Estimation of the pore-size distribution function from the nitrogen adsorption isotherm. Comparison of density functional theory and the method of Do and co-workers

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Abstract

A comparative analysis of the results for the estimation of the pore-size distribution based on the methods of Do and co-workers (ND) and density functional theory (DFT) is given. A new algorithm (ASA, Adsorption Stochastic Algorithm) is adopted and it is shown that this algorithm can be successfully applied for the determination of the PSD curve from the ND method. The obtained results show that, generally, the ND and DFT methods lead to almost the same PSD curves and this similarity is observed for carbons of different origin and possessing different pore structures. However, if the contribution of micropores to the PSD increases, the differences in the fit of ND and DFT to the experimental data are more pronounced.
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1. Introduction

Adsorption on heterogeneous adsorbents plays an important role in many fields of science and technology. Numerous processes of technological and scientific interest, such as catalysis, adsorption, membrane separations and noncatalytic gas–solid reactions, are strongly affected by the structural and/or energetic heterogeneity of surfaces. The pore-size distribution function is usually used as a quantitative characteristic of the porous structure of solid adsorbents with respect to their heterogeneity [1–4]. The pore-size distribution function of a porous medium is perhaps its most important characteristic, since it influences the transport and equilibrium of molecules adsorbed in the structure. As a rule, for the calculation of the pore-size distribution function, adsorption measurements of standard substances from the gas phase are carried out. In accordance with the patch-wise model of surface topography the experimentally measured adsorption isotherm is expressed mathematically as [1–4]

$$\Psi_t(p,T) = \int_{z_{min}}^{z_{max}} f(z)g_{theor}(z,p)\,\mathrm{d}z \qquad (1)$$

where z describes the heterogeneity of the adsorbent, and is related to one of the properties of the porous solid (as a rule, it is related to the adsorption energy or to parameters

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of the porous structure, the half-width d, the effective width H ($= 2d - \sigma_{ss}$), and the effective half-width x ($= H/2$), where $\sigma_{ss} = 0.3400$ nm for C atoms on a carbon surface); $f(z)$ is a distribution function; $g_{theor}(z,p)$ is the local adsorption isotherm (i.e. the kernel) which describes the adsorption process; and z_{min} is the smallest and z_{max} the largest value considered in the analysis.

Taking into consideration the different mechanisms of adsorption in the different ranges of physically effective pore half-widths x [5]:

$$\Gamma(p) = \int_{\Omega(x)} f(x) g_{theor}(x,p)\, dx$$

$$= \sum_k \int_{\alpha_k(x)} f(x) \beta_{k,theor}(x,p)\, dx \qquad (2)$$

where $\Omega(x) = \langle x_{min}, x_{max} \rangle$ corresponds to the smallest and largest effective pore half-width present in the adsorbent, $f(x)$ is the pore-size distribution function over the whole range of x, and k corresponds to the adsorption process characteristics for the pore range $\alpha_k(x)$ described by the theoretical local adsorption model $\beta_{k,theor}(x,p)$. As an example, when the investigated porous medium is strictly microporous the well-known Dubinin–Astakhov equation can be used as the local adsorption isotherm in the micropore range, especially for the description of the so-called 'primary micropore filling' process [6–8]. Assuming that Eq. (2) can be simplified for cases when adsorption in larger pores is negligibly small, one can write [1–4]

$$\Gamma(p) = W_0 \int_{\Omega(x)} f(x) \exp[-\mu A^n x^n]\, dx \qquad (3)$$

where W_0 is the micropore capacity; $A = -\Delta G = RT \ln(p_s/p)$ is the adsorption potential defined as the change in the Gibbs' free energy taken as negative; R is the universal gas constant; T is temperature; p and p_s denote the equilibrium pressure and the saturation vapour pressure of the adsorbate, respectively; $\mu = (\kappa \beta)^{-n}$ depends on the adsorbate and the kind of microporous structure [β is a similarity coefficient and κ is an empirical constant assumed to be 12 kJ nm mol^{-1}, connecting the pore width and the characteristic energy of adsorption (E_0)], and n is the equation parameter.

On the other hand, when the investigated porous medium is a micro-mesoporous material, Eq. (2) can be transformed into [5]

$$\Gamma(p) = W_0 \int_{\Omega(x)} f(x) \exp[-\mu A^n x^n]\, dx + \int_0^{x_k(p)} f(x)\, dx$$

$$+ t(p) \int_{x_k(p)}^{x_{r_{max}}} \frac{2f(x)}{x}\, dx \qquad (4)$$

where x_k is the mesopore radius, $x_{r_{max}}$ is the upper limit of the mesopore region and $t(p)$ is the statistical thickness of the adsorbate layer.

From the considerations given above it results that the complexity of the estimation of the pore-size distribution function from adsorption data strictly depends on the pore range [9–13]. Another difficulty associated with the problem of the estimation of the pore-size distribution from adsorption data is the ill-posed character of the adsorption Fredholm linear equation of the first kind [14,15]. Several advanced numerical algorithms have been adopted for solving the unstable adsorption integral equation [8,14–21]. Most of them (i.e. the Tikhonov regularisation method, the modified Galerkin method, orthogonal collocation, approximation methods, etc.) are both theoretically and computationally advanced, i.e. not simple for typical chemists.

For such reasons, developing new methods and algorithms describing the full range of the measured adsorption isotherm is very important. New possibilities in this field are two novel methods based on an advanced description of adsorption in carbon pores and computer simulations [22–24] [density functional theory (DFT) and Grand Canonical Monte Carlo (GCMC)], and the Nguyen and Do (ND) method [18,25–27]. Some authors have suggested that both methods lead to similar results [18,25–27], however a comparison on a wide scale has not yet been made.

In the current study we decided to put these two very promising approaches side by side. Both methods are used for the estimation of the pore-size distributions from low-temperature nitrogen adsorption isotherms determined at 77.5 K. To make the comparison as accurate and as wide as possible we chose different carbons and carbonaceous (for example, carbon/carbon-silica) materials. Therefore, not only modified and unmodified activated carbons of different kinds and origins possessing different porosities, but carbonaceous films and carbosils are also characterised using both approaches. The results are compared and conclusions have been drawn.

2. Theoretical developments

Do and co-workers [18,25–27] relied on both the Kelvin equation and statistical thermodynamics to develop a new model for estimating the PSD function from a single adsorption isotherm. In their method the n-BET/BET equation is used for the description of the process of layering in pores of any size, and the Kelvin equation is used for calculating the pore filling behaviour. The proposed methodology is similar to that used two decades ago to describe the mesopore size distribution. The significant difference is that Do and co-workers take into account the enhancement in the n-BET/BET equation constant due to the stronger dispersive forces in smaller pores, as well as

the enhancement in the pressure exerted by molecules occluded in the pores.

