Steam versus CO_2 Activation in the Development of the Porous Texture of Activated Carbons

F. Rodríguez-Reinoso, A. Linares-Solano, M. Molina-Sabio and I. Pérez-Lledo.

Universidad de Alicante. Alicante. Spain.

Introduction

The properties of activated carbons are a function of the carbonaceous starting material and the preparation conditions (activation method, temperature, length of reaction, etc) [1,2]. The major part of the commercial activated carbons are prepared by steam activation (in a two stage process, the first being the carbonization of the precursor) although both the activation with CO_2 and chemical activation are also used to a lesser extent[3]. Although laboratory scale the activation of the carbonized material with CO_2 is simple and convenient, allowing a good way of studying the effect of activation conditions on the porous texture of the final product it is interesting to compare it with the steam activation using a common carbonized precursor and to study the differences produced on the development of the porous texture of the activated carbon as a function of the extent in activation.

Experimental

The starting material selected for the preparation of the activated carbons was plum stones which has proven to be adequate for the production of high adsorptive capacity carbons [4]. The precursor was carbonized under a flow of nitrogen at different temperatures (800-950°C) for 2 h.[5]. The activation in CO_2 was carried out on the carbonized material (flow rate 80 $cm^3.min^{-1}$) at 800, 825 and 850°C and using different activation lengths to obtain a wide range of porosity. Steam activation was carried out in the 900-950°C temperature range (in order to have comparable activation rate to that of CO_2) and the time of reaction was selected to yield activated carbons with similar burn-off to those activated in CO_2; the partial pressure used was 12.3KPa, obtained by flowing N_2 (80 $cm^3.min^{-1}$) through oxygen free destilled water kept at 50°C.

The characterization of the porous texture of the activated carbons was carried out by means of adsorption of N_2 (77K) and mercury prosimetry.

Results and Discussion

Figure 1 includes some examples of adsorption isotherms (N_2 at 77K); carbons activated with CO_2 exhibit a gradual development of

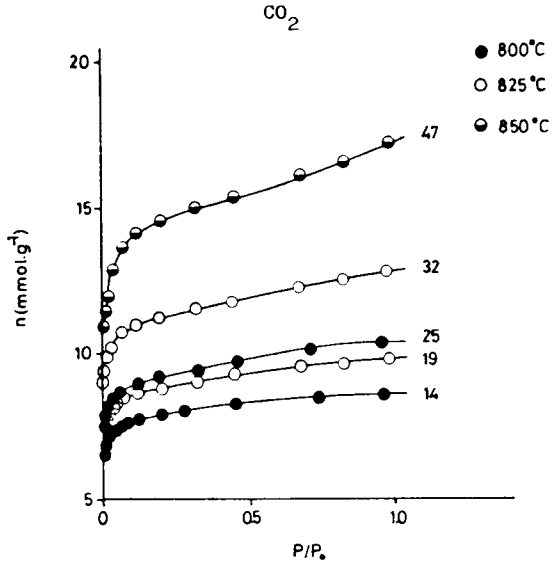

Figure 1a

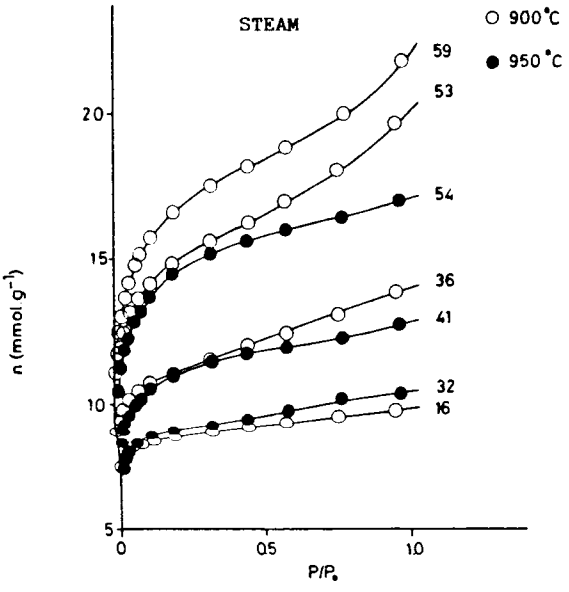

Figure 1b

the adsorptive capacity for increasing activation (% burn-off) independently of the activation temperature. However, in carbons activated with steam the largest burn-off does not necessarily corresponds with a larger amount-adsorbed, and the activation at 950°C yields carbons with lower adsorption capacity than carbons activated at 900°C with comparable burn-off (compare carbons 54-950 and 53-900 or 41-950 and 36-900 in Figure 1 and Table 1); a lower activation temperature develops in larger extent the mesoporosity of the carbons as seen in Figure 1; on the contrary, carbon 54-950 has a much larger contribution of microporosity.

