The comparative characterization of structural heterogeneity of mesoporous activated carbon fibers (ACFs)

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Abstract

The comparative analysis of the most widely used methods of mesoporosity characterization of two activated carbon fibers is presented. Not only the old methods are used, i.e. Barrett, Joyner and Halenda (B/H), Dubinin (the so-called first variant—\(D_{157}\) and the so-called second variant—\(D_{250}\)), Dollimore and Heal (DH), and Pierce (P) but the recently developed ones, i.e. the method of Nguyen and Do (ND) and that developed by Do (Do) are also applied. Additionally, the method of the characterization of fractality is put to use (fractal analog of FHH isotherm). The results are compared and discussed.

Keywords: Carbon fibers; Mesoporosity characterization; Pore size distribution; Fractal dimension

1. Introduction

Porous materials are usually heterogeneous both structurally and energetically. Among porous solids used in industry, activated carbons are the most complex ones. On the other hand, they are the most versatile due to their extremely high surface area and micropore volume. Activated carbon fibers (ACFs) are relatively novel fibrous adsorbents produced for example from pitch, cellulose, phenol resin and polyacrylonitrile [1–5]. Such a new generation of carbon materials can be utilized in different branches of chemistry, technology and industry. The adsorption/desorption characteristics of ACFs exhibit different behaviour according to the type of precursor used. The main advantage of these materials is a small fiber diameter, which minimizes diffusion limitations and allows rapid adsorption/desorption [6]. Typically, ACFs are characterized by a relatively narrow pore size distribution, very good mechanical properties (i.e. resistance to
abrasion, ability to form different shapes) and excellent adsorption capacity at low concentration comparing to commercial activated granular/powder carbons [7]. ACFs appear to be very promising materials for adsorption from solutions. As reported by Tamai et al., ACFs obtained from organometallics/pitch composites have excellent adsorption properties for larger molecules in the liquid phase [8].

The pore size distribution (PSD) of ACFs, together with the chemical composition of the surface layer, are perhaps the most important characteristics, that affect the transport and adsorption equilibrium. Other structural characteristics of the mentioned materials (for example, a specific surface area, a micropore/mesopore volume, mean micropore/mesopore radius and others) can be obtained from the PSD curve.

In the present study, some conventional and new (developed recently) methods of estimating PSD from a single nitrogen adsorption isotherm were adopted for characterizing ACFs. Not only the most popular older methods but also the newest ones are applied and the results are compared. What is also important is that the new numerical algorithm (called adsorption stochastic algorithm, ASA) for the calculation of the results from Nguyen and Do method is presented. Additionally, fractal analysis is used to study the surface roughness. The results are compared with those calculated using one of the newest method of porosity characterization, namely DFT theory. The main attention of the authors is paid to the comparative analysis of the methods of mesoporosity characterization.

2. Experimental

2.1. Adsorbents

Both activated carbon fibers were prepared following the method described in details previously [4,5].

2.2. Nitrogen adsorption measurements

A Micromeritics ASAP 2000 (Micrometrics Ins. Corp.) was used to measure nitrogen adsorption isotherms at 77.5 K. High purity nitrogen (99.99%) was used and before each measurement the samples were desorbed at 573.15 K for 2 h [4,5].

3. The methods of calculation

To compute the mesopore size distribution curves (MPSDs), a few iterative methods based on Cohan’s capillary condensation model (i.e. Barrett, Joyner and Halenda (BJH) [9], Dubinin (the so-called first variant—D_{1ST} [10] and the so-called second variant—D_{2ND} [11]), Dollimore and Heal (DH) [12], and Pierce (P) [13]) were used in the present study. All above mentioned methods are characterized with the computational algorithm described in details by Jagiello and Klinik [14]. If we denote for the \( n \)-th stage of desorption \( \Delta V_n \) (cm\(^3\)/g) as a change in the adsorption value (of liquid adsorbate); \( \bar{r}_n \) (cm) as the average pore diameter; \( \bar{r}_{kn} \) (cm) as the average Kelvin’s radius of the space between adsorbed layers; \( t_n \) (cm) as the average thickness of the adsorbed layer; \( \Delta t_n \) (cm) as the change in the thickness of the layer adsorbed on the pore walls for the considered stage of desorption; the change in the volume of empty pores for \( n \)-th stage of desorption \( \Delta V_p \) (cm\(^3\)/g) is given by the following equations.

