

## CARBON FIBER CARBON COMPOSITES FOR CATALYST SUPPORTS

J. W. Klett and T. D. Burchell

Carbon and Insulation Material Technology Group, Metals and Ceramic Division  
Oak Ridge National Laboratory  
PO Box 2008, Oak Ridge, TN 37831-6087

### INTRODUCTION

Gas separation, waste treatment, and catalyst supports are common industrial uses for active carbons. Settling, channeling, and pressure loss during operation are major problems associated with typical granular activated carbons. A novel process has been developed to produce a porous carbon fiber carbon composite with a density less than 0.2 g/cc. This composite can be activated to produce a significant volume of mesopores (2 to 50 nm). Furthermore, the rigid structure has macropores in the range of 50-100 microns which allow for excellent fluid flow through the sample, resulting in a low pressure drop. The rigid nature of the composite also eliminates channeling and settling, therefore making it a possible candidate for a catalyst support.

### EXPERIMENTAL

*Composite Fabrication.* The porous carbon fiber carbon composite was manufactured via a slurry molding technique, illustrated in Fig. 1, originally developed to produce high temperature thermal insulation. Fortafil P200 PAN-based carbon fibers were slurried in a water solution with phenolic DUREZ<sup>®</sup> resin at a ratio of 1.5:1 by mass. The slurry was then vacuum molded into a flat plate 12 x 12 x 2 inches and dried at 50°C in a convection oven. After curing for 3 hours at 130°C, the as-molded part was carbonized under flowing nitrogen at 5°C/min to 650°C.

*Steam Activation.* Samples were evacuated to 50 millitorr and then steam activated at 650 and 850°C for 60, 120, 240, and 480 minutes. Helium saturated with water vapor at 20°C was used as the activation gas.

*Characterization.* Both physical examination and mercury porosimetry were used to characterize the samples.

### RESULTS

*Carbonization.* The as-molded samples lost 18.3% by weight during the carbonization step, decreasing in density from 0.21 to 0.17 g/cc. Figure 2 is a SEM photograph of the carbonized preform illustrating the porous architecture of the composite. Significant macroporosity between the fibers allow for easy access to the mesopores in the fibers. Figure 3 illustrates both the bimodal distribution of the pores and the total mesopore volume in the as-received PAN fibers, the as-molded part, and the carbonized sample. Figure 4 is a plot of the cumulative Mercury surface area versus pore diameter. From this, it appears that the phenolic resin wets the surface of the fibers during the drying process and closes some of the pores, thus reducing the effective surface area. Upon carbonization, there is a rise in active surface area (572 m<sup>2</sup>/g) and mesopore volume (1.02 cm<sup>3</sup>/g), indicating a significant opening of pores in the fibers due to residual oxygen trapped

in the macroporous structure. During carbonization, this residual oxygen gassifies the fibers and increases the number of mesopores accessible to gas.

*Activation.* The percent burn-off versus the activation time, Fig. 5, illustrates consistent burn-off of the material at both activation temperatures. This indicates adequate diffusion of the steam into the samples and, thus, shows the potential as a catalyst support for gas-phase reactions. The average mesopore diameter increases slightly with activation, independent of the temperature (see Fig. 6). On the other hand, the surface area decreases substantially with burn-off, nearly 70% at burn-off's of 22% (see Fig. 7). Surprisingly, the volume of mesopores shows a similar decrease with burn-off, nearly 64% (see Fig. 8).

### DISCUSSION

Apparently, the PAN-based carbon fibers are not very reactive to steam at 650°C, but are consumed readily at 850°C. The decrease in both mesopore surface area and mesopore volume, combined with a very slight increase in pore diameter, suggest that steam activation did not etch the fiber and increase the pore size. Instead, the activation may have consumed the fiber radially, thereby decreasing the number of accessible pores. Examination with SEM revealed a decrease in some fiber diameters from 8.75 μm to about 5.2 μm. This diameter change would decrease the volume of the fiber by about 65%, which correlates to the decrease in both surface area and mesopore volume.

The large number of mesopores in the carbonized fibers seems reasonable because the fibril structure of PAN fibers [1] is conducive to large pore volumes in the mesopore range. The typical crystal size in PAN fibers is around 1.6 nm [2]. From the extensive folding and fibril nature of these crystals, as shown in Fig. 9 [1], there is likely a large fraction of mesopores in the size range of 2 to 10 nm, confirmed by Figs. 3 and 4.

