

## Computer analysis of microporous adsorbents with adsorption models of LBET class

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The reported research concerns applicability of new *LBET* models for heterogeneous multilayer adsorption to examination of microporous carbonaceous adsorbents. The models are based on a generalized *BET* theory presented in our earlier papers. They are aimed at drawing information on pore structure and capacity by analysis of adsorption isotherms of small molecule adsorbates.

In the theory adsorption of small, a nearly spherical molecules in irregular pores of molecular size is considered with side adsorbate-adsorbate interactions have being neglected. The molecules are located in pores by forming clusters, the size of which is limited by geometry of pores. The set of adsorbate molecules, which were adsorbed mainly due to adhesive interactions with the adsorbent matter, is treated as the first layer adsorption. Joining further molecules is viewed as the second, third, and following layer adsorption. The main idea of the presented approach to modelling of microporous structure consists in introducing of realistic relationships between geometrical properties of pores and adsorption energy.

The paper shows that a multivariant identification of adsorption isotherms, employing the *LBET* type formulas, gives an insight into pore size distribution and dominant pore shape, and provides more reliable evaluation of material surface area than the classical models.

## 1. INTRODUCTION

Modelling of adsorption processes on solid surfaces is of vital interest in surface science and chemical technology. Microporous carbonaceous materials are widely used as adsorbents, catalysts and supports in many industries and technology. At the present time, activated carbons occupy a prominent position among current carbonaceous adsorbents as versatile and universal materials, due to their specific properties [1]. The use of such materials in various fields of technology and science requires their characterization, which comprises determination of chemical composition, mechanical strength, description of porosity, surface texture and energetic heterogeneity. Also quantitative evaluation of the microstructure in porous materials is often a complicated step in design and application of materials for adsorption [2].

Adsorption of gases and vapours is one of the most widely used techniques for the characterization of microporous carbons. The first step is obtaining the adsorption isotherm and then quantifying the pore volume or surface area. There is a number of equations proposed to describe the adsorption equilibrium of small molecules with different aspects of the process being stressed and many theories of adsorption processes were elaborated [3]. For microporous materials the *Dubinin-Radushkevitch DR*, *Dubinin-Astachov DA* or *BET* equations are commonly recommended [4]. They are useful to obtain a measure of the material surface area on the basis of lower pressure physisorption data. However the results of surface structure and energy evaluation based on adsorption at higher pressures are doubtful. Together with the development of computer techniques more advanced methods of pore structure description were applied [5,6]. They use high tech numerical tools, e.g. optimization algorithms, advanced molecular simulations and approaches based on fractal geometry. Recently, significant progress has been made in the theoretical description of structural and energetic heterogeneity of porous solids [7]. Over the past few years the density functional theory *DFT* has become an interesting new tool for the characterisation of porous materials [8]. The approach is based on the established principles of statistical mechanics and necessarily assumes a solid structure model and pore topology.

Next, fractal geometry offers a new fashionable tool for the characterization of heterogeneous solids. To describe surface heterogeneity in the analysis the pores structure fractal dimension  $D$  is used. It depends on a surface available for adsorbate molecules ( $2 < D < 3$ ) [9,10,11]. The fractal dimension of the surface accessible for adsorption is a global measure of surface irregularity, and can be used to describe porous materials [12,13]. The fractal dimension  $D$  can be determined by other independent methods, although the comparison of fractal dimensions calculated from different adsorption models is problematic [14,15].

Further studies are necessary, particularly an advanced theoretical and experimental comparative analysis of the different methods of  $D$  calculation for porous materials possessing different types of porosity [14,15].

Effects of particular surface properties on the adsorption process are closely inter-correlated, so a specific shape of an isotherm may be formally explained with different adsorption mechanisms. Hence, in our opinion surface structure and adsorption energy distribution of irregular microporous materials can not be reliably determined, but only evaluated in semi-quantitative terms, by multilateral verification of alternative models of rather simple form, but handling main effects of random pore geometry on adsorption equilibrium. To this aim we elaborated an original *BET*-like mathematical model - *uLBET* formula, based on fundamental thermodynamics, and employing simple adsorption energy – pore geometry relationships. Its a bit simplified, analytical version - *LBET* type formulas was found to be accurate enough for examination of adsorption systems by fitting adsorption data [16].

The mentioned models for heterogeneous adsorption on microporous carbonaceous materials, applied in the presented research are based on general thermodynamics expressing changes of internal energy  $\Delta H$  and configurational entropy  $\Delta S$  due to the process. Adsorption of small nearly spherical molecules in irregular pores of molecular size is considered. The molecules are located in pores by forming clusters, the size of which is limited by a geometry of pores [17,18].

In the proposed approach the set of adsorbate molecules, which were adsorbed mainly due to adhesive interactions with the adsorbent matter is treated as the first layer adsorption. Joining further molecules is viewed as the second, third an following layer adsorption [19]. The clusters are formally constructed by adding consecutive layers being in equilibrium with the volatile phase. To overcome numerical problems, inherent in fitting of any more advanced adsorption model, a multivariant identification procedure is proposed, with a subset of parameters being fixed in each variant [20,21].

The proposed approach is recomendet to examination of adsorbents of random porous structure. It may be viewed as an alternative to classical techniques based on *BET* or *DR* equations and on the other hand, to more complicated *DFT* based techniques.