The comparison of both activations (Fig. 1 and Table 1) indicates that CO_2 develops the microporosity in a larger extent than steam which, in turn, develops preferently the mesoporosity.

Figure 2 includes some plots of cumulative pore volume determined by mercury porosimetry for carbons activated with CO_2 and steam and with comparable burn-off. Activation with CO_2 develops the macroporosity, specially in the pore size range 600-1500 nm. For pore sizes below 600 nm there is very little development of porosity and more or less similar for the percentages of burn-off covered in Figure 2. In the case of steam activation, again, the extent of activation (% burn-off) is not the only factor, but also the activation temperature. The porosity development is also very different to that of CO_2 activation, since now, as Figure 2 shows, that the pore dimensions being more developed correspond to the lower range measured by mercury porosimetry, mesoporosity, in agreement with the results obtained from the adsorption of N_2.

Table 1.

STEAM

% burn-off	$n_{0.95}$ (mmol.g^{-1})	$n_{0.1}/n_{0.95}$	V_0 (cm^3.g^{-1})	$V^*_{mesopores}$ (cm^3.g^{-1})	V_T^* (cm^3.g^{-1})
16	9.8	0.847	0.30	0.067	0.153
32	10.4	0.827	0.31	0.151	0.262
41	12.8	0.813	0.40	0.189	0.333
54	16.9	0.799	0.52	0.324	0.670
59	21.4	0.724	0.59	0.182	0.477

CO_2

% burn-off	$n_{0.95}$ (mmol.g^{-1})	$n_{0.1}/n_{0.95}$	V_0 (cm^3.g^{-1})	$V^*_{mesopores}$ (cm^3.g^{-1})	V_T^* (cm^3.g^{-1})
14	8.60	0.895	0.274	0.026	0.210
19	8.75	0.878	0.302	0.026	0.216
25	9.20	0.864	0.311	0.027	0.253
32	12.75	0.858	0.388	0.039	0.302
47	14.55	0.818	0.470	0.057	0.343

* From mercury porosimeter

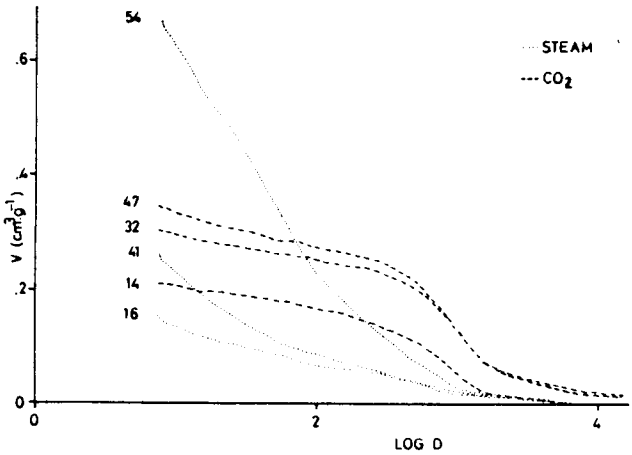

Figure 2

References

1. Smisek, M., and Cerny. S.; "Active carbon". Elsevier Amsterdam (1970).
2. Linares-Solano, A., López-González, J.D., Molina-Sabio, M. and Rodríguez-Reinoso, F.; J. Chem. Tech. Biotechnol., 30, 65 (1980).
3. Pierce, C. and Smith, R.N.; J. Phys. Chem., 57, 64 (1953).
4. Dubinin, M.M.; Izr. Akad. Nauk. SSSR. Otd. Khimmank, 750 (1961).
5. Lewis, I.C.; Carbon, 20, 519 (1982).