

# ACTIVATED CARBON FIBERS FROM PAN. I: STEAM AND KOH ACTIVATION

*I. Martin-Gullon, M. Jagtoyen and F. Derbyshire.*

*Center for Applied Energy Research, University of Kentucky  
3572 Iron Works Pike, Lexington, KY 40511, United States of America.*

## Introduction

Research in activated carbon fibers (ACF) has attracted increasing attention in the last several years in terms of their synthesis, and their suitability in different applications that include molecular sieving, solvent recovery, gas storage and catalysis [1]. A specific area of research has formed at the use of ACF as catalyst for the removal of flue gas SO<sub>2</sub> as sulphuric acid, via oxidation on the carbon surface [2-3].

Activated poly acrylo nitrile (PAN) based carbon fibers have been reported to exhibit a high activity for this reaction, and this might be attributable to their high nitrogen content [3-4]. It also appears that their catalytic activity is affected by the method of activation – namely, activation in steam versus chemical activation using KOH. In this paper, a study has been made to compare the effect of those two activation methods on the properties of PAN-ACF.

## Experimental

Commercial PAN fibers were obtained from RK Carbon Fibers Inc. (Milcar90 type PION18). Both steam and KOH activations were carried out in a stainless steel horizontal tubular reactor (2 inch diameter) placed inside an electric furnace. For steam activations, the fibers were precarbonized to temperatures between 600-1000°C in a flow of nitrogen (the as received fibers had been heat treated to about 600°C. Activations were conducted in a flow of 50% H<sub>2</sub>O/50% N<sub>2</sub> from 650-850°C.

KOH activations were carried out in the same reactor, placing in the inconel crucible the fibers mixed with a KOH solution. Runs were carried out in a nitrogen flow, from temperatures from 500 to 1000°C and reagent/fibers ratio of 1 and 3.

ACF's produced by both methods were characterized by 77K nitrogen adsorption isotherms (Coulter Omnisorp 610) and SEM (Hitachi 2700 with LaB<sub>6</sub>).

## Results

Upon steam activation, even to levels of burn-off of over 80%, the morphology of the parent fibers is preserved. This observation also holds for KOH activation using low reagent ratios. However, at a ratio of 3.0 the fiber form is completely disrupted at all heat treatment temperatures, as shown by the scanning electron micrographs in Figure 1. It appears that this drastic change is inherent to the development of very high surface areas, as discussed below.

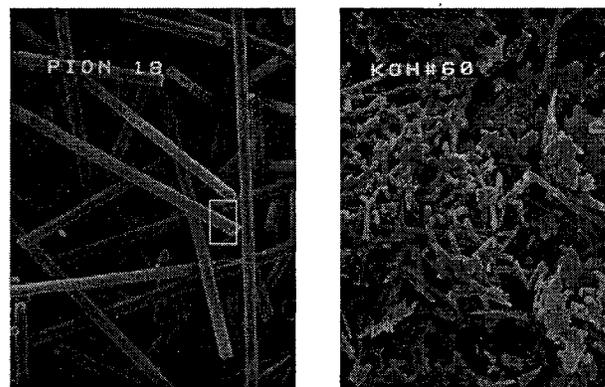


Figure 1. SEM micrographs of parent fibers (left) and activated with KOH at 700 and reagent ratio 3 (right).

A comparison of the extent of surface area development with burn-off (or weight loss for KOH activation) is shown for the two activation methods in Figure 2. The data shown for steam activation were obtained for samples at different carbonization temperatures and different activation temperatures. Although not evident from the figure, it was found that, as expected, increasing the carbonization temperature reduced the rate of activation. Nonetheless, all of the data follow the same trend and it is apparent that only modest surface areas are developed by this method of activation: even approaching 100% burn-off the surface area is only around 700 m<sup>2</sup>/g. Analysis of the adsorption isotherms shows that essentially all the pore volume is contained in micropores, and there is negligible mesopore

development. These findings are in contrast to the results we have obtained with the steam activation of isotropic pitch fibers, where high surface areas are developed at moderate levels of burn-off and porosity predominant microporous (5). Presumably, this distinction is related to fundamental differences in the structure and composition of PAN- and pitch-based carbon fibers.