(I) For the method of Barrett, Joyner and Halenda (BJH) [9]:

\[
\Delta V_p = \Delta V_n R_n - C \Delta t_n \sum_{i=1}^{n-1} \frac{2 \Delta V_i}{\bar{r}_i} (1a)
\]

where

\[
R_n = \left( \frac{\bar{r}_n}{\bar{r}_{kn} + \Delta t_n} \right)^2 \quad (1b)
\]

\[
C = \frac{\bar{r}_n - t}{\bar{r}_n} \quad (1c)
\]

(II) For the first variant of Dubinin’s method (D_{1ST}) [10]:

\[
\Delta V_p = \Delta V_n + \bar{r}_n \frac{2 \Delta V_n}{\bar{r}_{kn}} - \Delta t_n \sum_{i=1}^{n-1} \frac{2 \Delta V_i}{\bar{r}_i} (2)
\]

(III) For the second variant of Dubinin’s method (D_{2ND}) [11]:

\[
\Delta V_p = \left( \Delta V_n - \Delta t_n \sum_{i=1}^{n-1} \frac{2 \Delta V_i}{\bar{r}_i} \right) \left( \frac{\bar{r}_n}{\bar{r}_{kn}} \right)^2 (3)
\]
(IV) For the method of Dollimore and Heal (DH) [12]:

\[
\Delta V_n = \left( \Delta V_n - \sum_{i=1}^{n-1} \frac{2\Delta V_{pi}}{\bar{r}_i} + \Delta t_n \sum_{i=1}^{n-1} \frac{2\Delta V_{pi}}{\bar{r}_i^2} \right) \\
\times \left( \frac{\bar{r}_n}{\bar{r}_{kn} + \Delta t_n} \right)^2
\]

(4)

(V) For Pierce’s method (P) [13]:

\[
\Delta V_n = \left( \Delta V_n - \sum_{i=1}^{n-1} \frac{2\Delta V_{pi}}{\bar{r}_i} \right) \left( \frac{\bar{r}_n}{\bar{r}_{kn}} \right)^2
\]

(5)

Calculation of \( \Delta V_n \) at each step of desorption makes it possible to calculate the differential pore volume \( \Delta V_p/\Delta r \) and to draw the differential pore distribution curve for an adsorbent [15]:

\[
\frac{\Delta V_p}{\Delta r} = f(\bar{r})
\]

(6)

where \( f(\bar{r}) \) is a distribution function.

Additionally, the volume of mesopores can be calculated:

\[
V_{mes} = \sum_{i=1}^{n} \Delta V_{pi}
\]

(7)

and the surface of mesopores:

\[
S_{mes} = \sum_{i=1}^{n} \frac{2\Delta V_{pi}}{\bar{r}_i}
\]

(8)

In the current study, we also applied the method of Derjaguin–Broekhoff and de Boer, modified by Dubinin and Ulin. This method originates from the pioneering paper of Derjaguin [16] and, actually, is the modification of the Broekhoff and deBoer’s method [17–23]. In this modification Dubinin and co-workers assumed that the surface tension of an adsorbate is the function of the radius of the curvature of the meniscus of adsorbed nitrogen. They obtained the following equations [24]:

\[
\log \left( \frac{p_s}{p} \right) - \left( \frac{16.11}{r_e^2} \right) + 0.1682 \exp(-0.1137t_e)
\]

\[
= \frac{2.025}{r - t_e - 3.31}
\]

(9)

and

\[
r - t_e = \frac{4.05(r - t_e)}{(r - t_e - 6.62)\log(p_s/p) + (r - t_e)\log(p_s/p)}
\]

\[
\times \left\{ 32.22 \left[ \frac{r}{t_e} - 1 - \log \left( \frac{r}{t_e} \right) \right] \right. \\
- 2.964(r - t_e - 8.795)\exp(-0.1137t_e)
\]

\[
- 26.06 \exp(-0.1137r) \right\}
\]

(10)

where \( p \) and \( p_s \) denote the equilibrium pressure and the saturation vapor pressure, respectively, \( t_e \) is the average thickness of the adsorbed layer and \( r \) the mesopore radius.

