Characterising porous carbonaceous materials using the new methods. An attempt for estimation of micropore size distribution function from adsorption isotherm of nitrogen and benzene

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The study presents the analysis of adsorption data of nitrogen and benzene adsorption onto four microporous carbons. The most advanced methods of porosity characterisation, namely: the method of Do and co-workers (called Do), DFT, CONTIN, HK, and the methods basing on Dubinin’s potential theory of adsorption are put to use. It is shown, that the similarity between obtained results depends on the dispersion of microporosity of carbonaceous material, and if this dispersion is relatively high, all methods lead to very similar pore size distribution curves.

1. INTRODUCTION

Porous materials such as activated carbons, activated carbon fibres, molecular sieve carbons and others are used in several industrial processes such as purification and reaction processes, gas separation, gas storage, and so on. These materials exhibit remarkable structural and surface properties, determining the application in the processes mentioned above. It is generally accepted that solid surfaces are energetically and structurally heterogeneous to a

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greater or lesser extent. The surfaces of solids are both geometrically (i.e., fine pores of different size and shape, surface irregularities) and chemically (various surface groups, impurities) non-uniform [1-8]. A proper characterisation of porosity and surface properties of porous materials is a key factor of their successful synthesis and application. According to the "patch-wise" model of surface topography the experimental ("global") adsorption isotherm \( \theta_g(p,T) \) represents an average over all values of the pore dimension/adsorption energies existing on the gas - solid interface. Such formulation of the problem leads to the linear Fredholm equation of the first kind expressed in general by [1-8]:

\[
\theta_g(p,T) = \int_{\tau_{\min}}^{\tau_{\max}} g_{\text{local}}(\tau,p) f(\tau) d\tau
\]  

(1)

Here \( \tau \) describes the heterogeneity of an adsorbent, related to one of the properties of the porous medium (as a rule, of adsorption energy or structure); \( f(\tau) \) is a distribution function; \( g_{\text{local}}(\tau,p) \) is a local adsorption isotherm (i.e. kernel) describing the relative parameter of an adsorption process \( \tau \); \( \tau_{\min} \) is the smallest and \( \tau_{\max} \) is the largest value considered in the analysis. The proper choice of the kernel and integration boundaries in Eq. (1) seems to be a key problem in a proper description of structural and/or energetic heterogeneity of porous materials. Moreover, the solution of the linear Fredholm equations of the first kind formulated on the adsorption ground is a well-known "ill-posed" problem [9-13]. An ill-posed problem is one in which several solutions are consistent with the experimental data. Additionally, ill-posed problems exhibit also the property of being extremely sensitive to the perturbations in experimental data. Several methods of solving of Eq. (1) based on the condensation approximation method, Tikhonov regularisation procedure, optimisation algorithms, iterative algorithm, and others have been developed [9-24]. Each from the mentioned above methods possesses their own advantages and disadvantages.

As it was suggested by many authors Eq. (1) can be transformed to a discrete formulation with as a set of pore width and volume pairs. Such formulation of the problem leads to the classical non-linear optimisation method with constraints.

In the current study the MPSDs of four samples of activated carbons are obtained from benzene adsorption isotherms by means of the recently developed method of Do and methods based on the Dubinin's theory of micropore filling. The obtained results are compared. Additionally, for two samples of synthetic activated carbons labelled A and B, the MPSDs were derived from nitrogen adsorption isotherms by means of the method of Do, density functional theory (DFT), and Horvath and Kawazoe equation. The
results were compared with those obtained from the analysis of benzene adsorption isotherms.