The model developed by Do and co-workers is based on the following assumptions [18,25–27]:

(i) Activated carbon has pores of slit shape; this shape (although idealised) is generally accepted for micropores.
(ii) The adsorption mechanism comprises two steps in series: multilayering followed by pore filling.
(iii) The dispersive force is the dominant adsorption force [it is well known that this is generally true for the cases of non-specific (for example, nitrogen) adsorbates and for carbons].
(iv) The concentration of adsorbed phase in the multilayering step is described by an n-BET/BET-type equation, with allowance for the enhancement in the C constant. It is necessary to take this enhancement into account due to the changes in the value of the energy of adsorbate–adsorbate–adsorbent interactions resulting from the presence of pores.
(v) The pore filling step is described by the Kelvin equation.
(vi) The adsorbed phase density is the same as the corresponding liquid density.

Knowing the adsorption isotherms in individual pores of different dimensions and assuming the concept of a patch-wise model of the surface topography, one can again deal with the linear Fredholm equation of the first kind. Mathematically, the total amount adsorbed, in terms of volume of pores of effective width H $(= 2d - \sigma_{ss})$, taken up by adsorbate molecules is given by [27]

$$W(p) = \int_{\sigma_{ss}}^{H_k(p)} f(H)\,\mathrm{d}H + \int_{H_k(p)}^{H_{max}} \frac{2t(p,H)}{H - \sigma_{ss}} f(H)\,\mathrm{d}H \qquad (5)$$

where $t(p,H)$ is the statistical thickness of an adsorbed layer and $H_k(p)$ is the critical pore width calculated from

$$\Theta(p,H) = \begin{cases} \left(\dfrac{t(p,H)}{H/2} \right) & \text{for } p < p^* \\ 1 & \text{for } p > p^* \end{cases} \qquad (6)$$

where p^* is the critical pressure at which pore filling occurs.

3. Inverse problem of PSD determination

The solution of Eq. (5) is the well-known so-called 'ill-posed' problem. Actually, there is a large and growing number of papers on the numerical solution of integral equations with several monographs having been published. One reason for the sheer volume of this activity is that there are many different kinds of equations, each with

many different possible pitfalls; often, many different algorithms have been proposed to deal with a single case.

Although while composing each new algorithm the authors usually take into consideration the shortcomings of previous algorithms, an ultimate procedure for the solution of the linear Fredholm integral equation of the first kind has not yet been elaborated. Therefore, new efforts are needed to improve the methods for the analysis of this problem. First of all, the new proposed method should be fast, and enable one to attain approximately the same accuracy (it should reproduce the original multi-peak and complicated 'unknown' function with excellent accuracy). Secondly, such a formulation of the minimisation problem should prevent an unphysical value of an unknown and evaluated function (i.e. strong oscillations, a negative value of the probabilistic distribution function, the appearance of artificial peaks, etc.). Moreover, the program code should be simple, short and easily applied by a wide group of scientists. Therefore, in the current paper a special numerical algorithm based on the relaxation procedure is proposed. As reported by Do and co-workers [25], the problem of the solution of the integral Fredholm equation of the first kind may be replaced by a classical non-linear minimisation problem with constraints. Therefore, in general, we can define the expression describing a global adsorption isotherm as follows [25]:

$$\Psi_t(p_j) = \int_{H_{min}}^{H_{max}} g_{theor}(H_i,p_j)f(H)\,\mathrm{d}H \cong \sum_{i=1}^{N} w_i \cdot g_{theor}(H_i,p_j);$$

$$i = 1,2,\ldots,N; \; j = 1,2,\ldots,M \qquad (7)$$

where $g_{theor}(H_i,p_j)$ is the discrete form of a local adsorption isotherm (i.e. kernel) that describes the adsorption process in homogenous pores.

Based on both the theory of non-linear minimisation and the static penalty function, our task is to find $\bar{w}$ so as to minimise the functional $\Omega(\bar{w})$. Mathematically, minimise

$$\Omega(\bar{w}) = \begin{cases} \sum_{j=1}^{M} \left(\Psi_t(p_j) - \sum_{i=1}^{N} w_i g_{theor}(H_i,p_j) \right)^2 & \text{if } \bar{w} \in \Sigma \cap S \\ \sum_{j=1}^{M} \left(\Psi_t(p_j) - \sum_{i=1}^{N} w_i g_{theor}(H_i,p_j) \right)^2 + \sum_{i=1}^{T} C_i \delta_i & \text{otherwise} \end{cases}$$

$$(8)$$

with respect to $\bar{w} = (w_1, w_2, \ldots, w_N) \in R^N$, where

$$\begin{cases} \delta_i = 1 & \text{if constraint '}i\text{' is violated} \\ \delta_i = 0 & \text{if constraint '}i\text{' is satisfied} \end{cases} \qquad (9)$$

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

$$0 \leq l(i) \leq w_i \leq u(i); \; 1 \leq i \leq N \qquad (10)$$

The feasible search space Σ is assumed outside the defined N-dimensional rectangle. It should be noted that $\Omega(w_i)$ is the penalised objective function, and C_i is a constant imposed for violation of constraint i. We should point out that such a definition of the minimisation problem prevents unphysical solutions being obtained [i.e. negative values of the distribution function $f(H)$, unphysical oscillations of the distribution function $f(H)$, etc.]. Up to now we have only defined a minimisation problem of the functional $\Omega(\bar{w})$, but we have not stated anything about the construction of the minimisation procedures (Fig. 1).