Thus, the pore size distributions in this case can be calculated taking into account in Eq. (3) the relationships (9) and (10), and this method is denoted as Derjaguin–Broekhoff–deBoer–Dollimore–Dubinin–Ulin (DBdBDU).

Another method considered in this study was proposed by Nguyen and Do (ND) [25–28] and recently developed by Do [29–31]. They developed a new promising procedure for the evaluation of pore size distribution from adsorption data. Such a procedure is based on the combination of the Kelvin equation and the statistical adsorbed film thickness. The most important feature of this method is the possibility of analysis of the structural heterogeneity of porous solids without the need to distinguish the micropore range and the mesopore range. Additionally, it provides almost the same results as those obtained using the most sophisticated method of porosity characterization, namely the DFT method [25–32].

Following Nguyen and Do, the overall adsorption isotherm equation possesses the form as follows:

\[
a = \int_{r_{\min}}^{r_{\max}} f(R_p) \, dR_p + \int_{r_{\min}}^{r_{\max}} \frac{w}{(R_p - \sigma_\theta)/2} t(p, R_p) f(R_p) \, dR_p
\]

(11)

where \( r_{\min} \) and \( r_{\max} \) are the minimal and maximal half widths (or pore radii), respectively; \( w_{\text{NG}} = 1 \) for slit like pores and 2 for cylindrical pores; \( \gamma(p) \) is determined with the Kelvin equation (\( \gamma \) is the liquid surface tension; \( v_m \) the liquid molar volume; \( \theta \) the liquid–solid
contact angle; \( R \) the universal gas constant; \( T \) the temperature)
\[
n(p) = \frac{\sigma_s}{2} + t(p, R_p) + \frac{w_{NG} v_m \cos \theta}{RT \log(p_s/p)}
\]
(12)

where the statistical adsorbed film thickness is equal to
\[
t(p, R_p) = t_m \frac{c_B z_B}{1 - z_B} \left[ 1 + \frac{(n_B b/2) - (n_B b/2) z_B^{-1} - (n_B b + 1) z_B^n}{(c_B b/2 - b/2) z_B^n - (c_B b/2 + b/2) z_B^{n+1}} \right]
\]
(13)

describing a global adsorption isotherm as follows [26,33]:
\[
\Psi_i(p_j) = \int_{x_{\text{min}}}^{x_{\text{max}}} g_{\text{theor}}(x_i, p_j) f(x) \approx \sum_{i=1}^{N} w_i g_{\text{theor}}(x_i, p_j)
\]
(15)

where \( i = 1, 2, \ldots, N; j = 1, 2, \ldots, M; x \) describes the structural heterogeneity of an adsorbent; \( f(x) \) is the distribution function of a parameter \( x \); \( g_{\text{theor}}(x_i, p_j) \) the discrete form of a local adsorption isotherm (i.e. kernel) that describes the adsorption process in homogenous pores; \( x_{\text{min}} \) is the smallest and \( x_{\text{max}} \) is the largest value of a structural parameter (i.e. pore with, radius, half width). Based on both the theory of non-linear minimization and static penalty function our task is to find \( \bar{w} \) so as to minimize functional \( \Omega(\bar{w}) \). Mathematically:
\[
\text{minimize } \Omega(\bar{w}) = \begin{cases} 
\sum_{i=1}^{M} \left( \sum_{j=1}^{N} \Psi_i(p_j) - \sum_{i=1}^{N} w_i g_{\text{theor}}(x_i, p_j) \right)^2, & \text{if } \bar{w} \in \Xi \cap S \\
\sum_{i=1}^{M} \left( \sum_{j=1}^{N} w_i g_{\text{theor}}(x_i, p_j) \right)^2 + \sum_{i=1}^{H} C_i \delta_i, & \text{otherwise}
\end{cases}
\]
(16)

physical half width \( (R_p - \sigma_s/2) \), which is:
\[
\theta(p, R_p) = \begin{cases} 
\frac{t(p, R_p)}{R_p - \sigma_s/2}, & \text{for } p < p^* \\
1, & \text{for } p \geq p^*
\end{cases}
\]
(14)

where \( p^* \) is the critical pressure at which the pore filling occurs and it is obtained from the solution of modified Kelvin equation. Thus, the problem of the solution of unstable linear Fredholm integral equation of the first kind may be replaced by a classical optimization problem with constraints.

