# CO<sub>2</sub> versus N<sub>2</sub> as Adsorbates for the Characterization of Microporous Carbons

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## Introduction

A revision of the literature on the characterization of carbons by gas adsorption can show that two very common adsorptives are N<sub>2</sub> at 77K and CO<sub>2</sub> at 273 or 298K<sup>1,2</sup>. However, when the results obtained with both adsorptives on a wide range of activated carbons are compared a relatively large dispersion on apparent surface areas and/or micropore volume can be found<sup>3</sup>. In general terms, the results may be classified in three groups: i) SN<sub>2</sub>  $\leq$  SCO<sub>2</sub> (or V<sub>0(N<sub>2</sub>)</sub>  $\leq$  V<sub>0(CO<sub>2</sub>)): it is usually found with carbonized materials and coals; ii)SN<sub>2</sub>  $\geq$  SCO<sub>2</sub> (or V<sub>0(N<sub>2</sub>)</sub>  $\geq$  V<sub>0(CO<sub>2</sub>)), in carbons with low degree of activation and relatively narrow microporosity; iii) SN<sub>2</sub>  $\gg$  SCO<sub>2</sub> (or V<sub>0(N<sub>2</sub>)</sub>  $\geq$  V<sub>0(CO<sub>2</sub>)), in a carbons with a large degree of activation and relatively narrow microporosity; iii) SN<sub>2</sub>  $\gg$  SCO<sub>2</sub> (or V<sub>0(N<sub>2</sub>)</sub>  $\gg$  N<sub>0</sub>(CO<sub>2</sub>)), An additional problem is the uncertainty about the true values of cross-sectional area (A<sub>m</sub>) and density (d) of the adsorbate.</sub></sub></sub>

In order to clarify these discrepancies this work presents the comparison of adsorption data for  $N_2$  and  $CO_2$  on a series of activated carbons covering a wide range of burn-off.

#### Experimental

The activated carbons have been prepared from olive stones previously carbonized in  $N_2$  at 1123K for 2h; the activation has been carried out in  $CO_2$  at 1098K for different periods of time (7-71h) to cover the burn-off range 8-80%.

The adsorption of  $N_2$  (77K) and  $CO_2$  (273 and 298K) has been carried out in a conventional gravimetric system; the low relative pressure range in the adsorption of  $N_2$  (77K) has been studied using a high precision volumetric system.

## Results and Discussion

Table 1 shows the micropore volumes (D-R equation) for the carbonized olive stones (D-O) and the resulting activated carbons (D-X, where X is the burn-off). The D-R plots for N<sub>2</sub> at 77K are linear in the whole range for carbons D-O and D-8 but as from D-19 exhibit an upward deviation in the high relative pressure zone; such deviation starts at lower relative pressure of larger burn-off. This evolution is due to the development and widening of the microporosity with increasing activation

Table 1. Micropore volumes  $(cm^3.g^{-1})$ 

Muestra	$N_2$ at $77K^*$	CO <sub>2</sub> at 273K	CO <sub>2</sub> at 298K
D- 0	.02	.23	
D- 8	.26	.26	.35
D-19	.31	.30	.42
D-34	.39	.36	.52
D-52	, 50	.41	.57
D-70	.57	.48	.58
D-80	.62	.51	.59

N<sub>2</sub> liquid density = 0.808 g.cm<sup>-3</sup> CO<sub>2</sub> (273K) liquid density = 1.023 g.cm<sup>-3</sup> CO<sub>2</sub> (298K) liquid density = 0.700 g.cm<sup>-3</sup>

\* Determined for P/P<sub>O</sub> > 0.2

(burn-off) leading to a wider micropore size distribution, specially in carbons D-52, D-70 and D-80; in fact, the D-R plot for sample D-80 is almost curved in all the pressure range covered by the gravimetric system (down to  $P/P_0 = 10^{-2}$ ). The D-R plots for the adsorption data of CO<sub>2</sub> at both 273 and 298K are linear in almost all the range of relative pressure for the carbons with the largest burn-off.