## 2. THEORETICAL BASIS – LBET APPROACH, ULBET AND LBET TYPE MODELS

In the presented approach the adsorption is viewed as a clusterization of adsorbate molecules in pores of different shapes. Each cluster starts at a place (primary site) on a pore wall producing a local minimum of adhesion energy. Further molecules (the layers  $n > 1$ ) are joined due to cohesive and adhesive forces [20,21,22]. The maximum number of layers  $k$  (referred to as the cluster size) is determined by a space preassigned to another cluster (competitive clusterization - 1<sup>st</sup> type) or by a geometry of pore (2<sup>nd</sup> type). Possible branching of clusters is taken into account that is expressed quantitatively by the pore shape factor  $\beta_{\kappa n}$ . It can significantly affect adsorption isotherms.

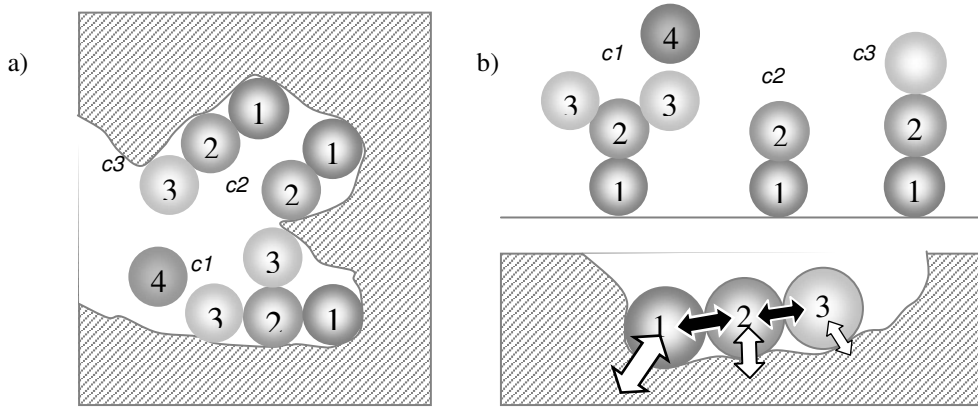


Fig. 1. Illustration of multilayer adsorption in presented approach: a)  $c1$  - an individual cluster with the third layer branched, limited to 3 layers by the pore geometry – 2<sup>nd</sup> adsorption type, because the 4<sup>th</sup> layer needs expansion of the pore, b) adsorbate molecules agglomeration mechanisms in micropores.

Assuming that each cluster can occupy only a space of a presumed structure and size, the general *BET*-like adsorption formula expressing the coverage ratio  $\theta_{\kappa n}$  of the  $(n-1)$ -th layer at clusters of a  $\kappa$ -th class was derived [20]:

$$\theta_{\kappa k} = \frac{\pi}{\pi + B_{\kappa k}}, \quad \theta_{\kappa n} = \frac{\Pi_{\kappa n}^*}{1 + \Pi_{\kappa n}^* - \theta_{\kappa n+1}} \quad \text{for } n=k-1, \dots, 1, \quad \theta_{\kappa k+1} \equiv 0 \quad (1)$$

$$\Pi_{\kappa n}^* \stackrel{def}{=} \frac{\pi}{B_{\kappa n} (1 - \theta_{\kappa n+1})^{\beta_{\kappa n+1}-1}}, \quad B_{\kappa n} \stackrel{def}{=} \exp\left(\frac{Q_{\kappa n}}{RT}\right) \quad (2)$$

where index  $\kappa$  counts  $k$ -th type clusters of identical energy profile across the layers  $n=1, \dots, k$ ,  $Q_{\kappa n}$  is the molar energy contributed by placing an adsorbate molecule at  $n$ -th layer of  $\kappa$ -th class clusters,  $\pi$  is the relative fugacity of adsorbate,  $R$  - gas constant,  $T$ - temperature.

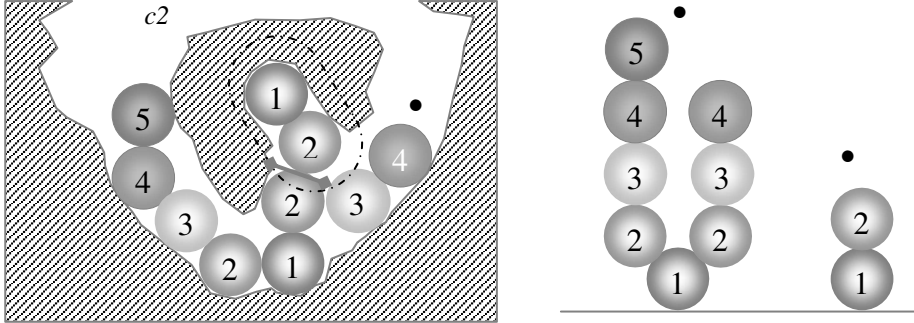


Fig. 2. Illustration of adsorbate molecules agglomeration mechanisms in micropores and types of clusters considered in the *LBET* approach: *c1* - a space of a agglomerate limited to two layers by the competing agglomerate *c2* - 1st type of adsorption, because the agglomerates are separated arbitrarily.

To make a model (1,2) useful in examination of adsorption systems of random porous structure with  $k=1, \dots, K \approx \infty$ , the following additional assumptions were made [20]:

- The layers  $n=2, \dots, k$  are homogeneous, i.e.  $\beta_{\kappa n} = \beta$  and  $B_{\kappa n} = B_C$  for  $k=1, \dots, K$ ,  $n=2, k-1$ ,

$$B_C \stackrel{def}{=} \exp(Q_C/RT), \quad Q_C \stackrel{def}{=} U_p (1 - 2 \cdot Z_{pp}) - Z_C \cdot Q_{cp} \quad (3)$$

where  $Q_{cp}$  is the molar adhesion energy in ideal adsorbent-adsorbate contacts,  $U_p$  - molar cohesion energy of adsorbate in bulk phase;  $Z_{pp}, Z_C$  - correcting factors.

