

DETERMINATION OF PORE SIZE DISTRIBUTION USING A MODIFIED DR EQUATION

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Introduction

N₂ adsorption at 77 K is of interest in that the pressure at which capillary condensation (or pore filling in micropores) occurs in a particular pore is related to the size of the pore. The correlation between condensation (filling) pressure P^* and corresponding (critical) pore size w^* was historically studied by the Kelvin equation. Kelvin equation becomes less accurate in micropores for the adsorption is enhanced due to overlap of the force field created by the opposing pore walls. Recently, based on the mean field theory (MFT), Seaton et al. (1989) proposed a unique statistical mechanical approach to extend the accuracy of the correlation between P^* and w^* in both mesopores and micropores. More recently, the nonlocal MFT by Lastoskie et al. (1993) gives even more accurate correlation between P^* and w^* especially for (ultra-) micropores by taking into account the short-ranged correlations in the fluid density, which is neglected in the local MFT (Seaton et al., 1989). This paper presents a simple technique, combining the numerical results by Seaton and Lastoskie, to calculate pore size distribution (PSD) on the basis of generalized adsorption isotherm (GAI). Adsorption density is introduced into the classic DR equation and used as the local adsorption isotherm in GAI. A modified normal distribution is developed and used as a distribution function for pore sizes on the domain $[0, \infty)$. The model is also compared with three typical methods: MP, JC and HK methods.

Two activated carbon fibers (ACFs-15 and 25) are selected to represent typical microporous materials (Cal, 1995). ACF-15 has the shorter activation time (lower burn-off and higher yield). A tire-based activated carbon is also selected to represent a typical adsorbent with a wide PSD and significant portions of mesopores and macropores (Sun et al., 1997). N₂ 77 K adsorption isotherms were measured for all the samples using a Quantachrome sorption analyzer (Quantachrome Corporation, Boca Raton, FL).

Model Description

A modified normal distribution has been developed,

$$f(x) = \frac{x}{\sqrt{2\pi}\sigma g} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] \quad (1)$$

where x is distribution variable, μ is mean, and σ^2 is variance and

$$g = \frac{\sigma}{\sqrt{2\pi}} \exp\left(-\frac{\mu^2}{2\sigma^2}\right) + \frac{\mu}{2} \left(1 + \operatorname{erf}\left(\frac{\mu}{\sqrt{2}\sigma}\right)\right) \quad (2)$$

The classic DR equation takes the form,

$$\theta = \exp[-(A/\beta E_0)^2] \quad (3)$$

where θ is defined as the fraction of pore filling V/V_0 . V represents the volume of adsorbate condensed within micropores at temperature T and relative pressure P/P_0 . V_0 is the total volume of micropores; $A = -RT \ln(P/P_0)$ is the differential molar work of adsorption; E_0 is the characteristic energy; and β is the affinity coefficient. According to Dubinin (1975), DR equation works only at moderate and high adsorptive pressures, and breaks down at low pressure (Henry's law region). It also assumes a continuous pore filling mechanism, which is not entirely correct for N₂ adsorption at 77 K. In this study we modify the DR equation by introducing the adsorption density particularly for N₂ 77 K

adsorption at pressures above the filling pressure ($P > P^*$),

$$\rho = \rho_l \exp[-(A/\beta E_0)^2] \quad (4)$$

where ρ is the density of adsorbed phase. ρ_l is the density of saturated liquid N₂. This modification makes sense in that pore 'filling' at $P > P^*$ is indeed continuous. In other words, adsorption density increases gradually at $P > P^*$ due to the compression of N₂ in the liquid-filled pore. In Eq 4 the fraction of pore filling is $\theta = \rho/\rho_l$ and θ approaches one at $P/P_0 = 1$ (complete pore filling).

At low pressure, monolayer is initially formed on pore walls. As pressure increases, multilayers are adsorbed to form liquid-like films. To estimate the adsorption density at $P < P^*$, the Cranston-Inkley (CI) method is a recognized approximation,

$$\rho_l = \rho_b + 2\rho_l t/w \quad (5)$$

where ρ_b is the bulk N₂ density, ρ_l again is the saturated liquid N₂ density (assumed to be equal to the adsorbed film density), and t is the thickness of the adsorbed film evaluated by de Boer empirical equation (1966). CI equation is based upon Kelvin theory and disregards the enhanced adsorption potential in micropores. In fact, due to this enhanced potential, the adsorbed phase becomes highly inhomogeneous within micropores (Evans and Tarazona, 1984). The phase transition from inhomogeneous state to the homogeneous liquid state occurs when the filling pressure is reached. Hence, the density of adsorbed phase is strongly dependent on the size of micropores at a given pressure. To take this enhanced potential into account, we put Eq 5 into the modified DR equation by replacing ρ_l with ρ_l .

