

Iron Catalyzed Activation of Almond Shells in CO₂

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Introduction

Almond shells are an excellent raw material for the preparation of activated carbons with large apparent surface area and very adequate for the adsorption of gases and vapours¹. Under the practical point of view an activated carbon must have, besides a large micropore volume, a well developed meso and macroporosity to facilitate the access of the molecules of the adsorptive to the micropores. Since the activated carbons prepared from almond shells are essentially microporous it is convenient to find methods of preparation that increase the development of meso and macroporosity. This paper presents the results obtained in the process of activation of almond shells using the catalytic effect of iron in the gasification C-CO₂-3.

Experimental

Almond shells, crushed and sieved to a 1.62-2.0mm particle size, were washed with a 10% H₂SO₄ solution and later impregnated at 25°C with Fe(NO₃)₃ solutions for 24h; the solutions had 0.1, 1 and 5% of iron. The samples were directly activated in CO₂ at different temperatures and lengths of reaction. The iron loading of the almond shells was analyzed spectrophotometrically on the dissolved ash. The characterization of the activated carbons was carried out by mercury porosimetry and adsorption of N₂ (77K) and CO₂ (273K).

Results and Discussion

Table 1 shows a selection of data for carbons prepared at 800°C (the nomenclature includes the percentage of iron in the Fe(NO₃)₃ solution and the length in hours of the activation process) and, for the sake of comparison, a carbon prepared at 850°C. The table shows that the increase in concentration of the Fe(NO₃)₃ solution means an increase in the iron content of almond shells (up to 0.4%).

The direct activation of almond shells in CO₂ at 800°C, which previous work⁴ showed to be equivalent to the conventional carbonization followed by activation, is catalyzed by the iron impregnating the raw material, as seen from the results of Table 1; the extent of activation considerable increases from 4% for the uncatalyzed (A-0-8) to 67%

for carbon A-5-8. Similar results have been found for the two other temperatures used (750 and 850°C). To show the long-term effect of the iron, the extent of activation has been plotted in Figure 1 as a function of activation time for the series A-5; Figure 1 shows that there is initially a considerable increase in the extent of the activation but after 8 h. of reaction the catalyst seems to lose effectivity and the rate of activation becomes comparable with that of uncatalyzed reaction.

The mercury porosimetry data for mesoporosity (7.5 < ϕ < 200nm) and the adsorption data corresponding to the micropore volume (by application of the D-R equation) are included in Table 1. The data for sample B-0-14 have been included in order to compare with carbon A-1-8 since both have similar extent of activation but one (B-0-14) has been uncatalyzed and the other (A-1-8) catalyzed by iron; the latter has been prepared at a lower temperature (800°C instead of 850°C) and in a shorter time (8h. instead of 14h.).

The porosity data of Table 1 and Figure 2 show that the catalytic gasification by iron is very effective, specially in the development of meso and macroporosity. This development increases with increasing iron content of the almond shells. Thus, a 0.01% iron on the almond shells doubles the mesopore volume of the resulting activated carbon. It is also interesting the comparison of carbons A-1-8 and B-0-14, both with similar burn-off; the former, catalyzed by 0.08% iron in the shells, has a much larger meso and macropore volume. The data of Table 1 for the series A-5, corresponding to carbons previously impregnated with 5% iron solution and activated for different lengths (2 to 12h.), show that the development of meso and macroporosity is very important up to sample A-5-6 but no development is taking place for more extended activation (this behaviour corresponds with that shown in Figure 1 for the evolution of activation as a function of time).

Although the catalytic gasification of almond shells clearly increases the meso and macroporosity of the resulting carbons, it does not seem to affect as much the develop-

ment of the microporosity (see Table 1), probably because the lack of accessibility of the iron solution to the interior of the almond shells particles.

References

1. F. Rodríguez-Reinoso, J.D. López-González and C. Berenguer; Carbon 20, 513 (1982).

Table 1.

2. P.L. Walker, Jr., M. Shelef and R.A. Anderson; Chemistry and Physics of Carbon, Vol. 4, Marcel Dekker, N.Y. (1968).
3. D.W. McKee; Chemistry and Physics of Carbon, Vol. 16, Marcel Dekker, N.Y. (1981).
4. F. Rodríguez-Reinoso, A. Linares-Solano, M. Molina Sabio and J.D. López-González; Adsorp. Sci. & Technol., 1, 211 (1984).

