

# PORE SIZE DISTRIBUTION OF ACTIVATED CARBON FIBERS DETERMINED BY A MODEL ISOTHERM EQUATION

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Pore size distribution (PSD) of microporous carbon is often associated with studies on gas separation and storage by physical adsorption, and heterogeneous catalysis. Many methods have been proposed to determine the PSD based on N<sub>2</sub> 77 K adsorption isotherm. Typical examples are MP (by Mikhail et al.), JC (Jaroniec and Choma), HK (Horvath and Kawazoe) and SNAP (by Seaton et al.) methods.<sup>1,2</sup> In this paper, an alternative way is proposed to calculate the PSD of three select activated carbon fibers (ACFs) using a model adsorption isotherm equation derived from statistical mechanical principles. Modeling results are compared with those obtained by three typical methods: MP, JC and HK. N<sub>2</sub> 77 K adsorption isotherms (Fig 1) for ACFs were taken from Cal.<sup>3</sup>

## The Isotherm Equation and PSD Determination

The semi-empirical DR and DA equations have been used successfully on adsorption in micropores, but they lack a rigorous theoretical basis<sup>4</sup> and they do not reduce to Henry's law at low adsorptive pressure.<sup>5</sup> Chen and Yang<sup>6</sup> have derived an isotherm equation for adsorption of gases in slit pores using a statistical mechanical approach.

$$\ln \frac{\rho^s}{\rho^f \Lambda} - \frac{7}{8} \ln(1-\eta) + \frac{2\eta}{(1-\eta)} + \frac{9}{8} \frac{\eta}{(1-\eta)^2} - \alpha(T)\eta + \frac{\Phi}{k_b T} = 0 \quad (1)$$

where  $\rho^f$  and  $\rho^s$  are adsorbate densities in the gas and 2-D adsorbed phases, respectively;  $\Lambda$  is the thermal wavelength;  $\alpha(T)$  is a function of  $T$ ; and  $\eta$  is the fractional surface coverage. The adsorbed phase is subjected to a mean force field  $\Phi$ . For adsorption in micropores with a high filling fraction the isotherm reduces to the DA and DR equations. At low pressure the isotherm reduces to Henry's law. In this study, we extend the derivation method of Chen and Yang<sup>6</sup> by introducing the 3-D Carnahan-Starling-DeSantis (C-S-D) equation of state<sup>7</sup> to describe adsorption density.

$$\ln \frac{\rho^s}{\rho^f} + \frac{8\eta - 9\eta^2 + 3\eta^3}{(1-\eta)^3} + \frac{1}{k_b T} \frac{a}{b} \left( \ln(1+4\eta) - \frac{4\eta}{1+4\eta} \right) + \frac{\Phi}{k_b T} = 0 \quad (2)$$

Eq 2 is a 3-D isotherm for a given pore size correlated with a mean force field  $\Phi$ . Parameters  $a$  and  $b$  are given by the C-S-D equation. The quantities  $\rho^f$  and  $\rho^s$  are number densities of the bulk fluid and adsorbed phases, respectively. The first term refers to Henry's law. The second term refers to the short range repulsive force between adsorbate molecules; the third term refers to the long range attractive force between adsorbate molecules; and the last term refers to the interaction between adsorbate and adsorbent molecules.

The experimental N<sub>2</sub> 77 K adsorption isotherm of a given adsorbent can be considered as the summation of the isotherms for the individual pores that make up the sample's pore structure. Mathematically, the experimental isotherm is the integral of the single isotherm multiplied by the pore size distribution,<sup>8,9</sup>

$$n(P^r) = \int_0^\infty \rho(P^r, w) f(w) dw \quad (3)$$

where  $f(w)$  is the distribution of pore volume as a function of pore size  $w$ .  $\rho(P^r, w)$  is the adsorbate density for individual pores at relative pressure  $P^r$ , which can be calculated using the model adsorption isotherm (Eq 2) by varying pore size  $w$ . The classic DS inverse relationship is chosen to prepare the adsorption potential from each pore size. By breaking down the integral (Eq 3) into a set of linear equations, PSD is determined by least-squares error minimization technique.

## Results and Discussion

PSD calculated by MP method are plotted in Fig 2. ACFs-15, 20 and 25 in order were made with increasing activation time. Increasing total pore volume and pore widening are expected with extended activation time. These features seem to be well interpreted by MP method. PSD for ACF-25 suggests that it is of bimodal nature, which is common for many activated carbons. Pore volumes for ACFs-15, 20 and 25 extracted from the PSD are 0.322, 0.702 and 1.109 cm<sup>3</sup>/g.

To obtain PSD using JC method (Fig 3), the experimental isotherms are fitted using the JC equation (Fig 1). Excellent fit exists for ACF-15 isotherm, but increasing deviations are observed for ACFs-20 and 25 whose structure presumably become more and more heterogeneous. Pore volumes for ACFs-15, 20 and 25 extracted from the PSD are 0.343, 0.63, 0.865 cm<sup>3</sup>/g.

The asymmetrical shape of PSD curve obtained by HK method (Fig 4) resembles that obtained by MP method, suggesting that ACFs are highly microporous. The lowest experimental relative pressures are  $2.5 \times 10^{-5}$ ,  $1.25 \times 10^{-4}$  and  $4.6 \times 10^{-5}$  for ACFs-15, 20 and 25. Their corresponding pore sizes are 0.53, 0.59 and 0.55 nm, respectively. Hence, Their PSDs may not extend below the sizes specified above. Pore volumes for ACFs-15, 20 and 25 extracted from the PSD are 0.336, 0.611 and 0.843 cm<sup>3</sup>/g. They do not include the volume of pores less than the specified sizes due to the experimental limitation.