To extract $f(H)$ from a measured global adsorption isotherm we can use genetic algorithms, evolutionary algorithms, simulated annealing, a taboo search, deterministic algorithms (i.e. the simplex strategy of Nelder and Mead, the strategy of Hook and Jeeves, etc.), gradient methods (i.e. the simple gradient method, etc.), and hybrid methods [28,29]. All of the powerful techniques mentioned above minimise all unknown variables simultaneously. In our new algorithm presented in this study, the adsorption stochastic algorithm (ASA), the well-known relaxation (a successive variation of the variables, parallel axis search, Gauss–Seidel strategy, alternating variable search, sectioning method) [30] was applied. The main purpose of such a minimisation procedure is successive minimisation in one dimension (i.e. minimise only one element from the $\bar{w}$ vector, see Fig. 1). Therefore, only optimising the first
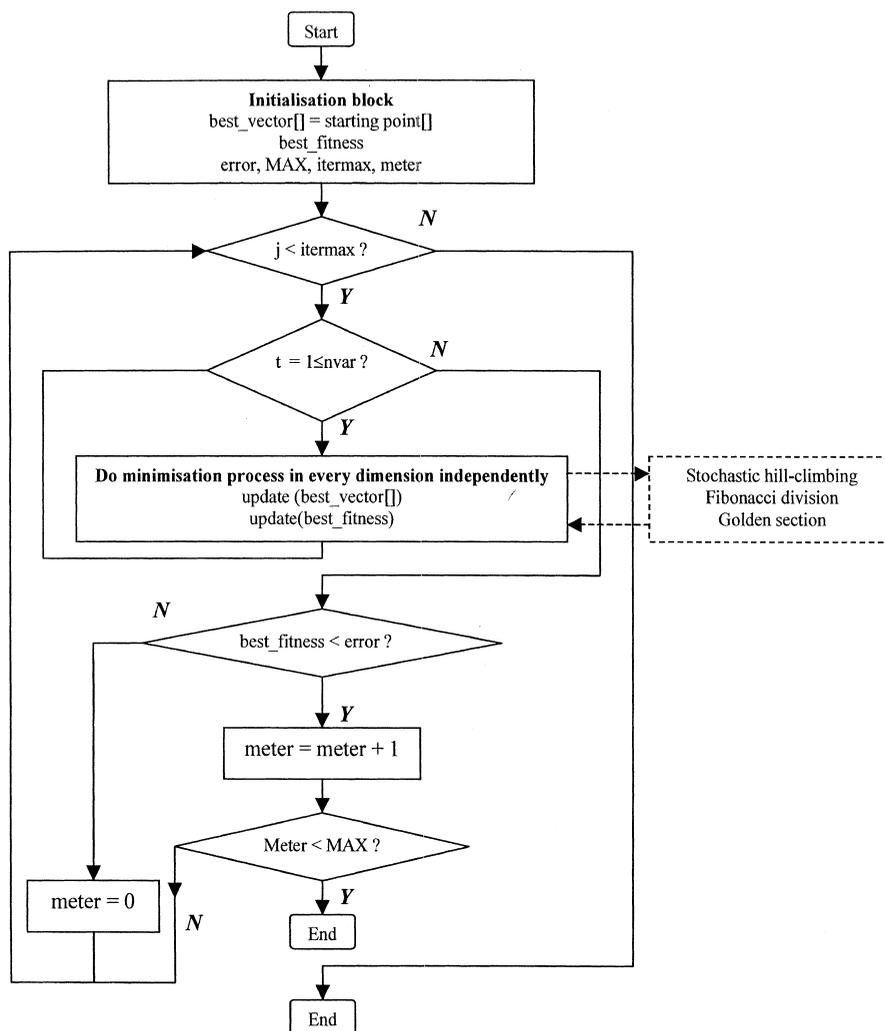

Fig. 1. Flow chart of the ASA algorithm. Legend: best_vector—$\bar{w} = (w_1, w_2, \ldots, w_{n\,var})$, for the starting point a uniform distribution of weights is assumed; best_fitness—the parameter characterising the fitness of the global theoretical isotherm to the experimental one; itermax—the maximum number of iterations; error—the accuracy of the fitness; MAX—the critical number of iterations according to the condition best_fitness<error.
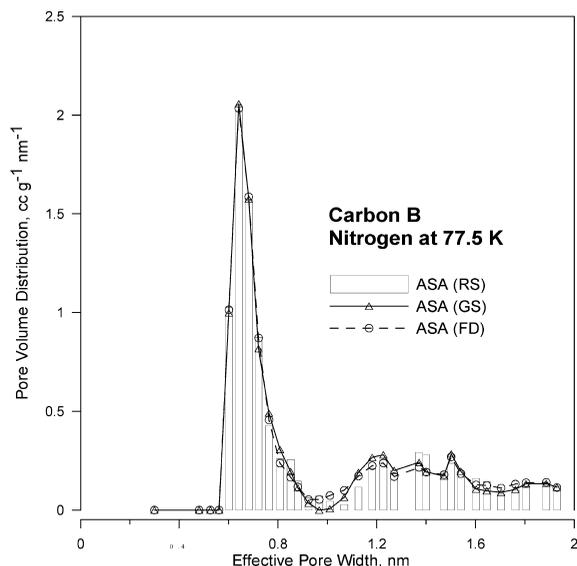
Fig. 2. Pore-size distribution of synthetic carbon B obtained by Do's method (optimisation by ASA). RS, Rechenberg–Schwefel; GS, golden section; FD, Fibonacci division.

elements of the optimisation variables, the $\bar{w}$ vector first carries out the optimisation. Once w_1 is optimised, w_2 is then optimised next until w_N has been optimised. Once this is completed, the process is then repeated until no further change in the functional is observed. In the ASA program, the well-known Rechenberg–Schwefel (RS), Fibonacci division (FD), and golden section (GS) procedures were used for estimating the relative minimum in one dimension. All such procedures give very similar results (as an example, see Fig. 2). We should point out that all minimisation routines applied with ASA give very similar results, but the time required for computation differs significantly.

4. Experimental

Nitrogen adsorption measurements were carried out using an ASAP 2010 volumetric adsorption analyser from Micromeritics (Norcross, GA, USA) at liquid nitrogen temperature (77.5 K) in the relative pressure range from about 10^{-6} to 0.999. Before measurement, the samples were outgassed for 2 h at 473 K. The analysed materials were divided into five groups according to the type of porosity or origin (four samples in each group were studied). Since some of the materials were not available commercially, the synthesis method is described more comprehensively. However, a detailed description of the preparation procedure can be found in the respective references.

4.1. Group I—Strictly microporous carbonaceous materials (Fig. 3)

These were materials possessing pores where it was shown (for example, from the shape of high-resolution α_s plots) that the primary micropore filling process predominated, i.e. four carbonaceous films obtained by the method of Zawadzki (the synthesis procedure can be found in Refs. [6,31]). The following materials were studied: C_{873}, $C_{873}Cu$, $C_{ox}Cu$, and $C_{ox}Ni$. Carbon samples were prepared from cellulose [6,31]. The raw material used for carbonisation was cellophane that had previously been purified in 20% HCl and washed repeatedly with distilled water. The charring experiments were set up as follows: cellulose samples carbonised at 573 K in air for 1 h were evacuated at 873 K for 1 h under dynamic vacuum. The following procedure was used to prepare oxidised carbon samples: the samples outgassed at 873 K (a standard pre-treatment) were exposed to 1000 hPa pure O_2 at 573 K for 1 h and evacuated at 873 K; they were then oxidised once more at 573 K (C_{ox}). Samples after outgassing at 873 K are denoted C_{873}. This film was used as the initial material for obtaining metal (Cu and Ni) loaded powdered oxidised carbon samples. They were prepared by an incipient wetness technique using aqueous nitrate solutions as a precursor. All samples were heated in vacuum at 473 K. The obtained samples were denoted $C_{ox}Cu$ and $C_{ox}Ni$. Moreover, sample $C_{ox}Cu$ was desorbed in vacuum at 873 K for 1 h and the obtained sample was denoted $C_{873}Cu$.

