

A STUDY OF THE EFFECTS OF AIR PREOXIDATION AND BURNOFF ON THE PREPARATION OF GRANULAR ACTIVATED CARBONS FROM A SEMIANTHRACITE

*B. Ruiz, J. J. Pis, J. B. Parra and J. A. Pajares
Instituto Nacional del Carbón. C.S.I.C.
Apartado 73, 33080-Oviedo (Spain)*

Introduction

The preparation of activated carbons from coals involves several steps: oxidation, pyrolysis and activation. The porous texture of the final products is conditioned by previous treatment. This work analyses the influence that air preoxidation of coal and the extent of burn-off during activation step have on the textural properties of the activated carbons.

Experimental

A semianthracite, from the Sovilla exploitation in the north of Spain, was used as raw material. The coal was ground and sieved to 1.0-3.0 mm. Representative samples were placed in trays and oxidized in an oven with forced circulation of air, at 270°C, for periods of time ranging from 1 to 7 days. The pyrolysis of fresh and oxidized coal samples was performed under nitrogen up to 850°C at a heating rate of 60 K min⁻¹. The activation of chars was carried out at 850°C with a flow rate of 9 cm³ min⁻¹ of CO₂ up to 51±2% burn-off. Activation of the char from coal which had been oxidized for 5 days was performed between approximately 16 and 81% of burnoff. Textural characterization of coals, chars and activated carbons was carried out by measuring the true (helium) and apparent (mercury) densities, mercury porosimetry, and physical adsorption of N₂ at 77 K, and CO₂ at 273 K. To determine the helium densities, a Micromeritics AccuPyc 1330 apparatus was used. Apparent densities were determined in a Carlo Erba Macropore Unit 120, with mercury at 100 kPa. Isotherms of adsorption of CO₂ and N₂ were made in a Micromeritics ASAP 2010.

Results and Discussion

It is well known that air oxidation introduces important modifications in the chemical composition and texture of coals (1,2). The oxidation of Sovilla semianthracite increases the oxygen content from 1.2 to 22.8% (Table I). The true density increases strongly from 1.34 to 1.57 g cm⁻³, while the apparent density increases slightly from 1.29 to 1.37 g cm⁻³, indicating a densification of carbonaceous matter. The specific surface area calculated from the adsorption of CO₂ at

273 K rises from 161 to 268 m²g⁻¹. N₂ adsorption at 77 K was insignificant.

The pyrolysis of fresh and oxidised coal samples produces a decrease in the oxygen content (Table II). The evolution of volatile matter made the closed porosity already present in the coals accessible. The values of true density of the chars indicate that preoxidation has a positive effect on densification (up to 1.78 g cm⁻³). The CO₂ surface area of char from the non-oxidised coal is 217 m²g⁻¹, while the char obtained from the most oxidised coal exhibits a surface area of 488 m²g⁻¹. The values of the surface area obtained from N₂ adsorption (BET) are insignificant for chars from less oxidised coals. However, values near to 400 m²g⁻¹ for the char obtained from the most oxidised coal clearly confirms the beneficial effect of preoxidation.

In the pyrolysis step a primary pore structure is developed. During the subsequent gasification-activation this structure leads to development of the final porosity of the activated carbons. The activation of the chars determines the higher densification of the carbonaceous matter (He density up to 2.06 g cm⁻³). Total porosity, calculated from the He and Hg densities, is 0.39 for AC0 and 0.60±0.05 for the other activated carbons. The N₂ (BET) and CO₂ (DR) surface areas of the activated carbons are included in Table III. Both parameters increase with the increase in the degree of coal preoxidation, tending to similar values for activated carbons obtained from higher oxidised coals. The values obtained for the N₂ surface area of activated carbons are higher than those obtained with CO₂, indicating a widening of the microporosity (3).

In a previous work (4) with the same coal but using steam as activating agent at 850°C and a soaking time of 1 hour in the pyrolysis step, activated carbons with higher CO₂ areas were obtained, underlining the more dominant role of microporosity. Taking into account that the use of CO₂ as activating agent favours the development of microporosity (5,6), it seems that the soaking time is the factor responsible for the smaller microporosity of the activated carbons obtained.

Furthermore, the effect that the degree of burnoff has on the textural development of activated carbons was studied. One sample of the fresh coal was oxidised for 5 days and after that pyrolysed in the same experimental conditions. Then, this char was activated to different degrees of burnoff between 16

and 81%. Figure 1 shows the N₂ adsorption isotherms of activated carbons with different degrees of burnoff. The increase in the degree of burnoff from 16 to 35% mainly develops the microporosity. Burnoff to 50% reduces the volume adsorbed at very low pressures, while it increases the volume adsorbed at higher pressures. The activation to higher degrees of burnoff continues to reduce the volume of micropores and to increase the volume of bigger pores. Activation up to 81% leads to a decrease in the total volume adsorbed, probably due to destruction of the walls of the pores.