For the top layer  $n=k$  we assume alternatively  $B_{\kappa k} < B_C$  such that  $\theta_{\kappa k} = \prod_{\kappa n}^*$  (1st type top layer adsorption) or  $B_{\kappa k} = B_C$  (the top layer adsorption of 2nd type) were assumed alternatively.

- The first layer adsorption energy is expressed in the following form [20]:

$$Q_{A\kappa} = U_p - Z_{A\kappa} \cdot Q_{cp}, \quad Q_A = U_p - Z_A \cdot Q_{cp} = \min_{k=1}^{def} (Q_{A\kappa}) \quad (4)$$

assuming that the factor  $Z_{Ak}$  is uniformly distributed over a range enlarging with growing  $k$ :

$$Z_{Ak} \in \langle Z_A(1-\zeta_{Ak}), Z_A(1-\zeta_{fk}) \rangle, \quad \zeta_{Ak} \geq \zeta_{Ak+1}, \quad \zeta_{fk} \geq \zeta_{fk+1}, \quad 0 \leq \zeta_{fk} \leq \zeta_{Ak}, \quad \zeta_{A1} \equiv 1 \quad (5)$$

The distribution function related to the energetic parameter  $B_{A\kappa} \in (B_{Ak}, B_{fk})$  is [20]:

$$f_k(B_{A\kappa}) = \frac{m_{hAk}}{\ln(B_{fk}/B_{Ak})} \frac{1}{B_{A\kappa}}, \quad B_{Ak} = B_A \cdot (B_{cp})^{Z_A(1-\zeta_{Ak})}, \quad B_{fk} = B_A \cdot (B_{cp})^{Z_A(1-\zeta_{fk})} \quad (6)$$

$$B_A = \exp(Q_A/RT), \quad B_{cp} = \exp(Q_{cp}/RT) \quad (7)$$

The coefficients  $\zeta_{Ak}$  and  $\zeta_{fk}$  in (5) are proposed to be calculated for clusters of  $k=1, \dots, K \approx \infty$ , according to appropriate formulas presented in our earlier papers [22,23]. By taking different options  $\{h, d, \eta\}$  ( $n=0 \dots 9$ ,  $d=\{0,1\}$ ,  $n \leq d$ ) one may produce a number of step-wise surface energy distribution variants [20,24].

- Exponential distribution of the cluster size is accepted. Thus, the number  $m_{hAk}$  of primary sites for the  $k$ -th type clusters is:

$$m_{hAk} = m_{hA}(1-\alpha)\alpha^{k-1}, \quad \alpha \in \langle 0, 1 \rangle \quad (8)$$

where  $m_{hA}$  stands for the total number of primary sites,  $\alpha$ - the distribution parameter.

The resultant isotherm equation  $m_p(\pi)$  has the following form (*uLBET* formula) [20]:

$$\begin{aligned}
m_p = m_{hA}(1-\alpha) & \left\{ 1 - \frac{1}{\ln(B_A / B_{f1})} \ln \left( \frac{B_A + \pi}{B_{f1} + \pi} \right) \right\} + \\
+ m_{hA}(1-\alpha) & \sum_{k=2}^K \alpha^{k-1} \left( 1 + \sum_{n=2}^k \prod_{j=2}^n (\beta \theta_{kj}) \right) \left\{ 1 - \frac{1}{\ln(B_{Ak} / B_{fk})} \ln \left( \frac{B_{Ak}(1-\theta_{k2})^\beta + \pi}{B_{fk}(1-\theta_{k2})^\beta + \pi} \right) \right\}
\end{aligned} \tag{9}$$

where  $\theta_{kj}$  are calculated with equations (1, 2).

The *uLBET* model involves five or six parameters:  $m_{hA}$ ,  $Z_A$ ,  $\alpha$ ,  $\beta$ ,  $B_C$  and optionally  $\zeta_{f\infty}$  to be adjusted by fitting eq. (9) to empirical adsorption data, with a chosen variant  $\{h, d, \eta\}$  of the surface energy distribution function. During such fitting the model is calculated thousands times [21]. Hence, to make the calculations more numerically effective, analytical formulas approximating the *uLBET* model (9) with negligible errors were elaborated [20]. They are referred to as the models of *LBET* type.

The formula (9) can be brought into an analytical form, providing that [20,21]:

- the coverage ratios  $\theta_{kn}$  are the same ( $\theta_{kn}=\theta$ ) for all  $k>1+d$ ,  $n>1+d$ ,
- the energetic parameters  $B_{Ak}$  and  $B_{fk}$  do not depend on  $k$ , at least for  $k>1+d$ .

Then the heterogeneous adsorption model of *LBET* type has the following form [20]:

$$\begin{aligned}
\frac{m_p}{m_{hA}} = (1-\alpha) & \left\{ 1 - \frac{1}{\ln(B_A / B_{f1})} \cdot \ln \left( \frac{B_A + \pi}{B_{f1} + \pi} \right) \right\} + \\
+ d \cdot \alpha(1-\alpha)(1 + \beta\theta_{22}) & \left\{ 1 - \frac{1}{\ln(B_{A2} / B_{f2})} \ln \left( \frac{B_{A2}(1-\theta_{22})^\beta + \pi}{B_{f2}(1-\theta_{22})^\beta + \pi} \right) \right\} + \\
+ \alpha^{d+1} \left[ d + (\beta\theta)^d \left( 1 + \frac{\beta\theta}{1-\alpha\beta\theta} \right) \right] & \left\{ 1 - \frac{1}{\ln(B_{A2+d} / B_{f\theta})} \ln \left( \frac{B_{A2+d}(1-\theta)^\beta + \pi}{B_{f\theta}(1-\theta)^\beta + \pi} \right) \right\}
\end{aligned} \tag{10}$$