2. THEORETICAL DEVELOPMENT

The method developed by do and co-workers. The process of adsorption in pores of various pore dimensions can be visualised as shown in Figure 1. For a given pressure (fugacity) in the bulk fluid phase, the interior of pore can be viewed as a space where higher density of molecules can be found, due to the external forces acting on them. For describing the interaction potential of a single fluid molecule inside a pore the well-known 10-4-3 potential function developed by Steele [25] can be used:

\[
\Psi(z,d) = \varphi_w \left\{ \frac{1}{5} \left[ \left( \frac{\sigma_{ks}}{d+z} \right)^{10} + \left( \frac{\sigma_{ks}}{d-z} \right)^{10} \right] - \frac{1}{2} \left[ \left( \frac{\sigma_{ks}}{d+z} \right)^{4} + \left( \frac{\sigma_{ks}}{d-z} \right)^{4} \right] \right\} - \left\{ \frac{\sigma_{ks}^4}{6\Delta(d+z+0.61\Delta)^4} + \frac{\sigma_{ks}^4}{6\Delta(d-z+0.61\Delta)^4} \right\}
\]

(2)

where \( z \) is the distance of the molecule from the central plane between the two surface layers, \( d \) is the half-spacing between the two lattice layers, \( \Delta \) is the graphite layer spacing, \( \sigma_{ks} \) is the collision diameter of two molecules "k" and "s", and \( \varphi_w \) is the wall potential energy parameter given by:

\[
\varphi_w = 4\pi\rho_s\sigma_{ks}^3\Delta \epsilon_{ks}
\]

(3)

Here \( \rho_s \) is the number density of the surface center per-unit volume, and \( \epsilon_{ks} \) is the Lennard-Jones well depth of the molecule and the surface. The heat of adsorption is equal to the minimum of 10-4-3 potential function taken with a minus sign:

\[
Q_{pore}(d) = -\min[\Psi(z,d)]
\]

(4)
Fig. 1. Schematic diagram of pore structure and adsorption mechanisms in Do’s method

As it can be seen from Figure 2, the heat of adsorption reaches a maximum that is equal to about twice the heat of adsorption on a flat surface when the pore half-width is close to the collision diameter $\sigma_{ks}$. As the pore size increases, the heat of adsorption decreases and reaches an asymptote—the heat of adsorption of a flat surface. Clearly, the enhancement of the heat of adsorption is
characteristic of micropores (i.e. pores characterised by $d < 1$ nm according IUPAC classification of pores) due to overlapping of two carbon surface potentials. All molecules (see Fig. 1) move around the pores, but statistically there is a spatial distribution of these molecules across the pore. This effect results from nonhomogeneity of the potential field in a pore. The density of these molecules is very high near the surface due to the strongest interaction between molecules and surface atoms, while away from the surface the density is lower and lower (statistically speaking). Do's model assumes that such a distribution is a step function, that is, uniform high density near the surface (adsorbed molecules) and uniform lower density near the center of the pore (occluded molecules).

The model developed by Do and co-workers and extensively applied for characterization many types of adsorbent [19, 26-33] is based on the following assumptions:

(i) Activated carbon has pores of slit shape.
(ii) The adsorption mechanism comprises of two steps in series: multilayering followed by pore filling.
(iii) The dispersive force is the dominant adsorption force.
(iv) The concentration of adsorbed phase in the multilayering step is described by a BET-type equation, with allowance for the enhancement in the $C$ constant.
(v) The pore filling step is described by the Kelvin equation.
(vi) The adsorbed phase density is the same as the corresponding liquid density.

With the above assumptions Do and co-workers proposed extending the well-known n-BET/BET and Kelvin theories describing the adsorption process on the flat surfaces and condensation in mesopores to the adsorption in micropores. The fractional filling of pore (i.e. local adsorption isotherm) having half width $d$ is defined as the ratio of the adsorbed layer thickness $t(p,d)$ to the maximum allowable physical half width $(d - \sigma_s/2)$, which is:

$$\theta(p,d) = \begin{cases} \frac{t(p,d)}{d - \sigma_s/2} & \text{for } p < p^* \\ 1 & \text{for } p \geq p^* \end{cases}$$