$$\rho = \rho_l \exp[-(A/\beta E_0)^2] \quad (6)$$

Eq 6 is then used to calculate the adsorption density at $P < P^*$. The combination of CI equation with DR equation is arbitrary to a certain extent, but the resulting model isotherms of N₂ adsorption at 77 K (Fig 1) calculated by Eqs 4 and 6 are surprisingly similar to those obtained by MFT (Seaton et al., 1989). As the pressure is increased from zero, adsorption begins to occur on the pore walls. The thickness of the adsorbed layer increases until the filling pressure is reached, at which point pore filling occurs, resulting in a discontinuous jump in the isotherm. The correlation of P^* with w^* is obtained from the numerical 'experimental' results by Seaton et al. (1989) and Lastoskie et al. (1993).

PSD Determination

The experimental N₂ 77 K adsorption isotherm of a porous sample can be considered as the summation of the isotherms for the individual pores that make up the pore structure of this particular sample. Mathematically, the isotherm is the integral of the single isotherm multiplied by the PSD (McEnaney, 1987),

$$N(P') = \int_0^\infty \rho(P', w) f(w) dw \quad (7)$$

where $N(P')$ is adsorbed N₂ at P' (P/P_0) that is obtained directly from the experimental isotherm. The PSD (unknown), $f(w)$, is the distribution of pore volume as a function of pore size w . $\rho(P', w)$ is the adsorption density at P' , which can be calculated using the modified DR equations (4 and 6) by varying the pore size w (Fig 1). To obtain a more realistic correlation between the adsorption potential and pore size, the DS inverse relationship (Dubinin and Stoeckli, 1980) is also modified in such a way,

$$E_0 = 2k/(w + d) \quad (8)$$

where k is 140 kJ-Å/mol and $d = 3.4 \text{ \AA}$ (diameter of a C atom).

Consequently, the modified DR equation can be rewritten as,

$$\rho = \rho_l \exp[-c(w + d)^2] \quad (9)$$

at $P > P^*$ and

$$\rho = \rho_t \exp[-c(w + d)^2] \quad (10)$$

at $P < P^*$, where

$$c = (RT \ln P^*/2\beta k)^2 \quad (11)$$

Plug Eqs 1, 9 and 10 into Eq 7, we have

$$n(P') = \int_0^{w^*} \frac{Vw}{\sqrt{2\pi}\sigma g} \exp\left[-\frac{(w-\mu)^2}{2\sigma^2}\right] \rho_l \exp[-c(w+d)^2] dw \quad (12)$$

$$+ \int_{w^*}^{+\infty} \frac{Vw}{\sqrt{2\pi}\sigma g} \exp\left[-\frac{(w-\mu)^2}{2\sigma^2}\right] \frac{2\rho_t t}{w} \exp[-c(w+d)^2] dw$$

where V is pore volume, and distribution of pore volumes $f(w)$ is represented as the product of V and Eq 1. $n(P')$ stands for the right hand side of GAI, which is broken into two terms due to the discontinuity in the local isotherms. For $w < w^*$, ρ_l is used in the modified DR equation; For $w > w^*$, ρ_t is replaced by ρ_t evaluated in Eq 5. N_2 bulk density ρ_b has a negligible effect and so is omitted in the derivation process. Integrating Eq 12 gives

$$n(P') = \frac{V\rho_l\sigma}{\sqrt{2\pi}g(1+2c\sigma^2)} (\exp[I] - \exp[II]) + \frac{V\rho_t(\mu - 2cd\sigma^2)}{2g(1+2c\sigma^2)^{3/2}} \quad (13)$$

$$\exp[III](\text{erf}[IV] - \text{erf}[V]) + \frac{V\rho_t t}{g\sqrt{1+2c\sigma^2}} \exp[III](1 - \text{erf}[IV])$$