The first condition is satisfied, if the top layer adsorption of 1<sup>st</sup> type is assumed. In this case the coverage ratios are:  $\theta_{kj}=\theta=\Pi_\infty^*$  for  $k>1$ ,  $j>1$  [8,9], where  $\Pi_\infty^* \in (0, 1/\beta)$  fulfils the equation [20,21]:

$$B_C \Pi_\infty^* = \pi (1 - \Pi_\infty^*)^{1-\beta} \quad (11)$$

If cluster restrictions are of geometrical/energetical nature (i.e. the 2<sup>nd</sup> type adsorption is considered – see Figure 1) the following averaging formula was found to be appropriate [20,21]:

$$\theta = \Pi^* \cdot \left( \frac{1 + w_H \cdot \Pi^*}{1 + \Pi^*} \right), \quad \Pi^* \stackrel{\text{def}}{=} (\pi / B_C (1 - \theta)^{\beta-1}),$$

$$w_H = \begin{cases} \frac{\alpha \cdot (1 + \alpha - \alpha^2)}{2 - \alpha} & \text{for } d = 0 \\ \frac{2 + \alpha}{3 \cdot (2 - \alpha)} & \text{for } d = 1 \end{cases} \quad (12)$$

In the energy distribution function proposed in [22,23] we assumed  $B_{Ak} = B_{A2+d}$ . To fulfil the second condition for the right hand side of the energy distribution ( $B_{fk}$ ) the following approximation was found to be adequate for  $B_{fk}$ ,  $k > 1+d$  [20,21]:

$$B_{fk} \cong B_{f\theta} = B_{A2+d} \cdot (B_{cp})^{Z_A (\zeta_0 - \zeta_{f\theta}) W_{d\eta}},$$

$$\zeta_{f\theta} \stackrel{\text{def}}{=} \zeta_{A2+d} - (\zeta_{A2+d} - \zeta_{f\infty}) \cdot W_{d\eta} \text{ for } k > 1+d \quad (13)$$

$$W_{d\eta}(\alpha, \beta\theta) = \frac{1}{1 - \frac{\ln(1-\alpha) - (\beta\theta)^{1+\eta} \ln(1-\alpha\beta\theta) + (d-\eta)\alpha(1-(\beta\theta)^{2+\eta})}{\alpha^{1+d-\eta} \frac{1-\beta\theta}{1-\alpha} \left[ d + (\beta\theta)^d \left( 1 + \frac{\beta\theta}{1-\alpha\beta\theta} \right) \right]}} \quad (14)$$

The parameters of the *LBET* type models are the same as in *uLBET* ( $m_{hA}$ ,  $Z_A$ ,  $\alpha$ ,  $\beta$ ,  $B_C$ ,  $\zeta_{f\infty}$  and energy distribution options  $\{h, d, h\}$ ). It is noteworthy, that the formula (10) needs only the clusters of  $k > 1+d$  to be exponentially distributed. Thus, the  $m_{hA1}$  and  $m_{hA2}$  (if  $d=1$ ) can be treated as the additional free parameters, so more diversified distributions might be also considered.

Energetic heterogeneity of microporous adsorption systems significantly worsens numerical conditioning of the system identification tasks. To overcome this problem we proposed to perform the identification procedures by multivariant fitting of the *LBET* model (10). The variants differ in the assumed



top layer adsorption type and in the options  $\{h, d, \eta\}$ , producing  $\zeta_{Ak}$  and the factor  $W_{\eta d}$  approximating energy distributions of different  $\zeta_{fk}$  [20,21].

The multivariant identification of adsorption systems, based on fitting of the *LBET* type models, was useful for examination of adsorption isotherms both simulated and received from the measurements.

### 3. NUMERICAL ANALYSIS OF THE EMPIRICAL ISOTHERM

The purpose of the numerical analysis and computer calculations was to verify the *LBET* class adsorption models and to test their applicability to the analysis of adsorption isotherm. The obtained results were compared to those calculated by classical equations. The research was divided into two stages. In the first stage numerical investigations of the multivariant identification procedure were carried out. The adsorption isotherms were generated by the *uLBET* formulas, using energetic and structural parameters taken from literature. Then, the parameters were identified, using the full set of variants of *LBET* formulas and selected popular classical equation.

Such simulations enabled us to evaluate reliably of the models properties on the basis of estimation error, which can be calculated as true values of the parameters were known. The identification of *uLBET* isotherms using the *LBET* class models shows an influence of simplifications involved in the analytical adsorption formulas (9), upon the identification quality indices. Moreover, it provides a basis for evaluation of reliability of parameters calculated for real adsorption systems by fitting the *LBET* model to empirical data.

