

## **SYNTHESIS AND CHARACTERIZATION OF ACTIVATED PITCH-BASED CARBON FIBERS**

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### **INTRODUCTION**

Recently there has been an increase in interest in activated carbon fibers (ACF) produced from pitch precursors. These fibers offer a number of advantages and because of their novel properties may be more suitable in certain applications than granular and powdered activated carbons. Being fibrous in form, they can be incorporated more easily into fabrics, filters and other articles which would require special designs to include a powder or granular product. The isotropic nature of pitch-based fibers makes it possible to create high specific surface areas in the region of 700 - 2000 m<sup>2</sup>g<sup>-1</sup>; because diffusion limitations are minimal, the fibers exhibit very high rates of adsorption and desorption, and they may be produced in a wide variety of woven and non-woven forms.

The adsorptive properties of petroleum pitch-based ACF are not as well-studied as other types of activated carbon fiber. This paper will discuss the manufacture and pore structure characterization by gas adsorption and mercury porosimetry of ACF derived from Ashland petroleum pitch.

### **MANUFACTURE OF ACTIVATED PITCH-BASED CARBON FIBERS**

Figure 1 is a block diagram of the method for producing ACF from petroleum pitch. The starting material is a heavy petroleum fraction from catalytic cracking which must be purified to remove catalytic fines, ash and other impurities. Pitch is produced by distillation, thermal cracking, solvent extraction or combined methods. Pitch is a complex mixture of polynuclear aromatic hydrocarbon species, with sulfur and nitrogen incorporated into the aromatic structure as heteroatoms. Short aliphatic substituents are present on the "typical" petroleum pitch molecule. Softening temperature [1] is a common test method for characterization. The softening point must often be increased by further distillation prior to fiber forming by melt spinning or melt blowing. In these fiber forming processes, the pitch is melted to a carefully controlled viscosity and then forced through a number of fine capillaries to produce the fiber as the pitch re-solidifies. The diameter of the fiber is controlled by drawing the fiber and winding it onto a reel for the case of melt spinning. In melt blowing, a stream of air is used to blow the fiber onto

a moving belt as it forms into a random mat. Extreme care must be taken to control temperature and other fiber forming conditions.

Once formed, the "green" pitch fiber is still fusible. In order to withstand the high carbonization temperature without remelting, it must first be heated gradually and carefully in an oxidizing atmosphere to render it infusible. The fiber can then be carbonized under an inert atmosphere until it contains about 95% carbon by weight. Activation of the carbon fiber is accomplished in much the same manner as for other types of activated carbon: by steam, by carbon dioxide or by chemical oxidation. The resulting chemical reactions attack the fiber surface and form pores, which are classified by diameter: micropores (< 2 nm), mesopores (2 - 50 nm) and macropores (> 50 nm).

#### CHARACTERIZATION OF ACTIVATED CARBON FIBERS

Several methods have been established and used to characterize activated carbon fibers of several types [2-6]. Frequently studied is the adsorption of gases (especially nitrogen and carbon dioxide), and of solvent vapors (e.g. carbon tetrachloride, benzene or toluene). Activated coal-tar pitch fiber was characterized by Kaneko *et al* [3], who obtained adsorption isotherms of nitrogen, benzene, NO, SO<sub>2</sub> and NH<sub>3</sub>, and then determined a number of surface characteristics. References were also cited in [3] on prior studies of activated fibers derived from cellulose, polyacrylonitrile (PAN) and phenol resin. Activated fibers derived from an unspecified pitch were characterized by Lee *et al* [4-5] and Ryu [6], who measured adsorption of nitrogen, CO<sub>2</sub>, iodine and methylene blue. Also contained in reference [6] were detailed discussions of methods used and measurements of the degree of activation as a function of burn-off, or weight percent lost during activation. Finally in [6], pore size distribution plots were compared for phenol resin-based ACF and a granular activated carbon.

The present paper describes the surface characteristics of petroleum pitch-based ACF as determined by mercury porosimetry and adsorption of nitrogen at 77 K and carbon dioxide at 195 K.

