STEAM AND CO_2 ACTIVATION OF BITUMINOUS COAL IN A FLUIDIZED BED REACTOR.

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Introduction

During the last five years, intensive research work has been carried out in our laboratory to analyze Spanish coals as raw materials for the preparation of activated carbons [1-3]. The aim of this study is not restricted to laboratory findings. The purpose is also to scale up the preparation to a pilot fluidized bed reactor (20-40Kg/day) designed and built at the University of Alicante [1, 4]. Since it is well known that the preparation of selective activated carbons need to control many variables and coals are highly heterogeneous precursors, many parameters (as coal rank, ash content, BO degree, activation agent, etc.) have been analyzed.

In this paper we shall present and discuss the effect that both the reactor type and the activation agent used have on the textural properties of the activated carbons obtained.

Experimental

An Spanish bituminous coal from Puertollano (María Isabel mine) with a 8 wt% in ash content was selected for this study. The activation process was carried out in two stages, i.e. carbonization followed by activation. Coal carbonization was performed in a nitrogen flow at 1123K during 1 hour, in a tubular furnace. The char was activated either in an horizontal or in a fluidized bed reactor. In the former, 3 or 4 g of char was activated at 1123K either in a steam/N_2 mixture or in a CO_2 atmosphere (100 ml/min). In the fluidized bed reactor, 14 g of char was either activated at 1073K in a pure steam flow (5.5 g H_2O/min) or in CO_2 (4000 ml/min) at 1123K. In each case, series of activated carbons, covering a wide range of BO, were prepared using different activation times. These activated carbons were characterized by means of physical gas adsorption (N_2 at 77K and CO_2 at 273K), mercury porosimetry and SEM.

Results and discussion.

Once variables such as fluidization conditions, particle size, and activation temperatures were established, the effect of the reactor type could be analyzed. Figure 1 shows, as a function of burn-off, the apparent surface areas obtained with both reactors and with both activating agents. The results for steam activation in both reactors and for CO_2 activation in the horizontal fixed bed reactor are similar and promising. The apparent surface area linearly increases with burn-off reaching for a 50 % BO, surface areas higher than 1000 m^2/g. From the results of this Figure it is deduced that steam activation is not affected by the reactor type. Therefore, with this activating agent the fluidized bed activation offers the advantage of being much faster (even using lower activation temperature, 1073 K, than in the fixed bed, 1123 K).

When activation is performed with CO_2 the results in the two reactors differ greatly, as can be noticed in Figure 1. Fluidized bed activation is much less favourable than its horizontal bed counterpart (surface area are 30 % lower). To analyze this negative influence of the reactor type, the effect of the CO_2 flow rate used during the activation process was studied. Figure 2 shows the CO_2 and N_2 apparent surface areas plotted as a function of the CO_2 flow rate. The plot also includes, for comparative purpose, the results of the fixed bed activation. The graph clearly indicates that activated carbons obtained in both reactors with a 80 ml/min flow have very similar apparent and microporous surface areas. However, the surface areas noticeably decrease when the flow, in the fluidized bed, reachs 500 ml/min.

This detrimental effect on the porosity development of the samples as a consequence of the CO_2 flow does not occur with steam. The different performance of CO_2 and steam must be related to the different way in which such agents operate and especially with the fact that H_2O molecules have greater accesibility to the inner porosity of char than CO_2, which in turn favours the activation process [5,6]. According to these results, the activation in the pilot fluidized bed reactor, should only be performed in steam. The use of CO_2 in this reactor is not recommended because its flow would have to be limited to values of 80 ml/min. The activation at this low flow rates will not occur under fluidization conditions and hence the activation time required will be excessively long.

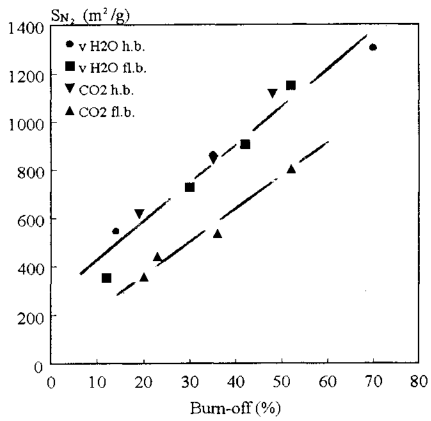

Figure 1. *Variation of the apparent surface area versus burn-off.*

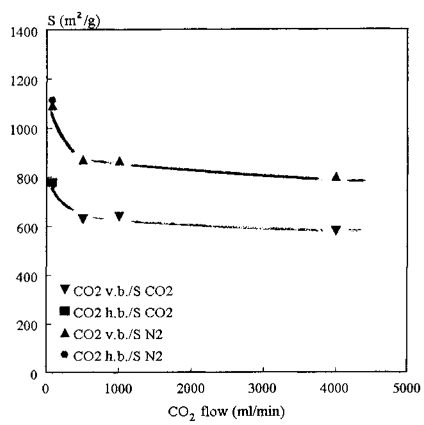

Figure 2. *Variation of the apparent surface area as fuction of CO_2 flows. (▲ N_2 BET, ▼ CO_2 DR)*

From the above results the pilot plant reactor is being operated with steam at 1073K. The results obtained in both laboratory and pilot scales are quite similar. Thus, in the pilot reactor using one or two hours of activation time, the % BO reached is near 50 % and the apparent surface area obtained are also above 1000 m^2/g .

Conclusions

The study of the effect of the reactor type in the preparation of activated carbons in both steam and CO_2 has allowed us to draw the following conclusions. It is possible to obtain activated carbons with acceptable adsorption characteristics from a bituminous spanish coal, with a 8 wt % ash content, using steam as activating agent in fluidized and horizontal bed reactors. The fluidized bed offers the advantage of requering a lower activation time, to reach a given activation degree, and a lower activation temperature. Fluidized bed reactor activation is not advisable with CO_2. The large flow rates used under fluidization conditions inhibit pore volume development.

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