Tab. 1. Options generating variants of the surface energy distribution used in calculations

Options	Variants of fitting <i>LBET</i> model and of <i>uLBET</i> model producing data																													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
$h_{LBET}$	0	1	2	3	3	3	5	5	5	7	7	7	9	9	9	0	1	2	3	3	3	5	5	5	7	7	7	9	9	9
$h_{uLBET}$	0	1	2	3	3	4	4	4	6	6	6	8	8	8	0	1	2	3	3	3	4	4	4	6	6	6	8	8	8	
$d$	0	0	0	0	1	1	0	1	1	0	1	1	0	1	1	1	0	0	0	1	1	0	1	1	0	1	1	0	1	1
$\eta$	-	-	-	0	1	0	0	1	0	0	1	0	0	1	0	-	-	-	0	1	0	0	1	0	0	1	0	0	1	0
Type	Top layer adsorption of 1 <sup>st</sup> type															Top layer adsorption of 2 <sup>nd</sup> type														

The isotherms have been generated for relative pressures  $\pi$  ranging to  $\pi_{\max}=0.8$ . For such data the standard constrained optimization procedure 'fmincon', offered by the MATLAB software package for nonlinear tasks, was found to be effective enough to perform identification of the examined adsorption systems by minimization of the fitting error dispersion  $\sigma_e$ . The

following quantities were selected to be adjusted during the optimization procedure:

- $V_{hA}$  - molar volume of the first layer region,
- $\alpha, \beta$  - geometric parameters of the porous structure,
- $Z_A, Z_C$  - correction factors used to calculate  $Q_A$  and  $B_C$ ,
- $Z_{f\infty}$  - optional parameter,

under constraints:

$$\alpha \in \langle 0, 1 \rangle; \beta \in \langle 1, 1.35 \rangle; Z_A \in (0.2, 1); Z_C \in \langle 1/12, U_p(1-2Z_{pp})/Q_{cp} \rangle; \pi_m(\beta, B_C) < \pi_{max}$$

(15)

Each time the identification has been started with the values of parameters:  $\alpha=0.01, \beta=1, Z_C$  giving  $B_C=1, V_{hA}$  and  $Z_A$  - according to  $m_{hA}$  and  $Q_A$  found by fitting the *Langmuir* equation to adsorption data of  $\pi < 0.1$ . The calculations were performed for a hypothetical microporous adsorbent with the solubility parameter  $\delta_c=28$  (realistic value for natural carbonaceous adsorbents), assuming  $Q_A/RT=-7.0$  and  $U_p=31.17$  kJ/mol,  $V_s=88.9$  cm<sup>3</sup>/mol,  $Q_{cp}/RT=38.29$ ,  $m_{hA}=1.33$  mmol/g,  $\beta=1.1, B_C=1.5$  and  $Z_{pp}=1/6$ .

The research was focused on the analysis of identification errors. The reliability of identification was assessed on the basis of residual dispersion and relative errors of parameters calculated for all 30 variants. To choose the best variants, the results were presented for three best fittings. Moreover, 10 from 30 well fitted variants were treated as acceptable results.

Tab. 2. The classical equations used in verification of the *LBET* class models [21,27].

Model name	Adsorption equation	Parameters of the models
Dubinin - Radushkevich <sup>1</sup>	$a = a_0 \exp \left( -B_{DR} \left( RT \ln \frac{p_0}{p} \right)^2 \right)$	$a$ - the volume of the adsorbate condensed within the micropores at temperature $T$ and relative pressure $p/p_0$ $a_0$ - the total volume of the micropores accessible to the given adsorbate $B_{DR}$ - energetic-structural parameter
Freundlich <sup>2</sup>	$a = k_{FR} p^{1/n_{FR}}$	$p$ - the partial pressure of the adsorbate $k_{FR}, n_{FR}$ - empirical constants characteristic for adsorbate-adsorbent system

BET <sup>3</sup>	$a = \frac{a_m C_{BET} \frac{p}{p_0}}{\left(1 - \frac{p}{p_0}\right) \left(1 + (C_{BET} - 1) \frac{p}{p_0}\right)}$	<p><math>a</math> - the amount in moles adsorbed on 1 g of adsorbent  <math>a_m</math> - the monolayer capacity (the adsorption of one molecular layer of the adsorbate on the adsorbent)  <math>p_0</math> - the saturation vapor pressure of the adsorbate  <math>C_{BET}</math> - the energy constant,</p>
Anderson <sup>4</sup>	$a = \frac{a_m C_{AND} \frac{p}{p_0} k_{AND}}{\left(1 - k_{AND} \frac{p}{p_0}\right) \left(1 + (C_{AND} - 1) k_{AND} \frac{p}{p_0}\right)}$	<p><math>C_{AND}, k_{AND}</math> - the Anderson equation constants, <math>k_{AND} \in (0,1)</math></p>
Hütting <sup>5</sup>	$a = \left(a_m C_{HUT} \frac{p}{p_0}\right) \left(1 + \frac{p}{p_0}\right) \cdot \frac{1}{1 + C_{HUT} \frac{p}{p_0}}$	<p><math>a</math> - the amount in moles adsorbed on 1 g of adsorbent  <math>a_m</math> - the monolayer capacity  <math>C_{Hut}</math> - the Hütting equation constant</p>
Kisarow <sup>6</sup>	$a = \frac{A_{KIS} B_{KIS} \left(\frac{p}{p_0}\right)^{n_{KIS}}}{1 + B \left(\frac{p}{p_0}\right)^{n_{KIS}}}$	<p><math>A_{KIS}, B_{KIS}</math> - empirical coefficients of equation obtained for analyzed adsorption system  <math>n_{KIS}</math> - the exponent <math>n</math> is parameter specific to the adsorption system</p>

<sup>1</sup> - Dubinin-Radushkevich approach conceived micropores, as space volumes in a porous material where the molecules successively adsorbed do not form adsorption layers, but rather adsorption is characterized by volume filling within the adsorption space. The adsorbed substance is present in the form of a liquid in a highly compressed state in the adsorption field [28,29,30],

<sup>2</sup> - the Freundlich equation is an empirical expression used to describe adsorption isotherms where there is a linear response for adsorption capacity as a function of partial pressure when this function is plotted on log-log scales. The valid concentration range for the Freundlich equation varies according to the adsorbate-adsorbent combination [21,27],

<sup>3</sup> - BET theory is based on a kinetic model of adsorption proposed by Langmuir and portrays a solid surface as an array of adsorption sites. Equilibrium occurs when the rate at which molecules arriving from the gas phase and condensing or adsorbing onto unoccupied adsorption sites is equal to the rate at which molecules evaporate or desorb from occupied sites [31],

<sup>4</sup> - Anderson equation is based on BET theory, but the equation has three parameters [32],

<sup>5</sup> - Hütting equation is based on BET theory, but assumed different mechanism of the adsorption-desorption process [33].