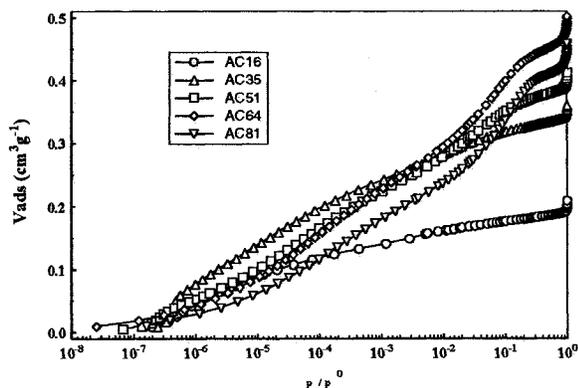


Figure 1. N₂ isotherms of activated carbons with different burnoff

Table IV shows the true and apparent densities and the specific surface area N₂ (BET) values for the activated carbons with different degrees of burnoff. Mercury densities decrease continuously with increasing burnoff, due to the generation of porosity in the activated materials. As for true density, a slight increase with the degree of burnoff was observed, as a consequence of the densification of activated carbons. Similar trends were found in another work (7) with the same starting coal but using steam in the activation step.

Conclusions

Air preoxidation of a semianthracite at 270°C modifies the texture of the subsequent materials obtained from oxidised coal to activated carbons. A densification of the carbonaceous matter and an increase in the volume of pores is produced.

There is an increase in the adsorption capacity with the burnoff up to 64%; a higher degree of burnoff destroys the walls of the micropores and generates mesoporosity.

Acknowledgments

The authors thank the DGICYT (Project PB94-0012-C03-01) for financial support.

Table I. Chemical analysis of fresh and oxidised coals (*).

Sample	OX0	OX1	OX2	OX5	OX7
% C	92.8	85.8	83.0	74.4	73.3
% O	1.2	8.7	11.8	21.3	22.8
% VM	15.1	19.6	22.5	32.6	34.4

Table II. Chemical analysis of chars (*).

Sample	PI0	PI1	PI2	PI5	PI7
% C	95.5	93.8	92.6	91.8	91.7
% O	1.2	2.5	3.7	4.3	4.2
% VM	3.6	3.3	3.3	3.7	3.4

Table III. Textural parameters of activated carbons. Preoxidation effect. (51±2% burnoff) (*).

Sample	AC0	AC1	AC2	AC5	AC7
ρ He (g cm ⁻³)	1.942	1.926	1.941	2.063	2.028
ρ Hg (g cm ⁻³)	1.19	0.74	0.72	0.85	0.92
S _{CO₂ DR} (m ² g ⁻¹)	73	157	226	649	688
S _{N₂ BET} (m ² g ⁻¹)	67	267	414	1039	1061

Table IV. Textural parameters of activated carbons. Burnoff effect (16 to 81%) (*).

Burnoff (%)	AC16	AC35	AC51	AC64	AC81
ρ He (g cm ⁻³)	2.011	2.070	2.079	2.087	2.060
ρ Hg (g cm ⁻³)	1.18	1.02	0.86	0.72	0.67
S _{N₂ BET} (m ² g ⁻¹)	461	842	913	1048	884

(*) Values are expressed in d.a.f. basis

References

1. Pis, J.J., Centeno, T.A., Mahamud, M., Fuertes, A.B., Parra, J.B., Pajares, J.A. and Bansal, R.C., *Fuel Proc. Technol.*, 1996, 47, 119.
2. Ruiz, B., Parra, J.B., Alvarez, T., Fuertes, A.B., Pajares, J.A. and Pis, J.J., *Appl. Catal.*, 1993, A 98, 115.
3. Garrido, J., Linares-Solano, A., Martín-Martínez, J.M., Molina-Sabio, M., Rodríguez-Reinoso, F. and Torregrosa, R., *Langmuir*, 1987, 3, 76.
4. Parra, J.B., Pis, J.J., Sousa, J.C. de, Pajares, J.A. and Bansal, R.C., *Carbon*, 1996, 34, 783.
5. Bansal, R.C., Donnet, J.B. and Stoeckli, F., *Active Carbon*, Marcel Dekker, New York, 1988.
6. Molina-Sabio, M., González, M.T., Rodríguez-Reinoso, F. and Sepúlveda-Escribano, A., *Carbon*, 1996, 34, 505.
7. de Sousa, J.C., Parra, J.B., Pajares, J.A. and Pis, J.J. in *Stud. in Surface Sci. and Catal.*, vol. 87, ed. J. Rouquerol et al. Elsevier Science B.V. Amsterdam, 1994, p. 603.