4.2. Group II—Microporous carbons (Fig. 4)

Micropores are mainly present in the structure (i.e. the 'external' surface is negligibly small compared to the apparent surface area of the micropores). However, the microporosity is dispersed over a relatively wide range. Two polymeric carbons (A and B), obtained from polyfurfuryl alcohol carbonised in vacuum, were studied [32,33]. The initial adsorbent (carbon A) was prepared by activation with carbon dioxide of the coke obtained in such a way, and this was followed by annealing in a flow of hydrogen. Such a procedure leads to a negligibly small concentration of oxygen groups on the surface of the carbon. Carbon B was obtained by nitric acid oxidation of carbon A. Additionally, commercial microporous carbons D55/2 (Carbo-Tech, Essen, Germany) and Row 0.8 Supra (Norit, Amersfoort, Netherlands) were analysed.

4.3. Group III—Micro-mesoporous carbons (Fig. 5)

These materials mainly contain micropores in the structure, however the mesopore content cannot be neglected: commercial carbons F 300 (ChemViron, NJ, USA) AHD and WD (commercial activated carbons from Hajnówka, Poland, de-ashed using the procedure of Korver) and D43/
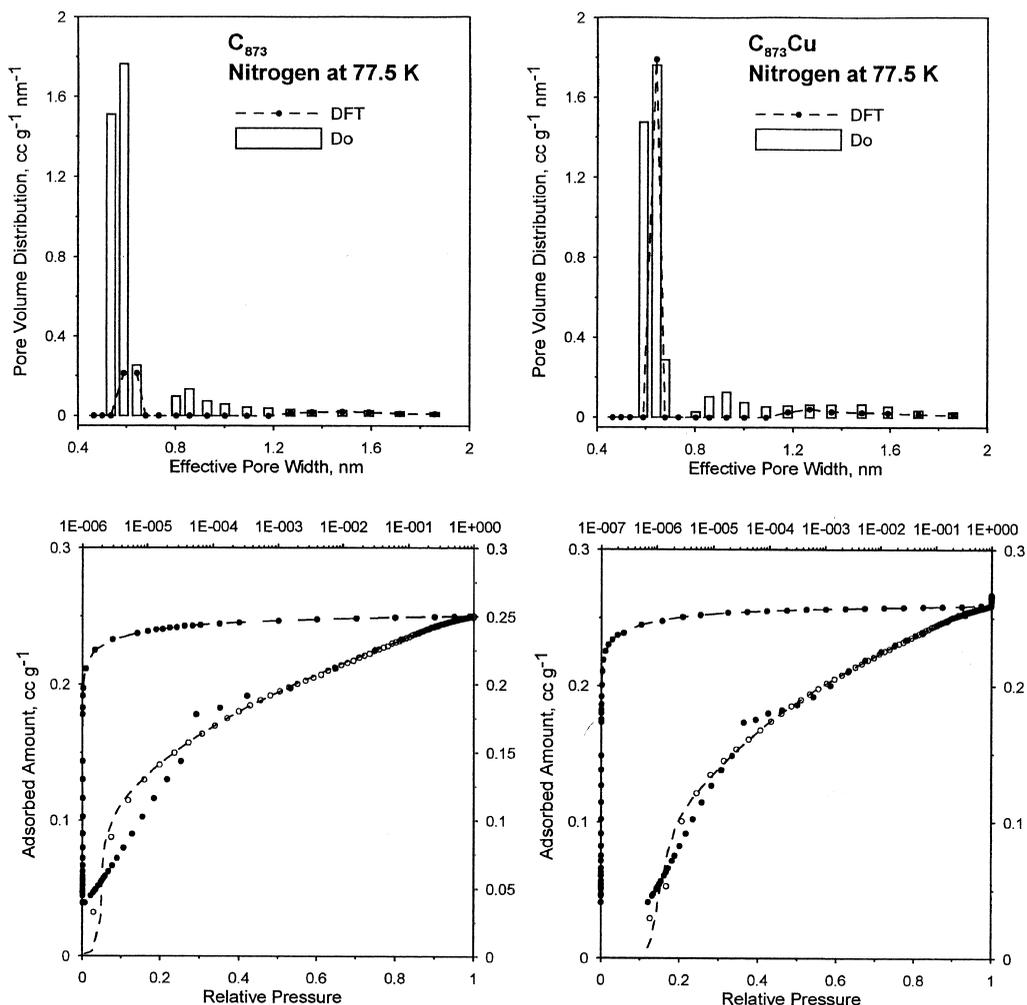
Fig. 3. The results of the comparative analysis of the PSD for some representative cases of the Group I—carbonaceous films. Lower panel shows the fit of the results obtained from the mehod of Do (●), DFT (○) to the experimental data (- - -). Note that in the lower panel also the data in the logarithmic scale are shown.

1 (Carbo-Tech) de-ashed by the procedure described earlier [34].

4.4. Group IV—Micro-mesoporous carbon fibres (Fig. 6)

In this group, four activated carbon fibres, PAN ACF 1–3 and Rayon ACF, were studied. They were synthesised by the method of Ryu and co-workers [35,36]. Poly-acrylonitrile was the initial substrate and carbons were obtained by continuous synchronism carbonisation and activation in steam, carbon dioxide and nitrogen gas atmospheres.

4.5. Group V—Micro-mesoporous carbosils (Fig. 7)

Mainly mesoporous, this group contained four carbosils

obtained by the method of Leboda and co-workers [37]. They were obtained from silica gel Si-60M (Merck, grain fraction 0.2–0.5 mm) by pyrolysis of CH_2Cl_2 (purity 99%, Polish Chemical Reagent Factory) under dynamic conditions in a stream of nitrogen (823 K for 6 h) for 0.5, 1, 2, and 3 h (labeled AB-i, $i = 1$–4). The carbon concentration (C_C) in AB-i was 1.5, 2.3, 5.9, and 10 wt.%, respectively, determined using differential thermal analysis.