To get a synthetic measure of the identification uncertainty, the following identifiability index  $w_{id}$  was defined [21]:

$$w_{id} = 1 - \frac{\sigma_{e \min}}{\frac{1}{10} \sum_{opt=1}^{10} \sigma_{e \opt}} \quad (16)$$

where:  $\sigma_{\text{emin}}$  and  $\sigma_{\text{eopt}}$  express the error dispersion of the best fitting and the sequence of increasing dispersion error of the ten well fitted models.

The optimal variant distinctivity index  $w_{id}$  is usually low, hence the well fitted variants should be treated as providing complementary information on possible properties of the examined system.

The detailed results of the analysis are presented in figures 3-8, illustrating fitting quality and optimal identification uncertainty for selected variants. The first column of the first row shows the fitted isotherm. Data are marked with circles "o", solid line "-" presents the theoretical isotherm calculated by the *uLBET* model with the parameters of the best fitted *LBET* variant. Dotted lines mean theoretical cover of the first adsorption layer.

The second figure in this row contains bar diagrams of the dispersion error of the fitting with different *LBET* model variants. The bold "o" refers to the best fitted one. Next "+" and "\*" mean the second and third fitting. Also the value of the identifiability factor  $w_{id}$  is shown. The more diversified highs of individual bars and the bigger the differences between the lowest bar and the remaining ones, the better identifiability of the adsorption system (the factor  $w_{id}$  reaches a value closer to 1).

The third figure in the discussed row shows values of the most important structure parameters, i.e.: monolayer capacity  $V_{hA}$ , obtained in individual variants. Three best fitted variants were marked in the same way as in the previous figure. The headline gives the name of the adsorption system i.e.: adsorbate symbol, the carbonaceous adsorbent symbol, the binary options  $h, d, \eta$  and parameters  $\alpha, \beta$  obtained with the best fitted variant. The figures in the second row present diversification of the model parameters, obtained in the ten well fittings. The mark "o" means the optimum fitting parameters, "\*", "+" – these of the second and third fitting quality, "x" the seven remaining parameters. They were presented in pairs at rectangular coordinate systems.

The third and fourth rows of figures shows fittings of six selected classical models. The fifth row of figures shows three best fittings of *LBET* models.

In headlines of the diagrams the symbol of the adsorption system was placed and the number of the *LBET* model variant or classical model name was divided by slash. In the lower part of each diagram the value of the fitting quality measure  $\sigma_e$  is located. In the sixth row the corresponding energy distributions are depicted. Vertical lines show the value of the adsorption energy on the second and next layers.

The proposed multivariant identification of adsorption systems, based on fitting of the *LBET* type models, was found to be useful for examination of empirical isotherms. The representative results of the full graphic illustration of fitting quality and optimal identification uncertainty for empirical isotherms  $N_2$ -AMB563 [26] are shown in Figure 8 in the same way as in the previous figure.