PSDs obtained by proposed method are plotted in Fig 5. The number of pore size interval (equal to the number of unknowns in the linear equations) are chosen to be seven to ensure maximum accuracy for the solution but still guarantee a reasonable PSD resolution. Pore volumes extracted from the PSDs are 0.3, 0.609 and 1.113 cm<sup>3</sup>/g. Increasing mean pore size and pore volume are observed for ACF samples. Because the three samples contain negligible non-microporous volumes, construction for continuous PSD is performed by changing the pore size interval down to 0.1 nm (Fig 6). In contrast to the PSDs by JC and HK, a marked bimodal PSD for ACF-25 is clearly revealed. Both peaks have the locations similar to the MP results. Pore volumes extracted from the PSD are 0.298, 0.606 and 1.067 cm<sup>3</sup>/g, which is in good agreement with those obtained from Fig 6.

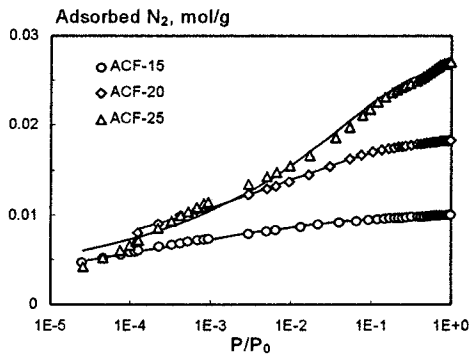
In summary of PSD for ACF-25, MP method gives a high micropore volume, due to the fact that MP method disregards the enhanced adsorption in micropores, that tends to overestimate the micropore volume. The PSD obtained by JC method is extended

further into the mesopore region (maximum at 1.6 nm) which presumably is the result of initial constraint associated with the assumption for the PSD mode. HK method gives the smallest PSD maximum and does not respond well to the pore widening by the extent of activation for ACF-25. This is due to the assumption of progressive pore filling mechanism made in HK theory. Part of the adsorbed  $N_2$  included to a specific pore, as determined by the HK method, should be attributed to the adsorption in pores larger than that particular pore.

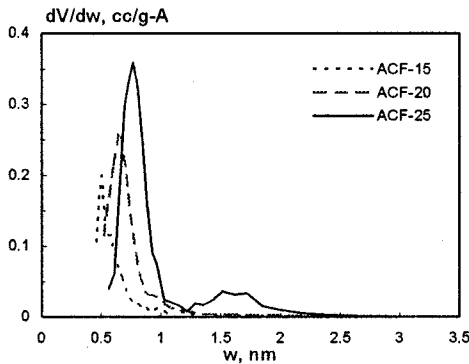
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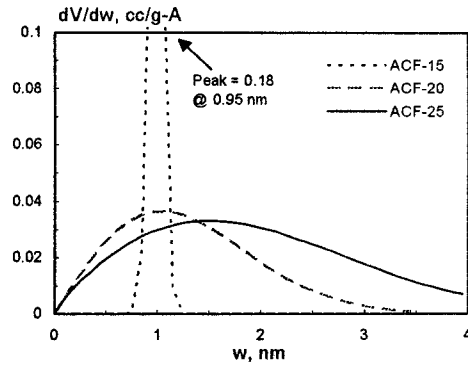
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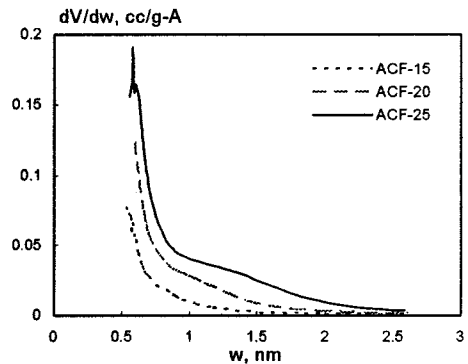
**Fig 1.**  $N_2$  77 K experimental adsorption isotherms (points) for the three ACFs plotted on log scale to highlight the low pressure region. Three isotherms are fitted with JC equation (lines).



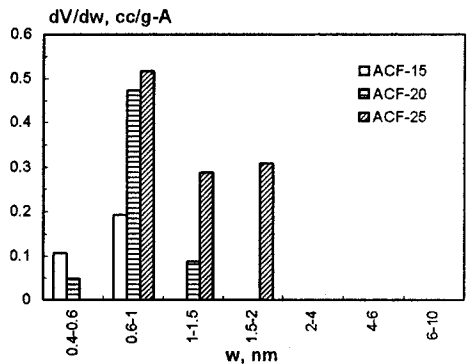
**Fig 2.** PSD of ACFs determined by MP method.



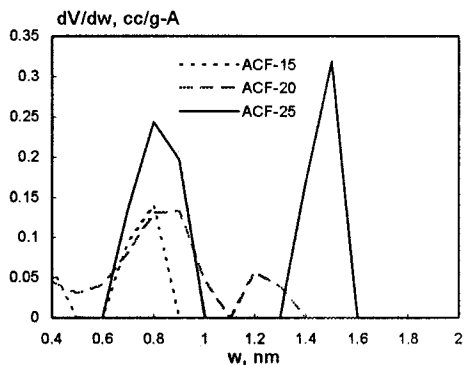
**Fig 3.** PSD of ACFs determined by JC method.



**Fig 4.** PSD of ACFs determined by HK method.



**Fig 5.** PSD (with 7 pore size intervals) of ACFs determined by the proposed method.



**Fig 6.** PSD (with 17 pore size intervals in micropore range) of ACFs determined by the proposed method.