5. Results and discussion

To make a comparison of the DFT and ND methods independent of the quantity of local isotherms, we used in the ND method the same number (82) of local isotherms (generating for the same effective widths changing from 0.465 to 233.9 nm) as in the DFT software (DFT PLUS
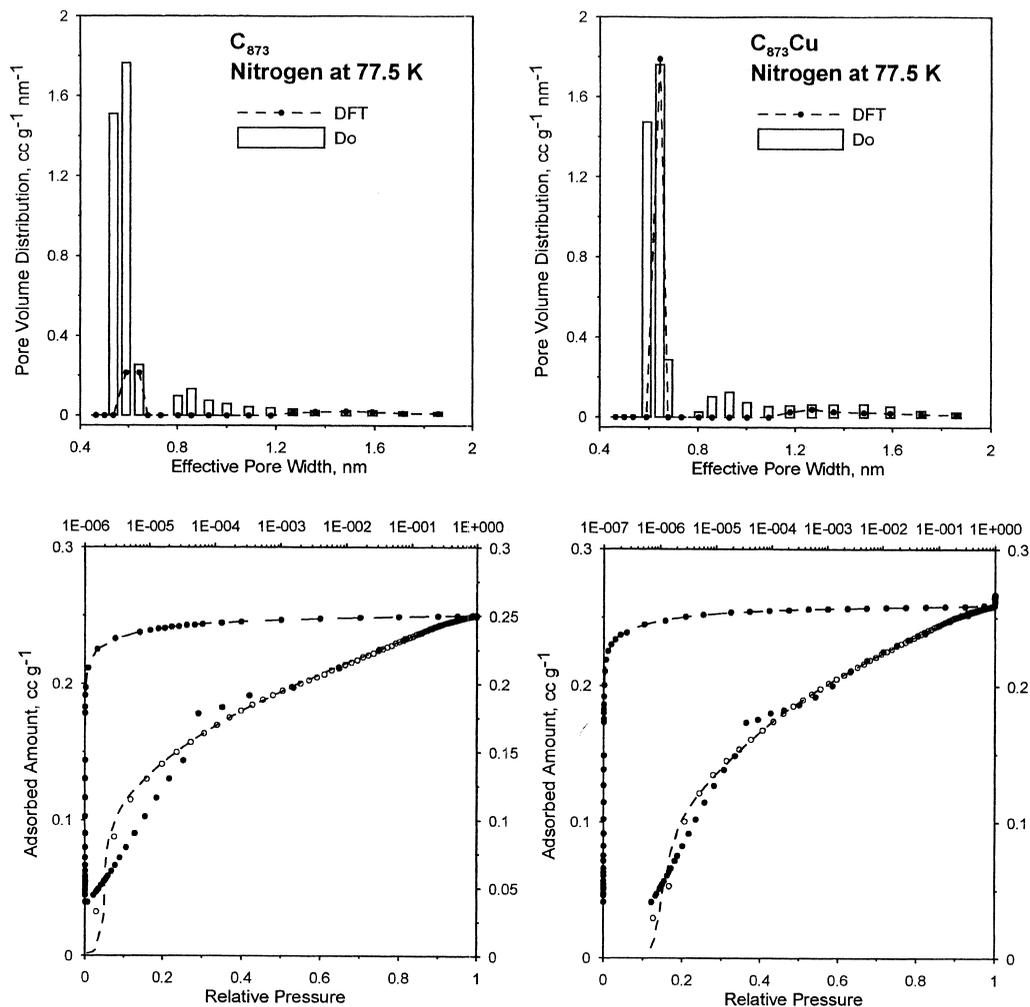
Fig. 4. The results of the comparative analysis of the PSD for some representative cases of the Group II—microporous carbons. Lower panel shows the fit of the results obtained from the method of Do (●), to the experimental data (- - -). For the cases where the value of the determination coefficient (for ND method) is smaller than 0.99, the results from the DFT method (○) are also presented.

software, ASAP 2010, Micromeritics). However, there are two main problems associated with a comparative analysis of the methods. First, associated with the DFT method is the choice of the so-called regularisation parameter, λ. It is well known that the regularisation parameter describes the weighting of 'the adsorption' and 'experimental error'. Therefore, the selection of this parameter plays a central role in finding a solution. Von Szombathely and co-workers [16] distinguished two principally different ways of determining the best choice: a manual choice by interactive judgment of the solution on a graphic displayed for several values of λ (applied in the INTEG algorithm), or the postulation of an aim function for the appropriate optimal regularisation parameter λ_{opt}, the choice of which can be automated by suitable search algorithms (applied, for example, in the CONTIN algorithm [18]). The first procedure is investigated in the current paper. Fig. 8 shows a comparison of the pore-size distributions obtained from the DFT method for different values of λ. It can be seen that there is a similarity between the DFT and the ND method for small values of λ. Moreover, Fig. 8 shows that the pore-size distribution becomes flatter as the effective smoothing parameter increases. The PSD shape changes from an initial modal distribution to a much flatter monomodal distribution. Davies and Seaton [38] suggested (analysing slit-shaped and rectangular models of pores) that, for large values of the effective smoothing parameter (compared with the average experimental error), the monomodal distribution is accurate and is the most probable.