Since in the present paper the new algorithm is applied to solve this problem we describe it in details below. In general case, we can define an expression

\[
\delta_i = 1, \text{ if constraint "i" is violated} \\
\delta_i = 0, \text{ if constraint "i" is satisfied}
\]
(17)

where \( H \) is the number of constraints, \( \bar{w} \in \Xi \cap S \). The set \( S \subseteq \mathbb{R}^N \) defines the search space and the set \( \Xi \subseteq \mathbb{R}^N \) defines a feasible search space. The search
space $S$ is defined as a $N$-dimensional rectangle in $\mathbb{R}^N$ (domains of variables defined by their lower and upper bounds)

$$l(i) \leq w_i \leq u(i), \quad 1 \leq i \leq N \quad (18)$$

The feasible search space $\Xi$ was assumed outside the defined $N$-dimensional rectangle. It is noted that $\Omega(\bar{w})$ is the penalized objective function and $C_i$ is a constant imposed for the violation of the constraint $i$. It is worthwhile to point out that such defining of a minimization problem always gives rise to physical solutions (i.e. negative value of distribution function $f(x)$, unphysical oscillations of distribution function $f(x)$, are avoided). We have defined a minimization problem of functional $\Omega(\bar{w})$, and we now turn to developing a minimization procedure. Obviously, for extracting $f(x)$ from measured global adsorption isotherm we can use genetic algorithms, evolutionary algorithms, simulated annealing, taboo search, deterministic algorithms (i.e. simplex strategy of Nelder and Mead, strategy of Hook and Jeeves, and so on), gradient methods (i.e. simple gradient method and so on), and hybrid methods [34]. All the above mentioned techniques determine all the unknown variables simultaneously. Developed by us and analyzed in this study are the new adsorption stochastic algorithm [35], the well-known relaxation (successive variation of the variables, parallel axis search, Gauss–Seidel strategy, alternating variable search, sectioning method [36]).

The main idea of such minimization procedure is the sequential minimization problem of one dimension (i.e. minimize only one element from $\bar{w}$ vector). So the optimization is first carried out by only optimizing the first element of the $\bar{w}$ vector. Once $w_1$ is optimized, $w_2$ is then optimized next until $w_k$ has been optimized. Once this is completed, the process is then repeated until no further change in the functional is observed. In the developing ASA program the well-known Rechenberg–Schwefel, Fibonacci division, and golden section procedures [37] were used for searching a local minimum in one dimension. All the procedures give very similar results.

Additionally, in the present study, the mesopore size distribution was calculated using the new method described in details by Do (Do) [38]. For the evaluation of the pore volume distribution of investigated ACFs, a bi-modal model of mesoporous structure was assumed. Following Do, the mesopore volume distribution was approximated by the combination of two gamma-type distributions:

$$f(r) = V_{S,1} \frac{x_{1}^{p_{1}+1}}{\Gamma(p_{1}+1)} r^{p_{1}} \exp(-x_{1}r)$$

$$+ V_{S,2} \frac{x_{2}^{p_{2}+1}}{\Gamma(p_{2}+1)} r^{p_{2}} \exp(-x_{2}r) \quad (19)$$

- **Fig. 1.** Experimental adsorption–desorption isotherms of nitrogen at 77.5 K on the Rayon and PAN activated carbon fibers.
Therefore, the amount adsorbed in mesopores is equal to:

\[ V(p) = V_{S1} \frac{\Gamma(p_1 + 1, z_1 r)}{\Gamma(p_1 + 1)} + V_{S2} \frac{\Gamma(p_2 + 1, z_2 r)}{\Gamma(p_2 + 1)} + 2V_{S1}(z_1 t) \frac{\Gamma(p_1, z_1 r_{\text{max}})}{\Gamma(p_1 + 1)} - \frac{\Gamma(p_1, z_1 r)}{\Gamma(p_1 + 1)} + 2V_{S2}(z_2 t) \frac{\Gamma(p_2, z_2 r_{\text{max}})}{\Gamma(p_2 + 1)} - \frac{\Gamma(p_2, z_2 r)}{\Gamma(p_2 + 1)} \]