(5)

where $\sigma_s$ is the collision diameter of surface atom, $p^*$ is the critical pressure at which the pore filling occurs, and it is obtained from the solution of the modified Kelvin equation ($\gamma$ is the liquid surface tension; $v_m$ is the liquid molar volume; $\theta$ is the liquid – solid contact angle):
where the statistical adsorbed film thickness is equal to:

\[
t(p,d) = \frac{c_B Z_B}{(1 - Z_B)} \left[ \frac{1 + (n_B b^2/2 - n_B/2)z^n_B - (n_B b + 1)z^{n+1}_B + (n_B b^2/2 + n_B/2)z^{n+1}_B}{1 + (c_B - 1)z_B + (c_B b^2/2 - b/2)z^n_B - (c_B b^2 + b/2)z^{n+1}_B} \right]
\]

(7)

\[\text{The Dubinin's theory of micropore filling.}\] The potential adsorption theory, originally proposed by Polanyi and developed by Dubinin and co-workers [8, 34-36], is classified as the “thermodynamic” approach since it is based on the phenomenological thermodynamics. The well-known Dubinin-Radushkevich (DR) adsorption isotherm equation was initially used for description of adsorption of vapours in homogenous activated carbons [3-5, 8, 34-36]:

\[
\theta = \exp \left[ -\left( \frac{A}{\beta E_o} \right)^2 \right]
\]

(8)

where \(\theta\) is the degree of micropore filling, \(A = R T \ln(p_s/p)\) is the differential free enthalpy of adsorption, \(\beta\) is the similarity coefficient, and \(E_o\) is the characteristic energy of adsorption. Later, this equation was found useful for the description of adsorption on a variety of adsorbents (for example silicas, zeolites and other materials [5, 36-38]) especially at low pore fillings.
As many authors reported, DR equation has not adequately described the experimental adsorption data on carbons, especially in the cases of high burnoff [39, 40]. To overcome this difficulty many authors applied the three-parameter Dubinin-Astakhov (DA) equation in the following form [3-5, 7, 8, 36, 40]:

\[
\theta = \exp \left[ -\left( \frac{A}{\beta E_0} \right)^n \right]
\]

(9)

where \( n \) is the empirical heterogeneity parameter. It can be used as a macroscopic measure of the sharpness of the micropore size distribution. For solids having a relatively narrow micropore size distribution curve, DA equation with \( n \) equal to 3 describes the experimental data well. Therefore, if the parameter \( n \) of a system deviates from 3 (usually smaller than 3), that system is called to be heterogeneous or having a wide micropore size distribution. A typical value of \( n \) for strongly activated carbons is between 1.2 and 1.8 [36].

Dubinin and Izotova proposed an alternative equation (DI) describing the adsorption isotherm on a heterogeneous and microporous solid [41]:

\[
\theta = \exp \left[ -\left( \frac{A}{\beta E_{10}} \right)^{n_1} \right] + \exp \left[ -\left( \frac{A}{\beta E_{12}} \right)^{n_2} \right] + \ldots + \exp \left[ -\left( \frac{A}{\beta E_{1M}} \right)^{n_M} \right]
\]

(10)

DI equation suggests a bi-porous structure of micropores. Two independent regions of a micropore system are characterised by DA or DR equation. This approach is one of the simplest approaches dealing with non-homogeneous solids. It is obvious that real heterogeneous solids are usually composed of several independents regions of micropores. Thus, Eq. (10) can be extended as follows [35]:

\[
\theta = \exp \left[ -\left( \frac{A}{\beta E_{10}} \right)^{n_1} \right] + \exp \left[ -\left( \frac{A}{\beta E_{12}} \right)^{n_2} \right] + \ldots + \exp \left[ -\left( \frac{A}{\beta E_{1M}} \right)^{n_M} \right] = \sum_{m=1}^{M} \exp \left[ -\left( \frac{A}{\beta E_{1m}} \right)^{n_m} \right]
\]

(11)

where \( M \) is the number of independent microporous regions. Consequently, when \( M \) tends to infinity the patch-wise character of topography of micropores is observed (i.e. the sum in Eq. (11) can be replaced by a continuous spectrum). In other words, micropores are grouped together into patches, which could be considered as independent adsorption sub-systems, forming the systems analogous to so-called “homotattic” surfaces.
For more complex microporous systems, Stoeckli [35] proposed a general form of adsorption isotherm equation (GAI) assuming DR (Eq. (8)) or DA (Eq. (9)) equation as a kernel:

$$\theta = \frac{1}{\Omega(B)} \exp\left[ -By \right] f(B) dB = \frac{1}{\Omega(B)} \sum_{t=0}^{\infty} \frac{(-By)^t}{t!} f(B) dB$$  