The second problem associated with both methods is the postulation of the value of the parameter C (BET equation), i.e. the choice of the reference material. It is well known that, in the DFT PLUS software STERLING FT-G [22], carbon black is the reference adsorbent. However, for
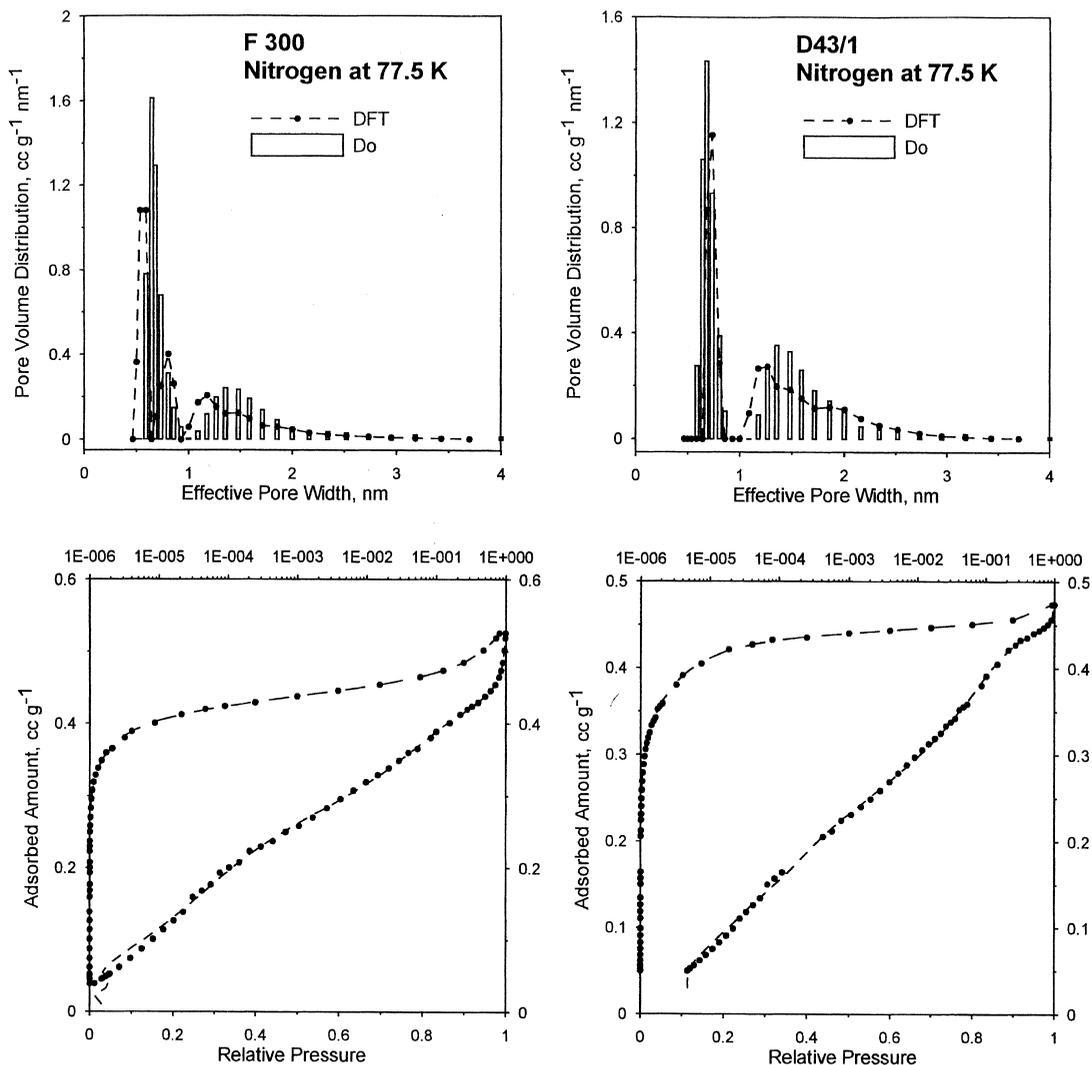
Fig. 5. The results of the comparative analysis of the PSD for some representative cases of the Group III—micro-mesoporous carbons. Lower panel shows the fit of the results obtained from the method of Do (●), to the experimental data (- - -).

nitrogen adsorption on this carbon the value of C is 23 [39]. On the other hand, the ND method assumes $C = 238$. Fig. 9 shows the influence of the value of C on the local adsorption isotherms calculated from the ND method for two different pore diameters. It can be seen that a small influence of C is observed for larger pores; however, for narrower pores this effect is larger. This can also be observed in Fig. 10, where we show the influence of C on the PSD calculated for one of the studied systems. It can be seen that the value of C determines the position of the peaks obtained from the ND method, however the influence is small. Summing up, the influence of the parameter λ is the most important, therefore to compare both methods we assumed $\lambda = 0.00001$.

The PSDs of some of the tested carbon materials determined by the method developed by Do and co-workers (applying the ASA algorithm presented in this study) and using DFT software are shown in Figs. 3–7. The lower panel in the figures shows the fit between the isotherms calculated from the ND method and the experimental isotherms. For the cases where the value of the determination coefficient (for the ND method) is smaller than 0.99, the results from the DFT method are also presented. The carbonaceous films (Group I) prepared by Zawadzki are characterized by a very small dispersion of micropores [6] (i.e. high homogeneity of the internal structure—Fig. 3). A bimodal character of PSD is observed for all the investigated samples. For this group, the
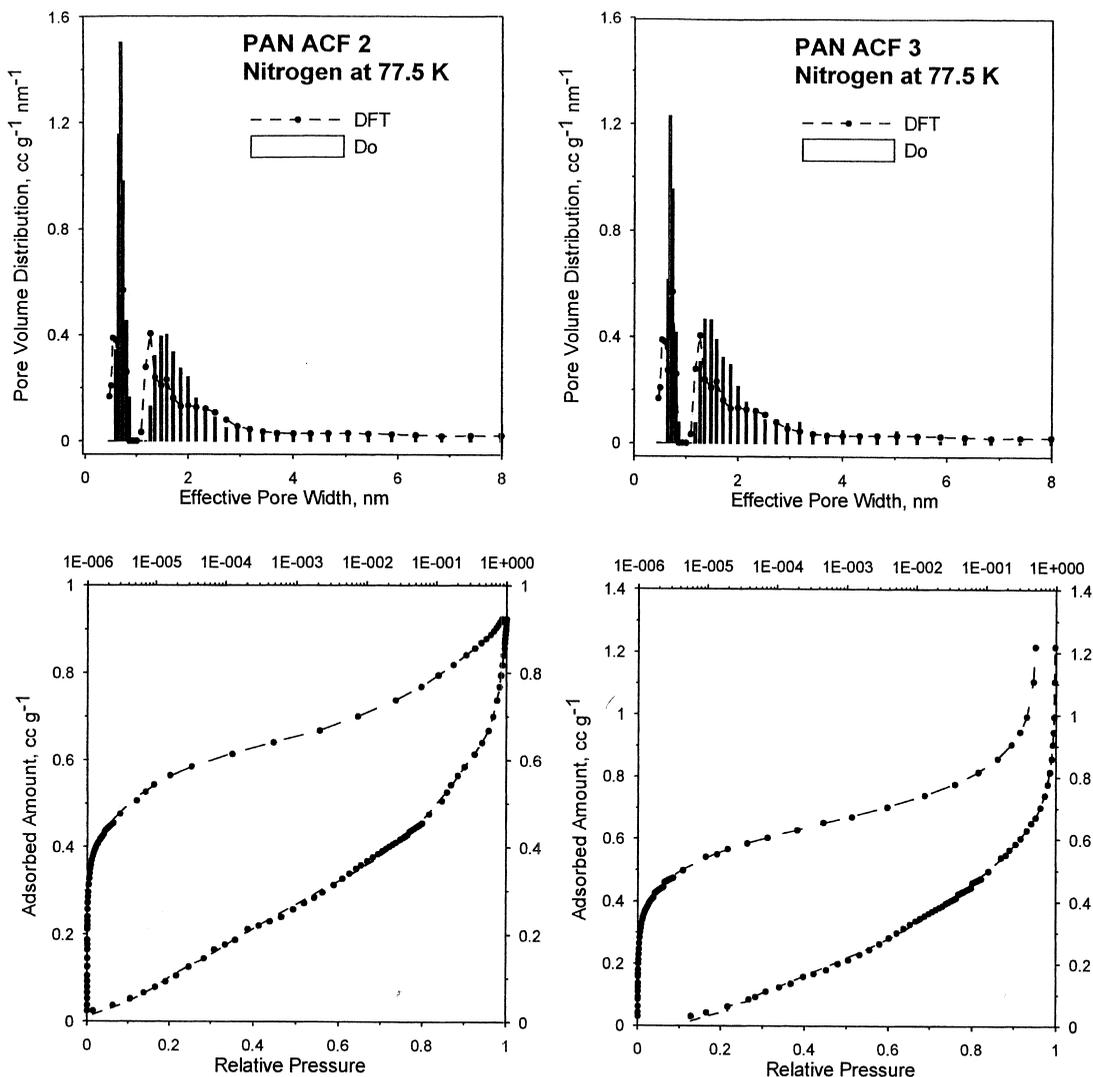
Fig. 6. The results of the comparative analysis of the PSD for some representative cases of the Group IV—mesoporous carbon fibres. Lower panel shows the fit of the results obtained from the method of Do (●) to the experimental data (- - -).