(20)

where \( \Gamma \) denotes gamma function, \( V_{Sj} \) is the \( j \)-th total pore volume, \( p_j \) and \( z_j \) are the \( j \)-th pore structural parameters, \( t \) is generally used as an estimate for the statistical adsorbed film thickness as a function of pressure for nitrogen adsorption at 77.5 K:

\[ t = 0.354 \left[ \frac{5}{\ln(p_s/p)} \right]^{1/3} \]

(21)

where 0.354 nm is the thickness of one nitrogen molecule. The threshold radius corresponding to a gas phase of pressure \( p \) is equal to:

\[ r(p) = \begin{cases} 
\frac{2v_m \gamma \cos \theta}{RT \ln(p_s/p)}, & \text{for desorption} \\
\frac{v_m \gamma}{RT \ln(p_s/p)}, & \text{for adsorption}
\end{cases} \]

(22)

Table 1
Main characteristics of the activated carbon fibers used in this study

<table>
<thead>
<tr>
<th>Theoretical model</th>
<th>Parameter</th>
<th>Rayon</th>
<th>PAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-BET (0.05) ( &lt; p/p_0 &lt; 0.25 )</td>
<td>( a_m ) (cc g(^{-1}))</td>
<td>0.88</td>
<td>0.50</td>
</tr>
<tr>
<td>FHH (0.54) ( &lt; p/p_0 &lt; 0.98 )</td>
<td>( \kappa )</td>
<td>1.1868</td>
<td>1.1254</td>
</tr>
<tr>
<td>Barrett, Joyner and Halenda (desorption branch)</td>
<td>( V_{\text{mes}} ) (cc g(^{-1}))</td>
<td>2.97</td>
<td>2.86</td>
</tr>
<tr>
<td>Dubinin (first variant) (desorption branch)</td>
<td>( S_{\text{mes}} ) (m(^2) g(^{-1}))</td>
<td>880</td>
<td>307</td>
</tr>
<tr>
<td>Dubinin (second variant) (desorption branch)</td>
<td>( V_{\text{mes}} ) (cc g(^{-1}))</td>
<td>0.58</td>
<td>0.28</td>
</tr>
<tr>
<td>Dollimore and Heal (desorption branch)</td>
<td>( S_{\text{mes}} ) (m(^2) g(^{-1}))</td>
<td>688</td>
<td>286</td>
</tr>
<tr>
<td>Pierce (desorption branch)</td>
<td>( V_{\text{mes}} ) (cc g(^{-1}))</td>
<td>0.58</td>
<td>0.51</td>
</tr>
</tbody>
</table>

![MPSDs of Rayon and PAN activated carbon fibers obtained by means of classical iterative methods (i.e. Barrett, Joyner and Halenda (BJH), Dubinin (the so-called first variant—\( D_{1ST} \) and the so-called second variant—\( D_{2ND} \), Dollimore and Heal (DH), and Pierce (P)).](image-url)
Finally, both the samples were also characterized by using a fractal geometry approach. The fractal dimension of the surface \((2 \leq D < 3)\) accessible for adsorption is an operative measure of the surface irregularity \([39–53]\). Calculating of the fractal dimension of the ACFs was performed on the basis of adsorption data in the capillary condensation region using the fractal analog of Frenkel–Halsey–Hill equation \((FHH\) method) \([44,45,48,49]\):

\[
\frac{a}{a_m} = \kappa [\ln(p_s/p)]^{-1/m}, \quad \text{and} \quad m = 1/(3 - D) \quad (23)
\]

where \(a\) is the amount adsorbed at a given relative pressure \(p/p_s\), \(a_m\) the amount required to form a adsorbed monolayer coverage (taken usually from Brunauer–Emmett–Teller \((BET)\) equation) \([54,55]\), and \(\kappa\) is a constant.