(12)

where $B = (E_0)^n$ is a structural parameter, $y = (A/\beta)^n$, $f(B)$ is an unknown distribution function of $B$ and $\Omega(B)$ is the integration range. Strictly speaking, the range of integration should reflect the properties of a microporous system i.e. the proper limit range should be between $B_{\text{min}}$ and $B_{\text{max}}$ (other parameters characterising the geometric and/or energetic heterogeneity) [42-53]. Different authors extend the integration range beyond this limit [7, 50-57]. In such cases simple adsorption isotherm equations can be obtained, applying Laplace transform or other uncomplicated inversion techniques. However, as it was mentioned by Cerofolini and Re [57] and clearly shown in numerical research by Wojsz [3], as well as by Gauden and Terzyk [50, 51, 53], extending of the integration range of Eq. (12) can lead to unphysical results and is questionable.

Many authors improved so-called optimisation solution of Stoeckli’s [35] integral equation. First of all Dubinin and Stoeckli [35] developed a new adsorption isotherm assuming that unknown distribution function $f(B)$ (or $f(x)$) can be approximated by Gaussian distribution and kernel of Eq. (12) can be described by DR formula. The Dubinin - Stoeckli (DS) equation [3, 35], which has been widely used in theoretical studies, can be written in the following form:

$$\theta(A) = \frac{1}{2\sqrt{1+2m\delta^2A^2}} \exp\left[ -\frac{m\delta^2A^2}{1+2m\delta^2A^2} \right] \left[ 1 + \text{erf}\left( \frac{x_0}{\delta\sqrt{2\sqrt{1+2m\delta^2A^2}}} \right) \right]$$  

(13)

where $m = (\beta\kappa)^2$, $\kappa$ is a proportional coefficient, $\beta$ is the similarity coefficient, erf is the error function [9], $\delta$ and $x_0$ are “dispersion” and mean of Gaussian distribution, respectively. Moreover, the relation between the parameter of micropore structure (mainly half-width $x$) and characteristic energy of adsorption, $E_0$ should be known. Up to the present, several empirical relations between the structural parameter and the micropore half-width have been proposed. Dubinin [35] postulated the most widespread indirect proportional relation, where for the adsorption of benzene on activated carbons $\kappa$ is assumed as equal to 12 [kJ nm/mol].
Knowing the parameters, the micropore size distribution may be generated using the formula [35]:

$$\frac{dW_0}{dx} = G(x) = \frac{W_0}{\delta \sqrt{2\pi}} \exp\left[ -\frac{(x-x_0)^2}{2\delta^2} \right]$$  \hspace{1cm} (14)

Wojsz [3] proposed another development of Dubinin's theory. First of all, he proposed several new equations assuming the DR/DA equation as a kernel of Eq. (12) and different forms of the micropore size distribution (Gaussian, Exponential, and others). Additionally, he incorporated physical boundaries in general form of integral equation with Dubinin's isotherm as a kernel, and proposed corresponding thermodynamic formulas. In the present study we used the well known equation proposed by Wojsz that can be treated as the corrected form of Eq. (13) (DA equation is considered as a kernel of Eq. (12) and it is assumed that the integration limit of the global adsorption isotherm and the normalization range of MSDs are the same: from zero to infinity) [3]:

$$\theta(A) = \exp\left[ \frac{\sigma^2}{2} \left( \frac{A}{\beta} \right) - \left( \frac{x_0 A}{\kappa \beta} \right) \right] \frac{\text{erfc}\left[ \frac{\delta}{\sqrt{2}} \left( \frac{A}{\beta} \right) - \frac{x_0^n}{\kappa^n \delta \sqrt{2}} \right]}{\kappa^n \delta \sqrt{2}}$$ \hspace{1cm} (15)