ND method leads to DC values close to 0.95, whilst the DFT gives values of 0.99. In this case the largest differences between the values of DC calculated for both methods are observed (however, both methods describe the experimental isotherms satisfactorily). Widening of the distribution of the microporosity (Group II—Fig. 4) does not change the above situation, i.e. the DFT method still leads to a better fit than the ND method, and the differences in the values of DC are around 0.03. If mesoporosity appears on the PSD curve (Group III—Fig. 5) the differences between the goodness of fit achieved from both methods vanish, and the DFT and ND lead practically to the same PSD curves. Further development of mesoporosity in the structure of activated carbons (Group IV—Fig. 6)

or carbosils (Group V—Fig. 7) leads to a decrease in the difference in DC values, which approach 0.0001 for the latter group.

6. Conclusions

The ASA algorithm can be successfully applied for the determination of the PSD curve from the ND method. This algorithm is simpler and faster than the INTEG algorithm applied in the DFT PLUS software. Moreover, the obtained results are independent of the regularisation parameter.

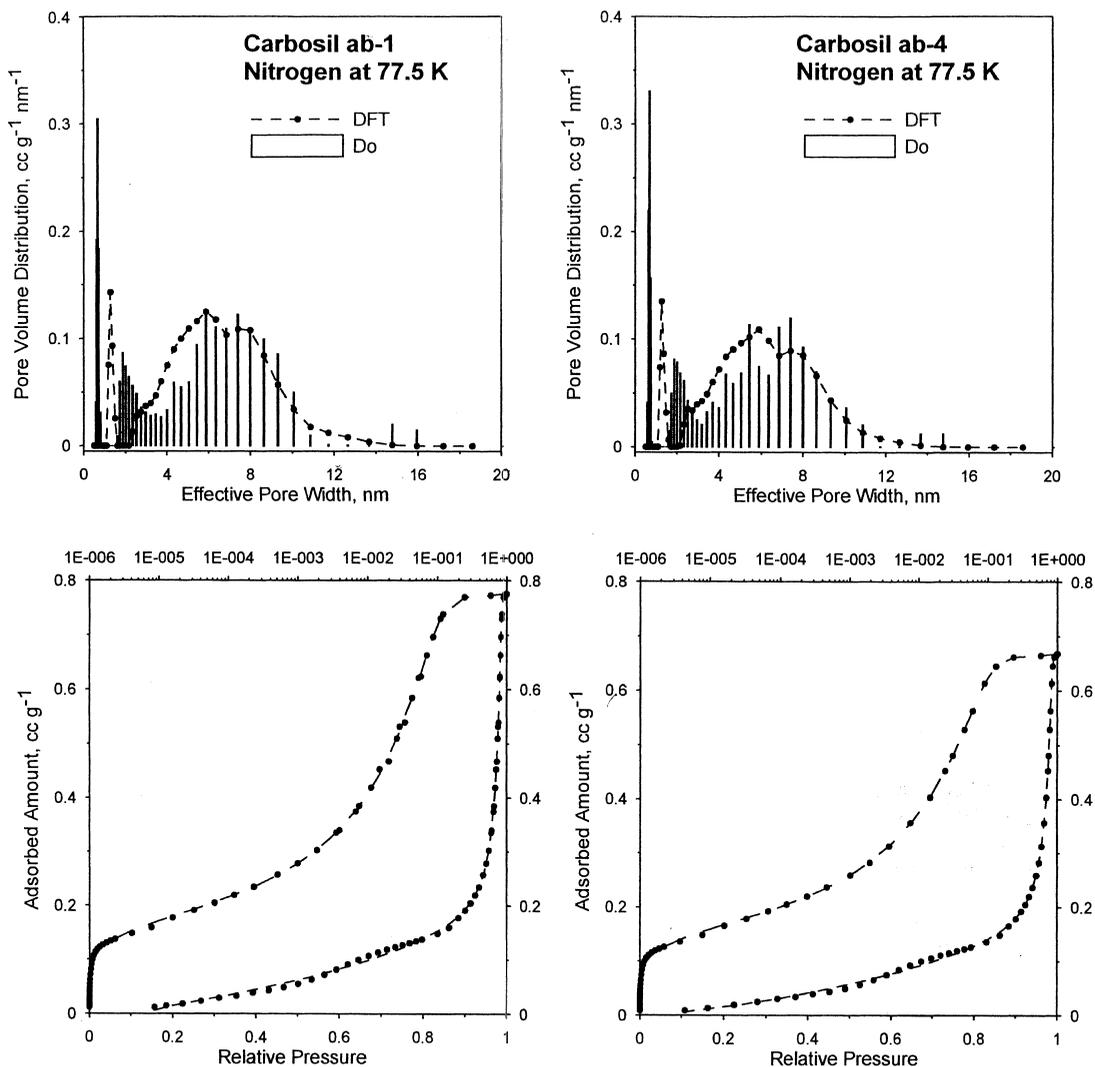Generally, the ND and DFT methods lead to almost the

Fig. 7. The results of the comparative analysis of the PSD for some representative cases of the Group V—mesoporous carbosils. Lower panel shows the fit of the results obtained from the method of Do (●), to the experimental data (- - -).

same PSD curves and this similarity is observed for carbons of different origin and possessing different pore structures. However, if the contribution of micropores to PSD increases, the differences in the fits of ND and DFT to experimental data are more pronounced. This leads to the conclusion that some aspects of the mechanism of adsorption assumed in the ND method in the range of fine micropores should be corrected. It is possible that, in the range of micropores possessing diameters close to that of the nitrogen molecule, the application of Steele's potential is incorrect. Instead, since for the molecules in those micropores possessing diameters close to the diameter of the nitrogen molecule the distance of the molecules from the surface is much smaller than the distance between surface atoms, summation should be used instead of integration. Additional differences between DFT and ND can also be produced by the assumption of the BET model as adequately representing the layering process. It should also be mentioned that the results of PSD obtained from the ND method depend on the value of C.