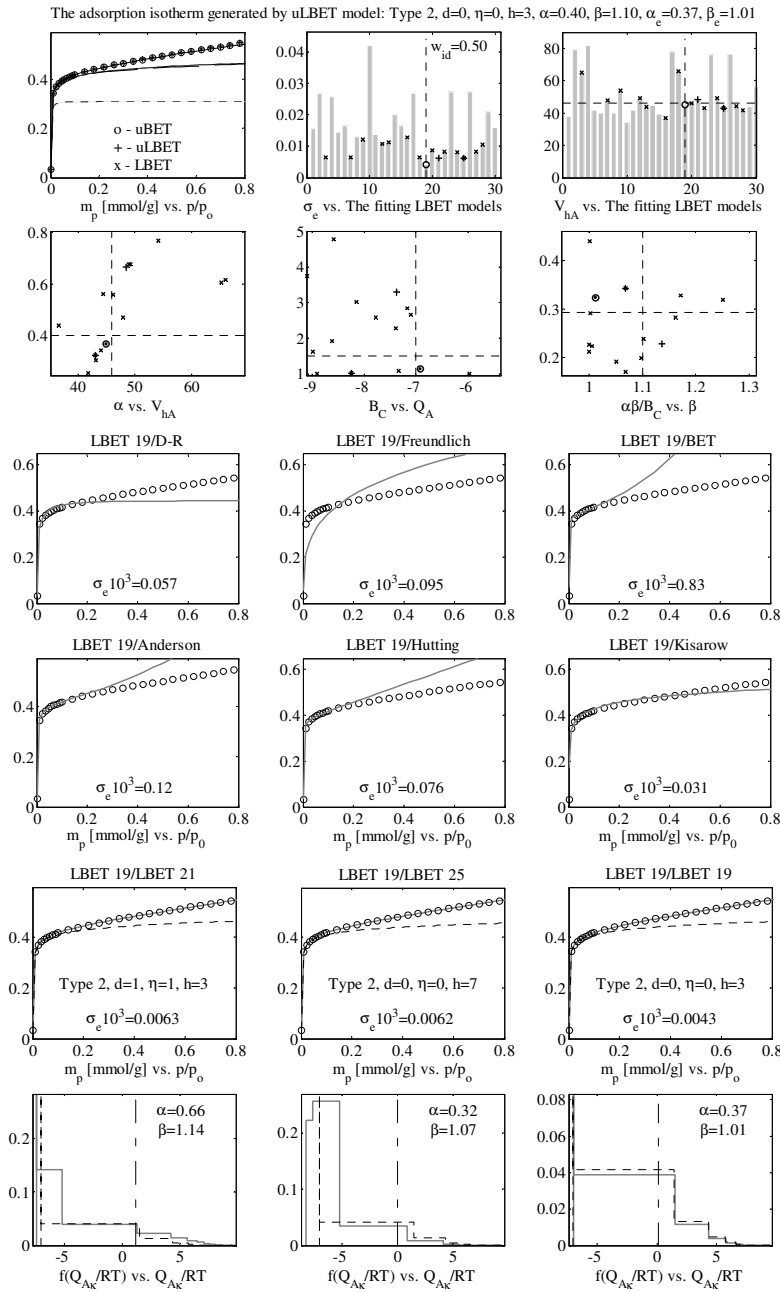


Fig. 3. The multivariate identification results for a single isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by chosen classical equation and *LET* formulas with five parameters.

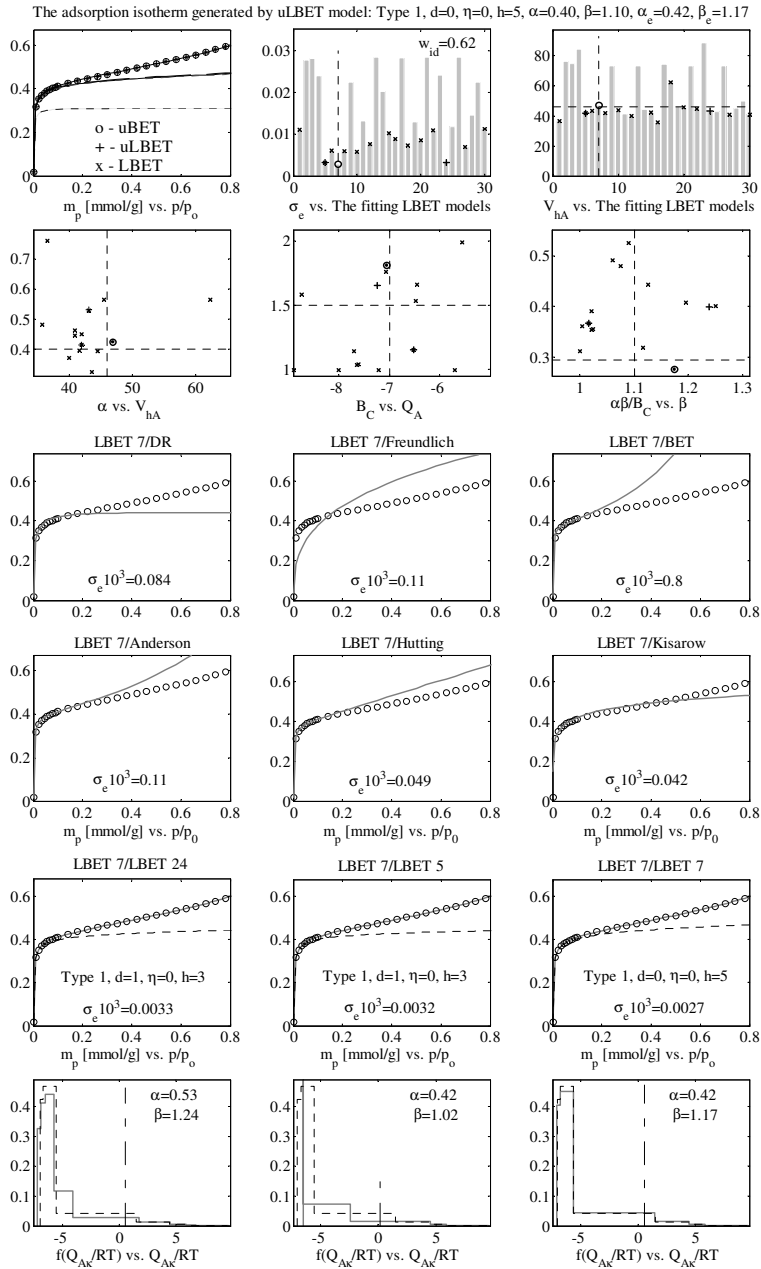


Fig. 4. The multivariate identification results for a single isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by chosen classical equation and *LET* formulas with five parameters.

