening of the microporosity, with an increasing contribution from V_w , which is about 33% in carbon D-80. All other carbons presented here have a wide range of contribution of V_w , ranging from less than 10% in carbon A to about 70% in carbons C and E. The case of carbon B, with a type II isotherm (see Fig. 1b) is different since the results of Tables 1 and 3 indicate that there is only a small proportion of narrow micropores, the rest of the adsorption process taking place in non-microporous surface ($577 \text{ m}^2\text{g}^{-1}$ of external surface area).

4. CONCLUSIONS

The results presented here for a wide range of activated carbons indicate that when N_2 (77 K) is used as adsorptive, the DR and α plots give similar value of micropore volume in carbons with narrow microporosity. As the porosity widens the values differ up to $V_{0(\alpha)} \approx 2(V_{0(DR)})$. On the other hand, it has been shown that both the n-nonane preadsorption and the DR plots for CO_2 (273 K) give the same value for the narrow microporosity. However, the n-nonane preadsorption results are conditioned by the degree of interconnectivity of the pore structure. Since the α plots for N_2 (77K) provide the total micropore volume and the DR plots for CO_2 (273 K) the volume of narrow micropores, the difference will correspond to the volume of wide micropores. Consequently, the distinction between narrow and wide micropores can be achieved using a rather simple experimental procedure, the adsorption of N_2 (77 K) and CO_2 (273 K) on the carbon under investigation.

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