Since the answer to the question concerning the reasons for the differences (for strictly microporous carbons) between the results from both methods needs extensive additional numerical studies, these aspects, as well as a detailed analysis of some assumptions of the ND method, will be the subject of our future communications.
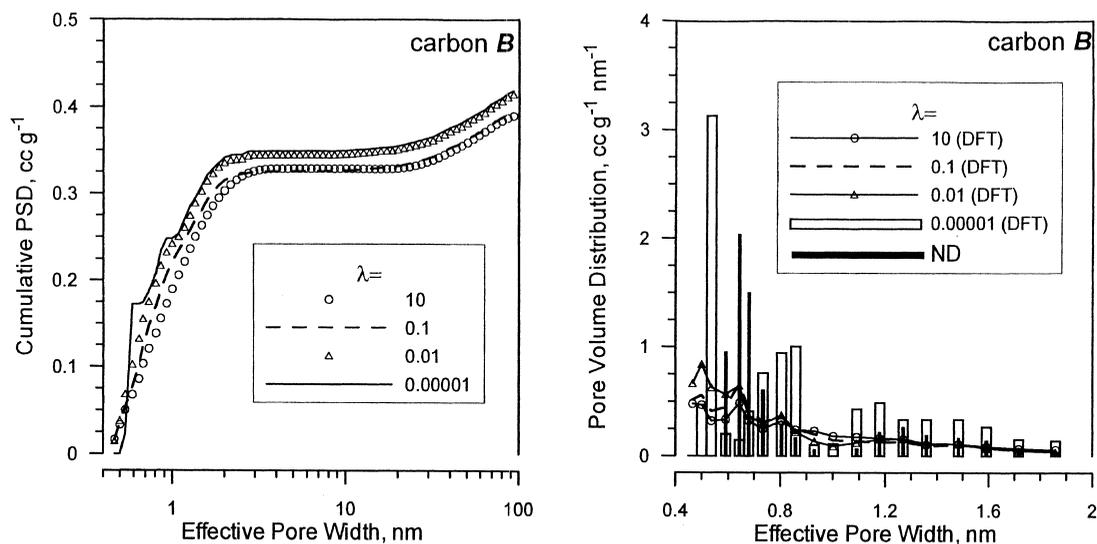
Fig. 8. Pore-size distributions of activated carbon B obtained using DFT (DFT Plus software) for different values of smoothing parameter λ (INTEG algorithms) and ND method.
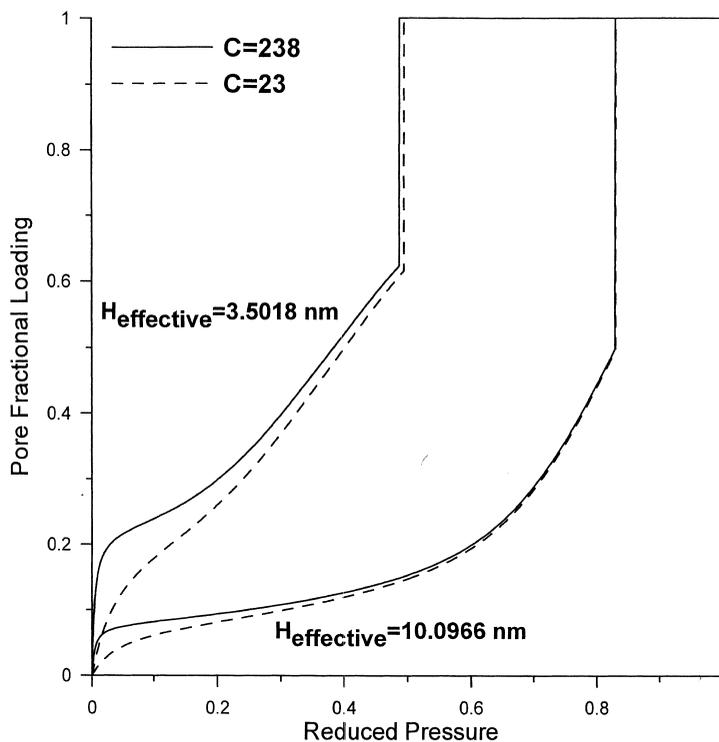

Fig. 9. Local nitrogen isotherms from the ND method calculated for two pore diameters and two different values of the parameter *C*.
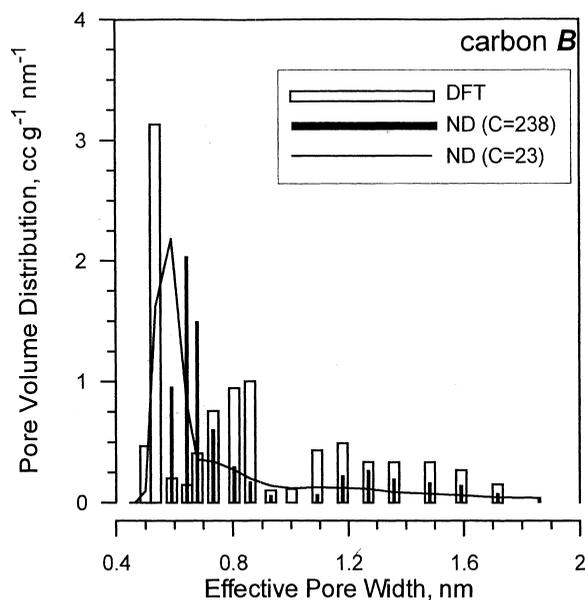
Fig. 10. Pore-size distributions of activated carbon B obtained using the DFT and ND methods. The results of the ND method were calculated for different values of the heterogeneity parameter (C) of the BET equation.

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