#### EXPERIMENTAL

Isotropic petroleum pitch-based non-woven carbon fiber mat was activated using steam to yield activated fibers with varying degrees of burn-off as indicated in Table 1. A sample of powdered coconut shell activated carbon (Pica G210) was chosen for comparison.

Specific volumes (cm<sup>3</sup>g<sup>-1</sup>) and surface areas (m<sup>2</sup>g<sup>-1</sup>) of macropores and mesopores were determined by mercury porosimetry using a Quantachrome Autoscan-60 porosimeter that attained a maximum pressure of 60 000 psig. Nitrogen surface area measurements at 77 K were carried out using a Quantachrome Autosorb 6 apparatus to provide a 40 point adsorption and a 40 point desorption isotherm. Isotherms were also obtained using carbon dioxide at 195 K. Specific surface areas were calculated from both the nitrogen and the carbon dioxide isotherms using the Brunauer, Emmett and Teller (BET) theory [2].

Micropore volumes and mesoporous surface areas were determined from the nitrogen data using the  $\alpha_s$  method [2]. A "notional" micropore surface area was taken as the BET surface area minus the mesopore surface area. Micropore volumes were also calculated from the  $N_2$  and  $CO_2$  adsorption data using the Dubinin-Radushkevich (DR) method [2].

## RESULTS AND DISCUSSION

A Type 1 isotherm is observed for ACF 86-1 and G210 carbon, Figure 2; similar isotherms were found for the other ACF samples. The ACF isotherm shows slight hysteresis extending to low relative pressures; the G210 isotherm shows similar hysteresis but with a step at  $p/p_0 \sim 0.45$ . These results suggest that the ACF contain mainly narrow micropores with little mesoporosity. G210 powdered carbon is also mainly microporous, but with larger mesoporosity than ACF. These qualitative observations are supported by  $\alpha_s$  analysis, Table 1, which shows that although  $S_{BET}$  values for the two carbons are similar, the mesoporous surface areas are 9 and 15  $m^2g^{-1}$  for ACF 86-1 and G210 carbon, respectively. Table 1 shows that it is possible to vary BET and mesoporous surface areas of ACF by varying the degree of activation.

Estimates of micropore radii,  $r$ , were made using the Dubinin-Stoeckli (DS) equation [7]:  $E_{or} = 14.8 \pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{nm}$ , where  $E_o$  is the characteristic energy obtained by application of the DR equation to nitrogen adsorption isotherms. Values of  $r$  increase progressively with increase in burn-off of the ACF, Table 1. Similar trends have been inferred from studies of granular activated carbons [8] and our results are consistent with those reported by Kaneko *et al* [3] for pitch-derived ACF with progressively increasing surface areas.

Higher BET surface areas are obtained in all cases from adsorption of  $CO_2$ , Table 2, showing that micropores in ACF and G210 carbon are more accessible to  $CO_2$  than to  $N_2$ . For both  $CO_2$  and  $N_2$  adsorption there is a linear correlation between  $S_{BET}$  and the extent of burn-off, Figure 3, as was also reported by Lee *et al* [4]; it follows from this that there is also a linear correlation between  $S_{BET}$  for  $CO_2$  and  $N_2$ . Micropore volumes for adsorption of  $N_2$  obtained from the DR equation are comparable to those obtained by the  $\alpha_s$  method. Although  $S_{BET}$  values for  $CO_2$  at 195 K are greater than those for  $N_2$  at 77 K, DR micropore volumes for  $N_2$  are comparable with those for  $CO_2$ . This trend has also been noted previously for granular carbons [9].

It was confirmed by mercury porosimetry that ACF samples contained no macropores, Table 3. In contrast, G210 carbon had a macropore volume of 0.28  $cm^3g^{-1}$ . Mesopores are found in both types of carbon using mercury porosimetry, Table 3. For both ACF and G210 carbon estimates of the mesoporous surface areas by the  $\alpha_s$  method are smaller than those estimated from mercury porosimetry at 60 000 psig. This may be due to breakdown of the pore structure under the high pressures used [10].