where erfc is the complementary error function [9]. This equation is rarely used due to slightly complicated form. The micropore size distribution can be obtained from the following relation:

$$\frac{dW_0}{dx} = G(x) = \frac{W_0 2n x^{n-1}}{\delta \kappa^n \sqrt{2\pi} \text{erfc}\left[ -\frac{x_0^n}{\kappa^n \delta \sqrt{2}} \right]} \exp\left[ -\frac{(x^n - x_0^n)^2}{2\delta^2} \right]$$ \hspace{1cm} (16)

According to Jaroniec and co-workers [7], all unknown distribution functions f(B) can be approximated by a shifted gamma distribution; and the kernel of Eq. (12) can be described by DR/DA equations. Basing on such assumptions and using integration range $\Delta_\theta \in (0, \infty)$ Jaroniec and co-workers proposed two simple adsorption isotherm equations (called JCh (n is the optimized parameter)) for the description of an adsorption process in the heterogeneous system of micropores [7, 51]:
\[ \Theta_{GR(b,\infty)} = \left( \frac{A^*}{\beta^* \rho} + 1 \right)^{-(\nu+1)} \quad (0 < b < \infty) \] (17)

(where \( \rho, \nu, \) and \( n \) are the parameters of the above equation) and the following form of the micropore–size distribution \( G(x) \):

\[ \frac{dW_0}{dx} = G(x) = \frac{W_0 n (\rho \zeta)^{\nu+1} x^{\nu(n+1)} \exp[-\rho \zeta x^n]}{\Gamma(\nu + 1)} \] (18)

Our considerations are limited to the simplest but frequently applied relationship, derived by Dubinin and co-workers (35), therefore:

\[ B = E_0^* = \frac{x^n}{\kappa^n} = \zeta x^n \] (19)

One should notice, that all the above mentioned methods of solution of the linear Fredholm equation of the first kind with Dubinin's equations as a kernel (as it was reported by Cerofolini and Re [57]) can be classified according to the optimisation methods. Clearly, the approximation of the real micropore size distribution by simple function (i.e. Gaussian, Gamma, Exponential, and so on) and the widening of the integration range (i.e. from zero to infinity) can lead to unphysical results [3, 50, 51, 53, 57, 58]. For this reason in the current paper we applied the well known CONTIN algorithm for solving the integral equation with Dubinin's kernel (Eq. (9)).

Developed by Provencher [16 – 18], CONTIN is a package for solving noisy linear integral equations of the first kind and a system of (possibly ill-conditioned) linear algebraic equations. This program is often applied for solving the integral equations for effectively continuous distributions of diffusion coefficients, molecular weights, relaxation times, electron densities, adsorption energy distributions, pore size distributions etc. [16-22, 59]. In the field of adsorption science the modifications of CONTIN algorithm were used by Puziy and co-workers [21, 22] for the estimation of the adsorption energy distributions, by Gun'ko and co – workers for the estimation of adsorption energy and pore size distribution [19, 20, 59], and in our recent studies, for the estimation of the pore size distributions [14, 24, 33, 60]. The description of the CONTIN package can be found in several papers [14, 16 – 22, 24, 33, 60].

The Horvath and Kawazoe method. The method proposed by Horvath and Kawazoe [61, 62], and improved by others [42, 63-69], is based on the principles of adsorption thermodynamics. The authors derived a relation
between the average potential energy of an adsorbate inside a slit-shaped micropore and the change of free energy upon adsorption:

\[
RT \ln \left( \frac{p}{p_s} \right) = U_0 + U_a
\]  
(20)

where \(U_0\) and \(U_a\) are the adsorbate-adsorbent and adsorbate-adsorbate interaction energy, respectively, averaged over the pore volume. The sum of \(U_0\) and \(U_a\) will depend on the choice of pore geometry and on assumed interaction potential. According to the earlier results, Horvath and Kawazoe [61, 62] assumed the slit-like model of micropores and they used the Everett and Powl 10-4 potential for the description of the adsorbate-adsorbent interactions [70-72]. For the system: nitrogen-activated carbon, the well-known non-linear HK equation can be written as:

\[
\ln \left( \frac{p}{p_s} \right) = \frac{62.38}{(L - 0.64)} \left[ \frac{1.895 \times 10^{-3}}{(L - 0.32)^3} - \frac{2.7087 \times 10^{-7}}{(L - 0.32)^5} - 0.05014 \right]
\]  
(21)

where \(L (\equiv 2d)\) is a micropore width. Eq. (21) relates the gas phase pressure in terms of the slit-shape micropore width. Thus, measuring the adsorption isotherm as a function reduced pressure:

\[
\theta = f(p/p_s)
\]  
(22)

MPSD can be obtained using simple transformations ((L-\(d_a\)) is the effective pore width and \(d_a\) is a diameter of carbon molecules equal to 0.34 nm):

\[
\theta = f(L-d_a)
\]  
(23)

and

\[
f(L - d_a) = -\frac{d\theta}{d(L - d_a)}
\]  
(24)

Although the HK method was originally developed for nitrogen adsorption, it has been extended [42, 63-69] for the cases of adsorption of other adsorbates, as well as for the cases of adsorption in the cylindrical zeolite and carbon pores.

**Density Functional Theory.** Pore size distributions (PSD and MPSD) were also calculated using the DFT software from Micromeritics (Norcross, GA).
A local mean field DFT was first used by Seaton and co-workers [73], and later Olivier [74] improved this method using a nonlocal mean field DFT. This method is considered by some authors [75-80] as the more quantitatively and accurate approach of the PSD determination.

3. EXPERIMENTAL

**Materials.** Four samples of activated carbons, characterised by significantly different porosity and the specific surface areas, were used in our considerations. Synthetic carbons A and B (irregular forms with the size: 0.30 – 0.43 mm) were obtained by Rychlicki [81] from polyfurfuryl alcohol. The detailed characteristics of those adsorbents and some adsorption properties were described previously [82-85]. Activated carbon A.U.G. Aktivekohle, (Germany) was produced from coconut shells [86]. The grains of A.U.G. Aktivekohle activated carbon have irregular shape with the size 0.5-0.71 mm. Activated carbon Norit N.V., (the Netherlands) is characterised of cylindrical regular grains with the size of 0.8 mm [86].

**Measurements.** Nitrogen adsorption isotherms were measured at 77.5 K using ASAP 2010 MicroPore System (Micromeritics, U.S.A). Before each measurement the carbon samples was desorbed in vacuum for 2 hours at the temperature of 473 K. The molar volume of liquid nitrogen is taken to be 34.666 cc mol$^{-1}$, and the density was 0.808 g cc$^{-1}$. The nitrogen data for carbons A.U.G. Aktivekohle and Norit N.V. has not been measured yet and will be published in a future correspondence. Benzene adsorption isotherms were measured at 293 K using a volumetric (for carbons A and B) apparatus with Baratron pressure transducers (MKS Instruments, Germany) and gravimetric Bakr-McBain balance (A.U.G. Aktivekohle and Norit N.V.).