Chemical activation with KOH produces much higher surface areas in the PAN-based fibers. At high levels of weight loss, the BET surface area approaches 3500 m<sup>2</sup>/g which is similar to that found in the seminal work by Wennerberg and O'Grady [6] and that has been reported by many other researchers. As already noted, the very high surface areas are only obtained at the expense of altering the physical form from that of a fiber to a fine powder. The surface area passes through a maximum with increasing extent of activation - an outcome that is produced by increasing the heat treatment temperature, and can also be obtained by increasing the reagent ratio (ref). The maximum corresponds to a widening of the pore structure, in which micropore volume is reduced while there is an increase in mesopore volume, such that the total pore volume continues to increase over this range of conditions, Figure 3.

#### Literature.

1. Suzuki, M. *Proc. 21st Biennial Carbon Conference*, 1993.
2. S. Kisamori, K. Kuroda, S. Kawano, I. Mochida, Y. Matsamura, M. Yoshika. *Energy & Fuels*, 8, 1337, 1994.
3. Y. Fei, Y. Sun., E. Givens, F. Derbyshire. *ACS proc.*, 40(4), 1051, 1995
4. G. Kimber, F. Derbyshire, M. Jagtoyen, Y. Fei. *Carbon '95*, 518, 1995.
5. Wennerberg, A. N, Grady, T. M.(1978), *United States Patent* 4 082 694 .

**Acknowledgements.** This work was sponsored by the Fossil Energy AR&TD Materials Program, US Department Energy, under contract no. SC19X-SN719C. The authors also thank Danny Turner for his valued help.

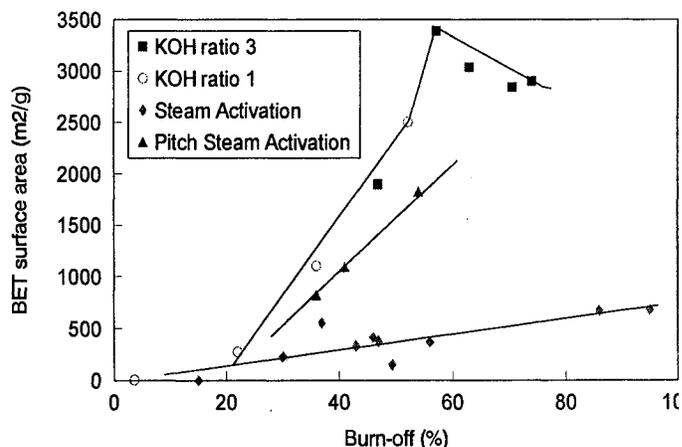


Figure 2. Development of surface area with degree of activation in steam and with KOH.

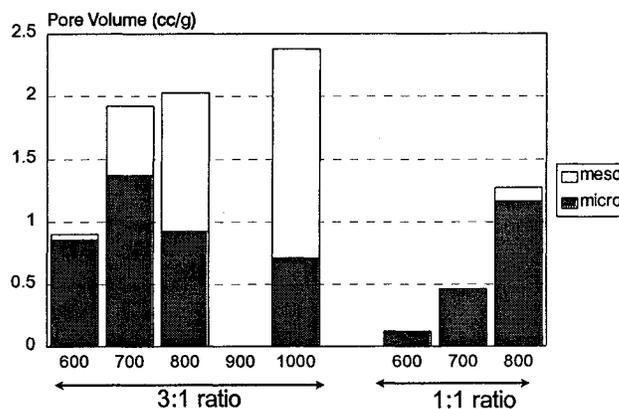


Figure 3. Change in pore size distribution of KOH activated carbon fibers as a function of reagent ratio and heat treatment temperature.