4. Results and discussion

The experimental nitrogen adsorption–desorption isotherms at 77.5 K on PAN and Rayon activated
carbon fibers are shown in Fig. 1. Both isotherms are characterized by the presence of hysteresis loop in the condensation capillary region (i.e. these samples of ACFs possess considerable contribution of mesopores). Additionally, from Fig. 1 it is clearly seen that these samples of ACFs differ significantly, in terms of total pore volume as well as pore structure. The basic parameters describing of ACFs properties were obtained by applying the methods described in the previous section and \( n\)-BET and \( FHH \) equations (see Table 1). It can be noticed that the mesopore surface area of Rayon activated carbon fiber is two times greater than that of PAN ACF, while the mesopore volumes are comparable. All iterative methods developed on the ground of both Kelvin and \( t\)-curve equations give similar result of mesopore size distributions (Fig. 2). Rayon is characterized by a bi-porous structure of MPSDs. The main fraction of mesopores is located in the range 1–1.5 nm of pore radius. The second peak appears around a pore radius of 2 nm. PAN is characterized by considerably greater quantity of larger mesopores (i.e. greater than 5 nm).

Fig. 3 shows that the most advanced method of porosity characterization, proposed by Nguyen and Do, gives similar results as those obtained from \( DFT \) analysis. This was also observed for other systems mainly for microporous and mesoporous ones [25–32,56]. The main difference is the intensity of the peak located at 2 nm. In both the cases \( ND \) method leads to a larger intensity of this peak, and a small shift towards larger pore diameters. As it can be seen in Fig. 3, the fit of the \( ND \) method to experimental isotherms is very good, and this leads to the conclusion that, proposed in this paper, the numerical procedure (ASA) of fitting the model to experimental data is very effective.

In Fig. 4, MPSDs obtained by the method proposed by Do are shown. It can be noticed that this method leads to a more regular MPSD curve. Both PAN and Rayon are characterized by a single peak but the dimension and quantity of mesopores differ significantly. As it was concluded from the results of the methods presented above this method also shows that PAN is characterized by a larger quantity of wider mesopores (i.e. pore radius >4 nm). The results obtained from adsorption and desorption data are very similar for both solids in this case.

Interesting results are shown in Fig. 5 where the comparison of the results obtained from the \( ND \) and \( DBdBD\) methods is presented. Although it may seem strange, MPSDs obtained from the \( ND \) (and \( DFT \)) and \( DBdBD\) methods are almost the same. In the current study, only two adsorbents were analysed. Thus, it is hard to postulate that the both methods always lead to the same results, however,
it seems to be very probable. Thus, in the case of the studied systems, and for the range of mesopores, the time-consuming and advanced mathematically DFT and or ND methods can be effectively replaced with a simpler DBdDDU method.

**Fig. 5.** MPSDs of Rayon and PAN activated carbon fibers obtained by means of methods: DBdDDU—Derjaguin–Brockhoff–deBoer–Dollimore–Dubinin–Ulin, ND—Nguyen and Do.

**Fig. 6.** shows that the fit of BET and FHH fractal analog to the experimental data is good. However, for Rayon carbon, which is more heterogeneous, the fit for FHH equation is worse. The value of the surface fractal dimension for the two samples of

**Fig. 6.** Adsorption of nitrogen in mesopores of PAN and Rayon activated carbon fibers: Exp—experimental points, fitting by Brunauer–Emmett–Teller (n-BET) equation, and fitting by fractal Frenkel–Halsey–Hill (FHH) equation.
ACFs is high. This suggests large surface heterogeneity.

5. Conclusions

The mesopore volumes calculated from different models are comparable, while larger differences are observed in the values of pore surface area. All iterative methods lead to similar mesopore size distribution curves. Do’s method leads to a more regular PSD curve as obtained from iterative methods, and the differences between the results calculated from adsorption and desorption branches of isotherm are small. The most sophisticated methods of porosity characterization, namely DFT and ND lead to practically the same results, and small differences are observed in the intensity of the peak located in the upper range of micropores. The new numerical strategy of fitting of ND method to experimental data is very effective and can be successfully used for the characterization of porous carbonaceous materials.

The method proposed by Derjaguin–Broekhoff and de Boer, modified by Dubinin and Ulin is probably the most sophisticated method among older methods of mesoporosity characterization. It leads to almost the same results as DFT and ND. Thus, in the range of mesoporosity characterization, for carbons the time-consuming and advanced methods can be effectively replaced with a very simple one. Since only two mesoporous adsorbents are studied in the current paper the question arises about the comparable results of these two methods for other systems. This will be the subject of our future correspondence.

References