Results for a lower mercury pressure, 50 000 psig, Table 3, show better agreement for the ACF materials.

#### CONCLUSIONS

Activated petroleum-pitch-based carbon fibers are predominantly microporous, showing very little mesoporosity and no macroporosity. This is consistent with previously published results for ACF from coal-tar pitch and other sources. On the other hand, the mesopore and macropore structures of a powdered activated carbon are more highly developed. This work has shown that it is possible to vary BET and mesoporous surface areas of ACF by varying the degree of activation.

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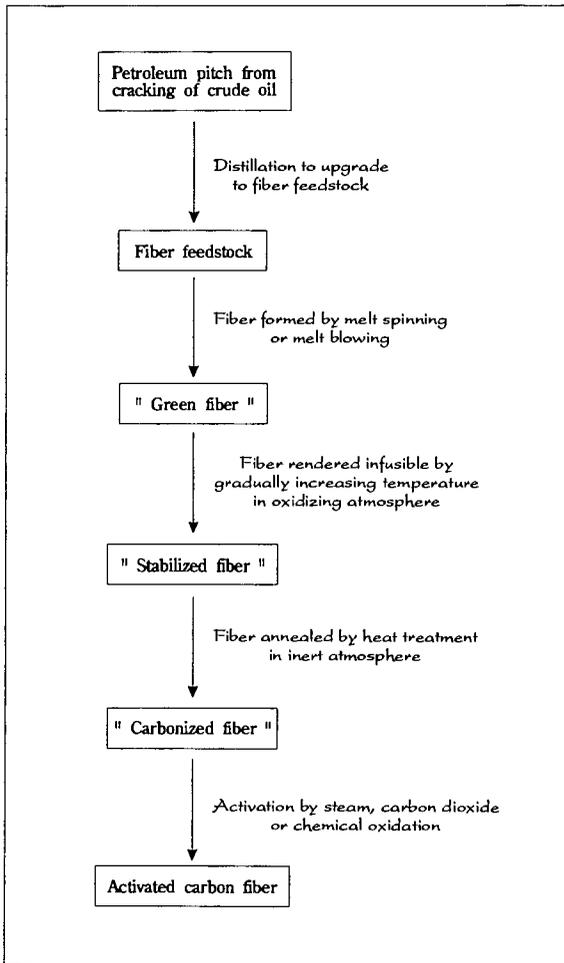


Figure 1 : Schematic diagram of the production of activated carbon fibers from isotropic petroleum pitch

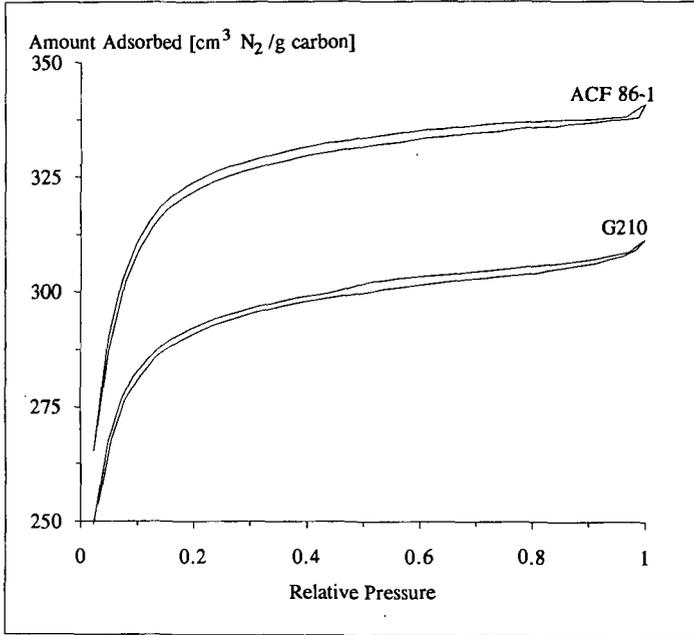


Figure 2 : Sorption isotherms for nitrogen at 77 K of G210 powdered activated carbon and ACF 86-1.