For typical active carbons, the external surface area (associated with pores greater than 2 nm in diameter) averages approximately 100 m<sup>2</sup>/g and rarely exceeds 200 m<sup>2</sup>/g [3, 4]. In addition, some active carbons contain mesopore volumes in the range of 0.4 to 0.5 cm<sup>3</sup>/g [4, 5]. However, most active carbons exhibit pores mainly in the micropore range (<2 nm) with the total mesopore volume accounting for only 0.05 cm<sup>3</sup>/g [3], compared to >0.4 cm<sup>3</sup>/g produced in this study.

### CONCLUSIONS

Due to the porous nature of the as-molded part and the fact that the sample was not evacuated prior to carbonization, residual air may be trapped inside the macropores of the structure during carbonization. The residual oxygen attacks

the surface of the PAN fibers and exposes the majority of the mesopores present in the as-received fibers and, therefore, produces (572 m<sup>2</sup>/g). Unfortunately, it appears that the PAN fibers do not etch well with steam. Instead, the fiber is consumed radially, thereby decreasing the mesopore volume and active surface area substantially upon steam activation. Fortunately, because this material does not need to be activated to produce large active surface areas and mesopore volumes, a substantial decrease in cost can be realized. Furthermore, activation with either oxygen or carbon dioxide may prove beneficial, unlike steam.

### LITERATURE CITED

1. Diefendorf, R. J., and E. W. Tokarsky, *Polymer Eng. Sci.*, **15**, 150 (1975).
2. Donnet, J-P, and R. C. Bansal, *Carbon Fibers*, Marcel Dekker, Inc., New York (1990).
3. Bansal, R. C., J-P Donnet, and Fritz Stoeckli, *Active Carbon*, Marcel Dekker, Inc., New York (1988).
4. Dubinin, M. M., and D. V. Fedoseev, *Izv. Akad. Nauk. SSSR (ser. Khim.)* p. 246, (1982).
5. Andreeva, G. A., Polyakov, N. S., Buvvinin, M. M., and K. M. Nikolaev, *Izv. Akad. Nauk. SSSR (ser. Khim.)* p. 2193, (1981).

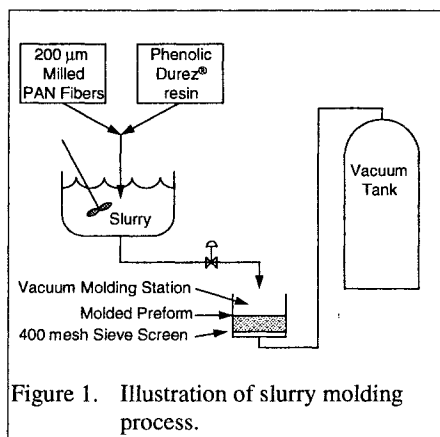


Figure 1. Illustration of slurry molding process.

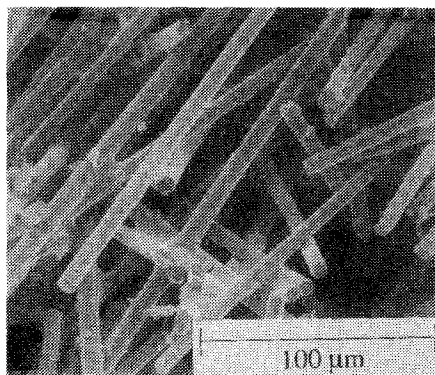


Figure 2. SEM photo of the porous carbonized composite.

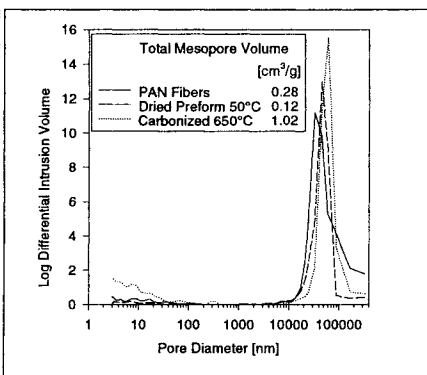


Figure 3. Pore distribution in PAN fibers, molded and carbonized parts.