where $[I] = -\mu^2/2\sigma^2 - cd^2$; $[II] = -(w^* - \mu)^2/2\sigma^2 - c(w^* + d)^2$; $[III] = -c(\mu + d)^2/(1 + 2c\sigma^2)$; $[IV] = (2c\sigma^2 w^* + w^* + 2cd\sigma^2 - \mu)/\sigma(2 + 4c\sigma^2)^{0.5}$; $[V] = (2cd\sigma^2 - \mu)/\sigma(2 + 4c\sigma^2)^{0.5}$. Eq 13 is the GAI for a porous sample with a heterogeneous PSD skewed to the right. In practice, a multiple (up to four) modal distribution is used,

$$f(w) = \sum_{i=1}^m \frac{V_i w}{\sqrt{2\pi}\sigma_i g_i} \exp\left[-\frac{(w-\mu_i)^2}{2\sigma_i^2}\right] \quad (14)$$

where $f(w)$ is a multimodal distribution with m modes, V_i is the volume of pores in distribution i , and μ_i and σ_i determine the

shape of the distribution. To obtain a sample's PSD, Eq 13 (with multiple modes) is fitted to the experimental isotherm by a simple least-squares error minimization criterion.

$$E = \frac{1}{n_e} \sum_{j=1}^{n_e} [n(P'_j) - N(P'_j)]^2 \quad (15)$$

where n_e (~50) is the number of points on the experimental isotherm. The total pore volume V_T is given by

$$V_T = \int_{w_{min}}^{w_{max}} f(w) dw \quad (16)$$

where w_{min} (3.5 Å) and w_{max} ($+\infty$) are the minimum and maximum pore sizes present in the adsorbent. In most cases, there is negligible pore volume with $w < 3.5 \text{ \AA}$ which is the diameter of a N_2 molecule. Practically, $V_T = \sum V_i$.

PSD Results

PSD results for ACFs-15 and 25 and tire-based carbon are plotted in Figs 2 and 3. PSD for ACF-25 is also determined by MP, JC and HK methods and the results are presented in Fig 4 along with that obtained by the proposed model.

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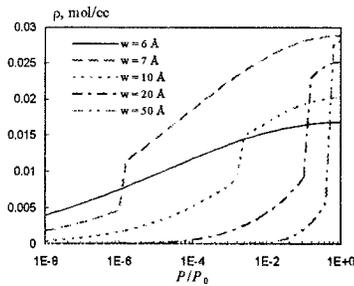


Fig 1. Model isotherms calculated using the modified DR Eqs (4 and 6).

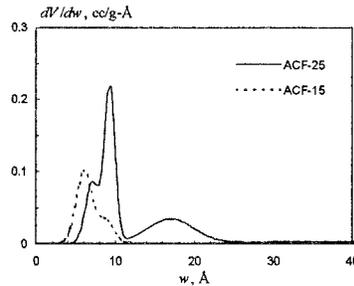


Fig 2. (b) PSD for ACFs determined by the model.

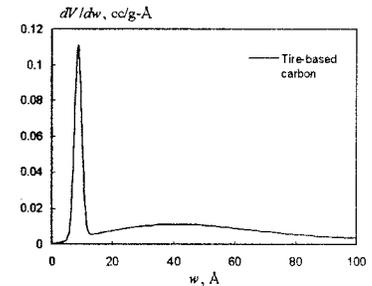


Fig 3. (b) PSD for tire-based carbon by the model.

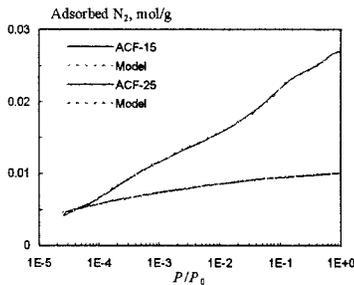


Fig 2. (a) Experimental and calculated isotherms for ACFs.

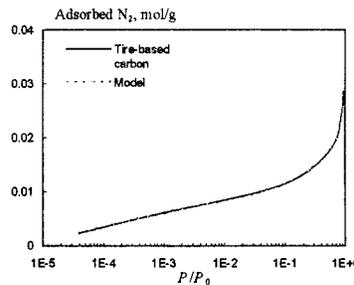


Fig 3. (a) Experimental and calculated isotherms for tire-based carbon.

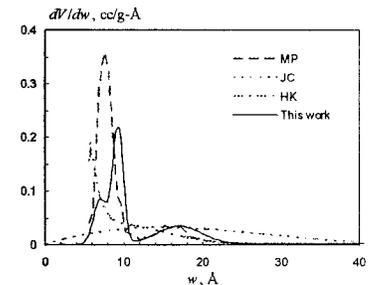


Fig 4. Comparison of PSD for ACF-25 by MP, JC, HK and the model.