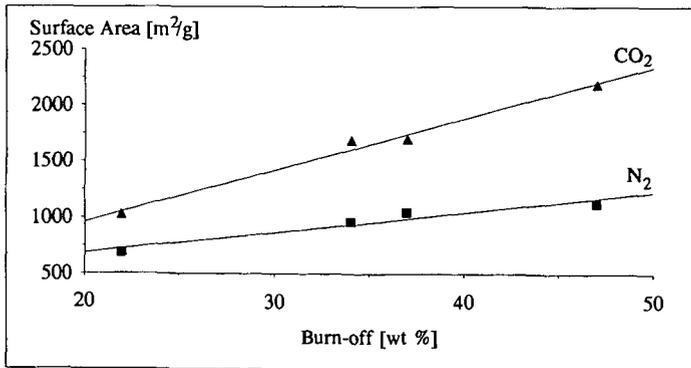


Figure 3 : BET surface areas from nitrogen ( 77 K ) and carbon dioxide ( 195 K ) adsorption on ACF as a function of burn-off.

Table 1. Pore structure analysis of activated carbons from N<sub>2</sub> adsorption data.

Sample	Burn-off (wt %)	BET Surface Area (m <sup>2</sup> /g)	Mesopore Surface Area <sup>1</sup> (m <sup>2</sup> /g)	Notional Micropore Surface Area (m <sup>2</sup> /g)	Micropore Volume <sup>1</sup> (cm <sup>3</sup> /g)	Micropore Volume <sup>2</sup> (cm <sup>3</sup> /g)	DS Mean Micropore Radius <sup>3</sup> (nm)
G210 Powdered Carbon	Not available	1193	15	1178	0.44	0.45	0.9
Carbon Fiber 41-1	22	685	2	683	0.26	0.26	0.4
Carbon Fiber 85-1	34	960	6	956	0.36	0.36	0.7
Carbon Fiber 70-1	37	1046	6	1040	0.39	0.40	0.8
Carbon Fiber 86-1	47	1123	9	1114	0.42	0.45	0.9

1 Calculated from the  $\alpha_s$  method [Ref. 2]

2 Calculated from the Dubinin - Radushkevich (DR) equation [Ref. 2]

3 Calculated using the Dubinin - Stoeckli (DS) equation  $E_{or} = 14.8 \pm 0.6 \text{ kJ.mol}^{-1}.\text{nm}$  [Ref. 7]

Table 2. Pore structure analysis of activated carbons from CO<sub>2</sub> adsorption data.

Sample	Burn-off (wt %)	BET Surface Area (m <sup>2</sup> /g)	DR Micropore Volume <sup>1</sup> (cm <sup>3</sup> /g)
G210 Powdered Carbon	Not available	1736	0.37
Carbon Fiber 41-1	22	1025	0.28
Carbon Fiber 85-1	34	1689	0.38
Carbon Fiber 70-1	37	1697	0.40
Carbon Fiber 86-1	47	2188	0.44

1 Calculated from the Dubinin - Radushkevich (DR) equation [Ref. 2]

Table 3. Pore structure analysis of activated carbons from mercury porosimetry.

Sample	Burn-off ( wt % )	Macropore Volume ( cm <sup>3</sup> /g )	Mesopore Volume ( cm <sup>3</sup> /g )	Mesopore Surface Area 50 000 psig ( m <sup>2</sup> /g )	Mesopore Surface Area 60 000 psig ( m <sup>2</sup> /g )
G210 Powdered Carbon	Not available	0.28	0.08	37	55
Carbon Fiber 41-1	22	0	0	5	13
Carbon Fiber 85-1	34	0	0.04	6	21
Carbon Fiber 70-1	37	0	0.04	9	32
Carbon Fiber 86-1	47	0	0.05	13	49