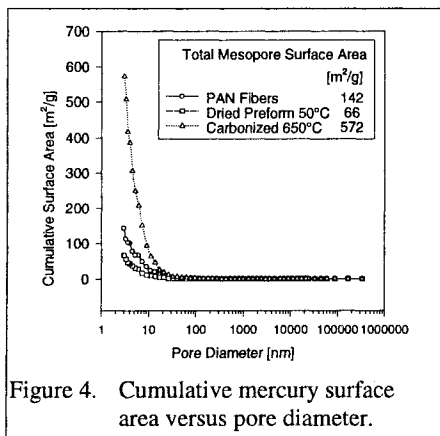


Figure 4. Cumulative mercury surface area versus pore diameter.

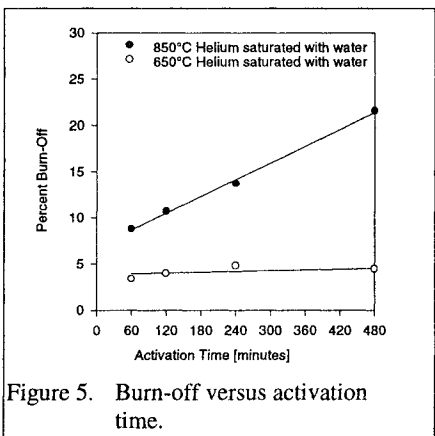


Figure 5. Burn-off versus activation time.

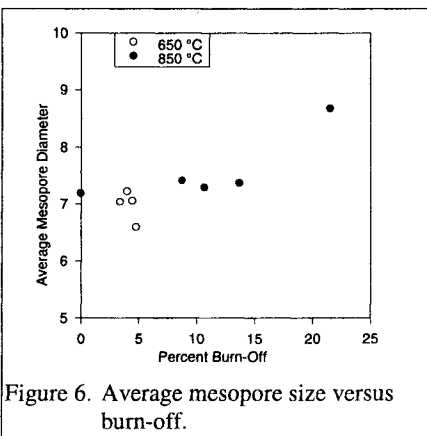


Figure 6. Average mesopore size versus burn-off.

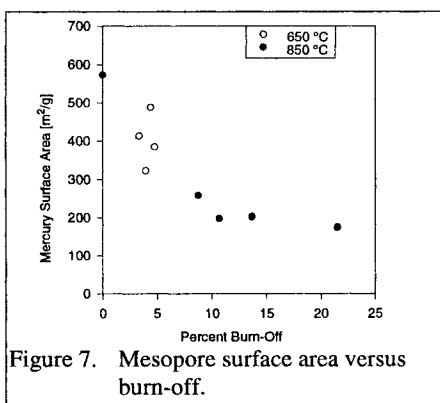


Figure 7. Mesopore surface area versus burn-off.

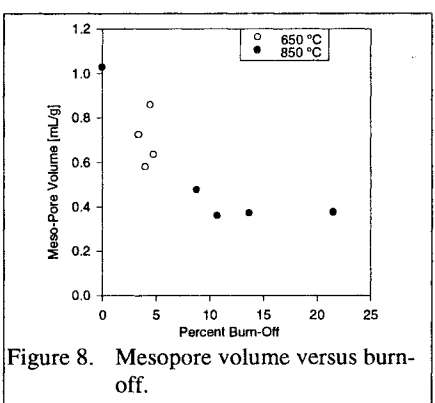


Figure 8. Mesopore volume versus burn-off.

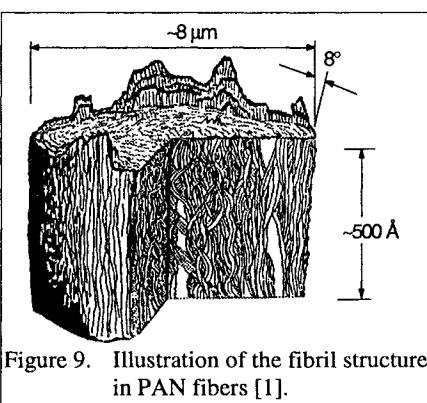


Figure 9. Illustration of the fibril structure in PAN fibers [1].