4. RESULTS AND DISCUSSION

As it was described by Do and co-workers [27, 30] adsorption in the pores occurs via layer mechanism followed by the pore filling pressure. Obviously, the pressure at which pore filling occurs is lower for smaller pores. Figure 3 shows the pore filling pressure for nitrogen adsorption in pores at 77.5 K and benzene (at three temperatures; 293, 303, and 333 K) as the function of effective pore half-width [27, 29, 32]. As it was reported earlier by Do and co-workers [29, 26-33] the agreement between Do's theory and DFT method (data from Lastoskie et. al. [87]) is remarkable. It is worthwhile that Horvath and Kawazoe method not considerably shifted the pore-filling curve to the smaller values of the effective pore half-width. Up to the effective pore half width equal 3 nm all the methods give similar value of pore filling pressure.
For adsorption of benzene molecules the pore filling pressure curve is shifted to the larger value of the effective pore half-widths, comparing to nitrogen [27, 29, 32]. One should notice that the temperature does not affect significantly the pore filling pressure (presented as reduced pressure) curve for benzene [27, 29, 32]. The one calculated for larger temperature is above that for smaller temperature, meaning that for a given effective pore half width the reduced pressure at which the filling occurs is slightly higher for larger temperature.
In Figure 4 both experimental (solid line) and theoretical, points (calculated from Do’s and DFT methods (the DFT PLUS software)) adsorption isotherms at 77.5 K on synthetic carbons A and B are shown. The method proposed by Do and co-workers predicts very well nitrogen data for the whole relative pressure range. The small deviations of the Do’s model at very low pressures at first could be attributed by experimental errors; however, our recent study [88] showed that there are other reasons for this behaviour. We made a comparison between DFT and ND method for 20 different (porosity (microporous and mesoporous) and origin) carbonaceous materials (nitrogen adsorption) and it was concluded, that if microporosity of a carbon increases, the differences between the two methods become more pronounced, while DFT software fits the experimental data for such systems better. Figure 5 shows the comparison of the pore volume distributions obtained by DFT software, the method of Do and HK procedure. The agreements between all three methods, (especially between Do’s and DFT ones) are observed for nitrogen adsorption on synthetic samples of strictly microporous activated carbons.

Very interesting results were obtained for the case of adsorption of benzene at 293 K. First of all, the Dubinin’s approximation methods describe the experimental adsorption data of benzene on strictly microporous synthetic activated carbons poorly, except DA and JCh equations (see Figure 6 and Table 1). As one can observe in Figure 7 all the methods (except JCh equation) reduce to the delta Dirac function (i.e. suggest homogeneity of micropore system) and give the pore widths around 1.25 – 1.50 nm for both tested carbons. The Jaroniec and Choma equation give unstable results for the adsorption of nitrogen on the above-mentioned carbons. First of all, unphysical values of gamma-type MPSD parameters are observed for generated MPSDs for solids with very small amount of mesopores that are characterised by a relatively small value of dispersion (i.e. heterogeneity) [58]. Moreover, this equation describe experimental adsorption isotherms well but optimised gamma-type MPSD parameters possess unphysical meaning and lead to questionable results (the impossibility of the generating the micropore-size distribution functions). Although DA equation (just like Do’s method) approximates the benzene data very well, it gives similar pore half widths to remaining Dubinin-type methods. This can be explained by the fact that in simple relation between structural parameter and micropore with the parameter "n" of the DA equation is not taken into account.

Tab. 1. Sorption characteristics of investigated activated carbons. Benzene vapour adsorption isotherms were described in the rage of relative pressure (\(p/p_0<0.1\))
HK analysis leads to smaller pore diameters than obtained from Dubinin's approximation methods. Also Do’s method shifts MPSDs of the activated carbons to the smaller values of micropore widths. The disagreement between Do method and CONTIN computations for carbons A and B can be seen in Figure 8. The MPSD for carbon A and B are obtained using the CONTIN package for different values of an empirical parameter of the DA equation ("n" of DA equation was fixed in this case as constant starting parameter in this advanced numerical program; the values of "n" were taken as equal to two, three and the third value was taken from best fitting of DA equation to nitrogen isotherm data (see Table 1)).
Fig. 4. Theoretical points obtained by fitting of Do’s and DFT methods to the experimental data (Exp) measured on synthetic activated carbons A and B (lines)
Fig. 5. Pore sized distributions of activated carbons A and B obtained from the fitting of nitrogen adsorption data at 77.5 K (DFT – density functional theory, Do – Do’s method, HK-Horvath and Kawazoe equation)
Fig. 6. The results of the fitting of experimental benzene adsorption isotherm determined at 293 K (Exp – experimental points, Do – Do’s method, DR – Dubinin and Radushkevich equation, DA – Dubinin and Astakhov equation, DS – Dubinin and Stoeckli equation, W – the equation proposed by Wojsz, JCh – the equation of Jaroniec and Choma)
Fig. 7. Pore sized distributions of activated carbons A and B obtained from the fitting of benzene adsorption data at 293 K (Do – Do’s method, HK – Horvath and Kawazoe model, DR – Dubinin and Radushkevich equation, DA – Dubinin and Astakhov equation, DS – Dubinin and Stoeckli equation, W – the equation proposed by Wojsz). The Jaroniec and Choma equation gives unstable results for the adsorption of nitrogen and unphysical values of gamma-type MPSD parameters are observed at the same time.
It means that we are assuming different forms of the kernel and different models of adsorption in homogeneous patches of the considered adsorbents. The obtained results indicate that the influence of the DA heterogeneity parameter on the position as well as on the shape of the MPSD is not large. Moreover, this parameter affects the MPSD of the considered activated carbons in a different way. So it seems obvious that the differences between the two most advanced methods i.e. CONTIN algorithm and Do's procedure are caused by the type of the relationship between pore diameters and the characteristic energy of adsorption. In fact we have shown recently [14] for nitrogen adsorption data that the type of this relation influences obtained PSDs significantly.