Sample	%Fe *	%Activation **	Pore Volumes (cc.g ⁻¹)			
			V _{total} *** (7.5 < ϕ < 1500nm)	V _{meso} *** (7.5 < ϕ < 200nm)	V _{micro}	
					N ₂ (77K)	CO ₂ (273K)
A-0 -8	0	4	0.12	0.07	0.25	0.27
A-0.1-8	0.01	22	0.31	0.15	0.28	0.27
A-1-8	0.08	37	0.60	0.26	0.34	0.27
A-5-8	0.4	67	1.11	0.32	0.30	0.26
A-5-2	0.4	17	0.59	0.19	0.24	0.24
A-5-4	0.4	43	1.01	0.32	0.26	0.24
A-5-6	0.4	57	1.14	0.39	0.32	0.28
A-5-12	0.4	70	1.15	0.29	0.30	0.28
B-0-14	0	35	0.36	0.08	0.47	0.44

* Expressed per gram of dry almond shells.

** % of activation is referred to a theoretically carbonized material.

*** From mercury porosimeter.

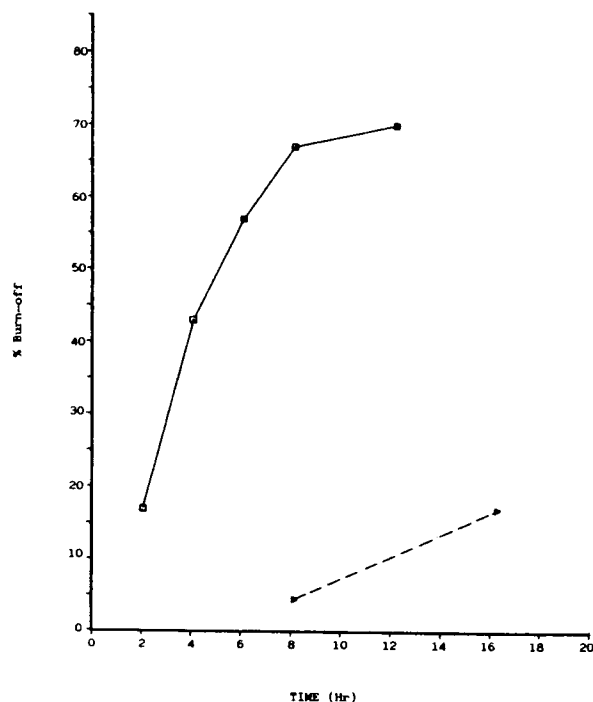


Figure 1

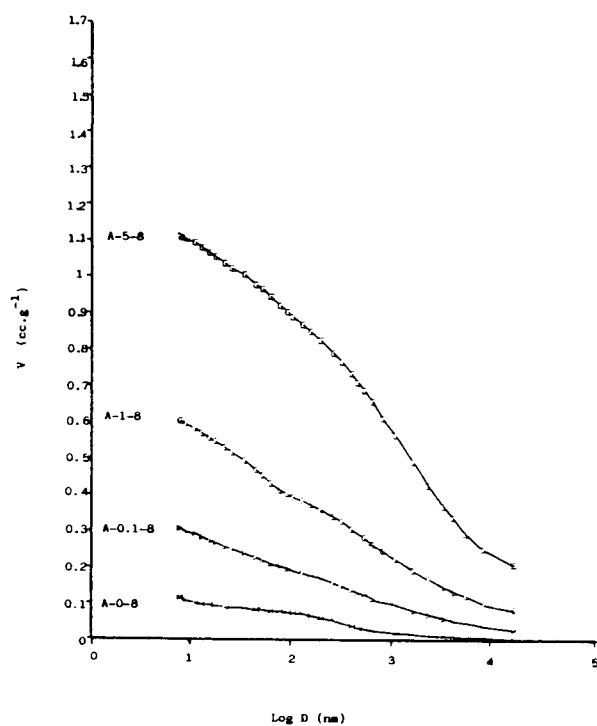


Figure 2