The data of Table 1 shows that  $V_0(N_2) < V_0(CO_2)$ for the carbonized olive stones (D-O); this behaviour, is typical of carbonized agricultural by-products<sup>4</sup> in which the constrictions of the micropores are of the same dimensions than the adsorptive molecular and, consequently, the adsorption of  $CO_2$  (at a higher temperature) is kinetically favoured. The comparison of of  $V_0$  values obtained with N<sub>2</sub> at 77K and  $CO_2$  at 273K shows that they are very similar for samples D-8, D-19 and D-34 but they differ (always  $V_0(N_2) > V_0(CO_2)$ ) for larger burn-off; the contrary occurs with the  $V_0$  values for  $CO_2$  at 298K and N<sub>2</sub> at 77K, since both values approach with increasing burn-off. The larger value of  $V_0(CO_2)$  at 298K in respect of the corresponding  $V_0(CO_2)$  at 273K can not be interpreted as due to an activated diffusion since, as shown previously for similar carbons<sup>5</sup>, the adsorption of hydrocarbons such as benzene and n-butane (larger molecular dimension than  $N_2$  or  $CO_2$ ) leads to  $V_0$  values similar to those of  $N_2$  at 77K; furthermore, if the amount adsorbed is expressed as mmole/g the amount of  $CO_2$  adsorbed at 273K is always larger than at 298K. According to this, it is obvious that the  $V_0$  values obtained at 298K for the adsorption of  $CO_2$  are too large.

A good way to compare the results for the adsorption of  $N_2$  and  $CO_2$  is to use the corresponding characteristic curves as in Figure 1 for carbon D-19 taken as example; the curves for  $N_2$  at 77K and  $CO_2$  at 273K are very coincident when the low pressure  $N_2$  adsorption data are included. Consequently, the extrapolation of the data corresponding to both adsorbates will be similar.

These results for the samples with lower burn-off (up to 34%), indicate that the  $V_0$ values obtained from the adsorption of  $N_2(77K)$  and  $CO_2$  at 273K are coincident because the microporosity is narrow and the characteristic curves are coincident. For larger extent of burn-off and, consequently, wider microporosity size distribution, the values of  $V_0$ obtained from the adsorption of N2 (covering relative pressure above 0.01) is larger (see Table 1) than the  $V_0$  from the adsorption of  $CO_2$  because the former is obtained by extrapolation of adsorption data at these relatively high relative pressures. If, as expected, the low relative pressure adsorption data for  $N_2$  would fit with the  $CO_2$  data as for sample D-19 then the  $V_0$  value would be the same for both adsorbates. Consequently, care has to be taken when comparing micropore volumes obtained with these adsorbates if the same relative pressure range not used.

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In the case of the adsorption of  $CO_2$ at 298K, the characteristic curve (except for very low relative pressures) is above and almost paralell to that of CO<sub>2</sub> at 273K, leading to a larger V<sub>0</sub> value. Since, on the other hand, the amount adscrbed at the micropores is larger at 273K than at 298K if expressed in mmole/g, the difference in the D-R plots is probably due to the fact that the density normally used for CO<sub>2</sub> at 298K (0.700g.cm<sup>3</sup>) is not correct. The corrected density value for samples with to 34% burn-off is rather constant, around 0.98g.cm<sup>-3</sup>, in agreement with the fact the micropore size distribution of these carbons is rather narrow. For samples D-70 and D-80, with a much wider micropore size distribution, the corrected would be lower, around 0.85 and 0.81g.cm<sup>-3</sup>, respectively. The use of the corrected density brings to  $V_0$  obtained with  $CO_2$  at 298K to a very similar values to those obtained at 273K.

### References

- S.J. Gregg and K.S.W. Sing; "Adsorption, Surface Area and Porosity". 2th Ed. Academic Press. London (1982).
- 2. T.G. Lamond and H. Marsh; Carbon <u>1</u>, 281 (1964).
- 3. P.L. Walker, Jr. and M. Shelef; Carbon, 5, 7 (1967).
- F. Rodríguez-Reinoso, J.D. López-González and C. Berenguer; Carbon <u>20</u>, 513 (1982).
- A. Linares-Solano, J.D. López-González, J.M. Martín-Martínez and F. Rodríguez-Reinoso; Ads. Sci. Techn., <u>1</u>, 123 (1984).



Figure 1.- The adsorption of  $N_2(77K)$  and  $CO_2(273 \text{ and } 298K)$  by the D-19 active carbon.