For remaining activated carbons (i.e. Norit N.V. and A.U.G. Aktivekohle) the observations are also very interesting. First of all, Dubinin's methods fitted low region (p/p₀<0.1) of experimental data very well (see Figure 9 and Table 1). Moreover, as one can see in Figure 10, MPSDs obtained by different Dubinin-type methods are very similar each other and similar to Do's method results. This is caused by a greater dispersion of micropores of those carbons, comparing to synthetic A and B activated carbons. One should notice, that in this case CONTIN algorithm leads to the MPSDs that are very similar to MPSDs obtained by Do's method (Figure 11). All the observations suggest that for benzene adsorption on micro-mesoporous materials the Do method and CONTIN solution of integral equation with DA/DR as a kernel give realistic picture of internal structure of porous materials. Additionally, for adsorption of nitrogen at 77.5 K the results of Do's methods are very similar to DFT ones.

Finally, we want to point out that many questions concerning the determination of the structural heterogeneity of porous materials arise. For example, similar results of DFT computations (i.e. two peaks placed in the micropore region and the absence of micropores having pore half width equal about 1 nm). The latter problem occurs also in some PSDs obtained from Do method. It was discussed by Olivier [89], as well as by Jagielło and Tolles [74]. In our opinion, this can be caused by neglecting the heterogeneity of pore walls, both in computer simulations as well in Do’s method. On the other hand, taking the effect of heterogeneity of the pore walls into account is slightly complicated problem therefore, we will try to solve it in our future studies.

**Acknowledgment:** Authors thank to Ms. Dorota Palijczuk (WICHIR, Warsaw) for experimental data of benzene adsorption on carbons Norit N.V. and A.U.G. Aktivekohle.
Fig. 8. Pore size distributions of activated carbon A and B obtained from the fitting of benzene adsorption data measured at 293 K. The comparison of CONTIN computations with DA and Do’s method results.
Fig. 9. Results of the fitting of experimental benzene adsorption isotherms determined at 293 K (Exp – experimental points, Do – Do’s method, DR – Dubinin and Radushkevich equation, DA – Dubinin and Astakhov equation, DS – Dubinin and Stoeckli equation, W – the equation proposed by Wojsz, JCh – the equation of Jaroniec and Choma)
Fig. 10. Pore size distributions of activated carbon Norit N.V. and A.U.G. Aktivekohle obtained from the fitting of benzene adsorption data at 293 K (Do – Do’s method, HK – Horvath and Kawazoe model, DR – Dubinin and Radushkevich equation, DA – Dubinin and Astakhov equation, DS – Dubinin and Stoeckli equation, W – the equation proposed by Wojsz, JCh – the equation of Jaroniec and Choma)
Fig. 11. Pore size distributions of activated carbon Norit N.V. and A.U.G. Aktivekohle obtained from the fitting of benzene adsorption data at 293 K. The comparison of CONTIN computations with DA and Do's method results.

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