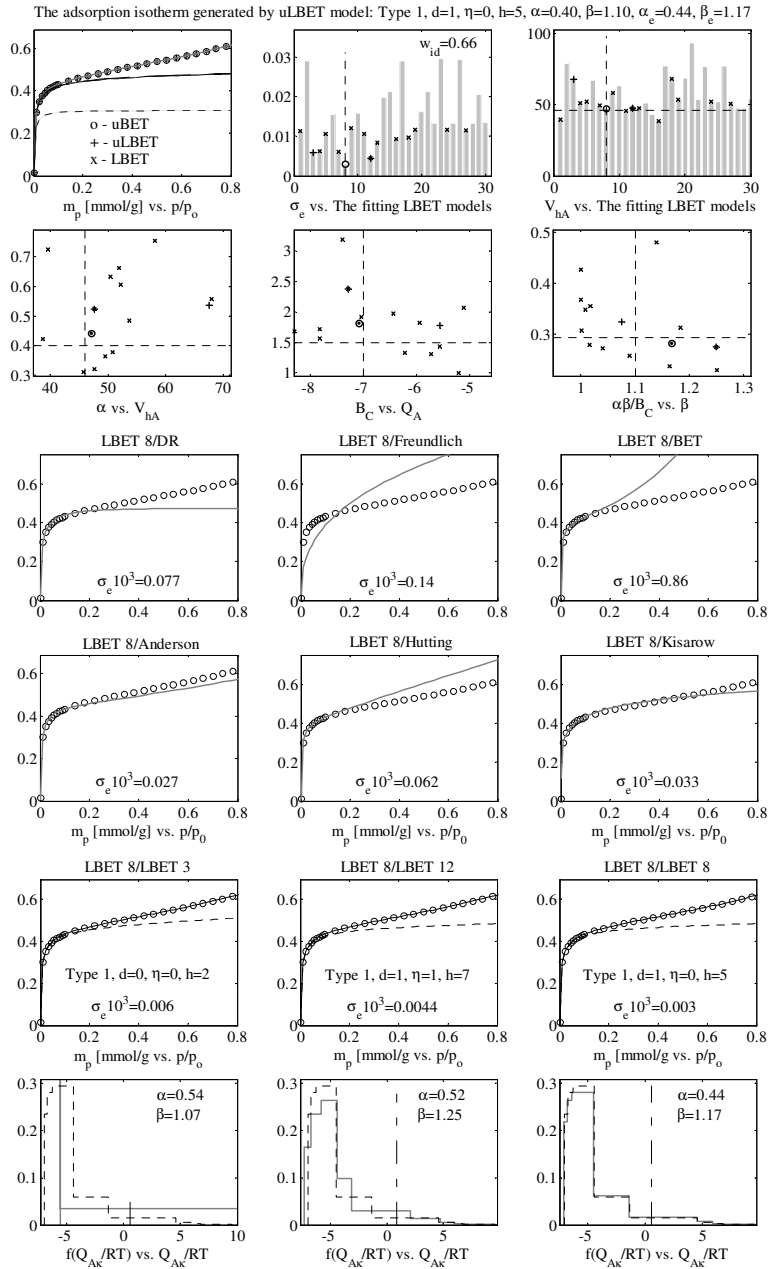


Fig. 5. The multivariate identification results for a single isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by chosen classical equation and *LET* formulas with five parameters.

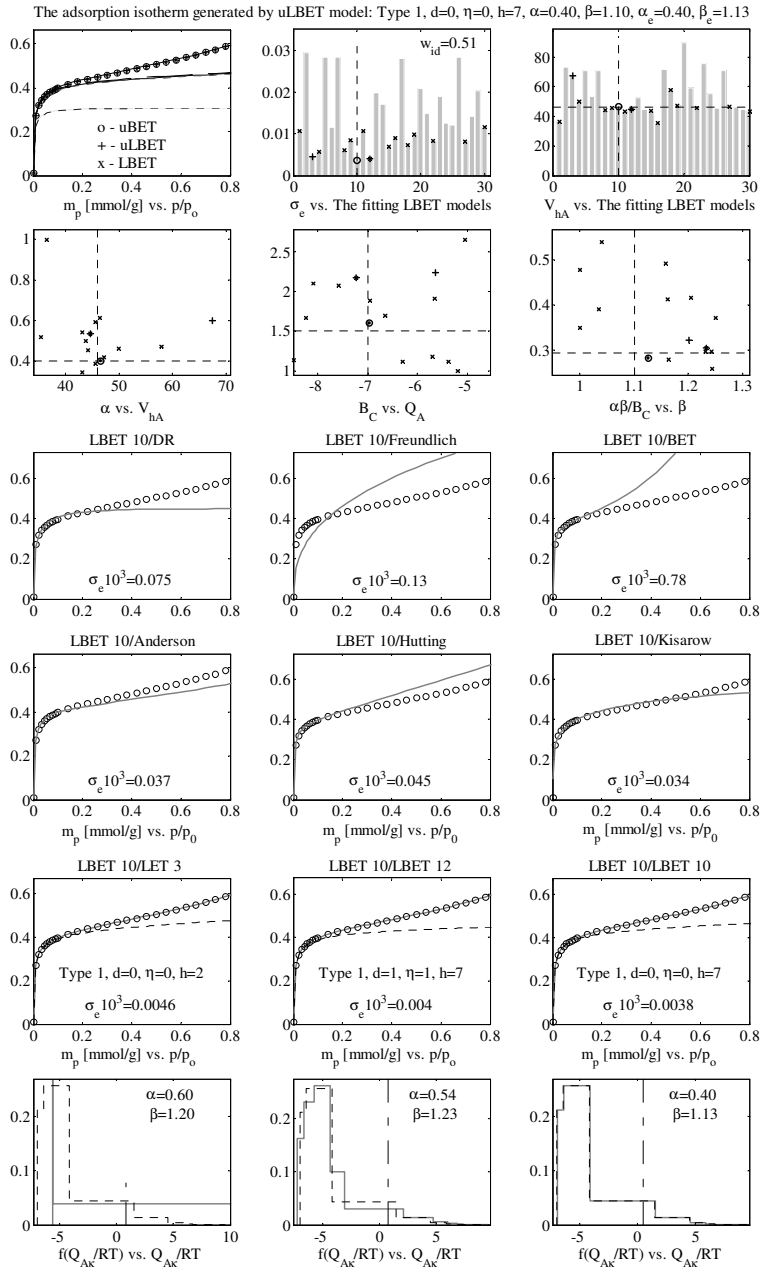


Fig. 6. The multivariate identification results for a single isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by chosen classical equation and *LET* formulas with five parameters.



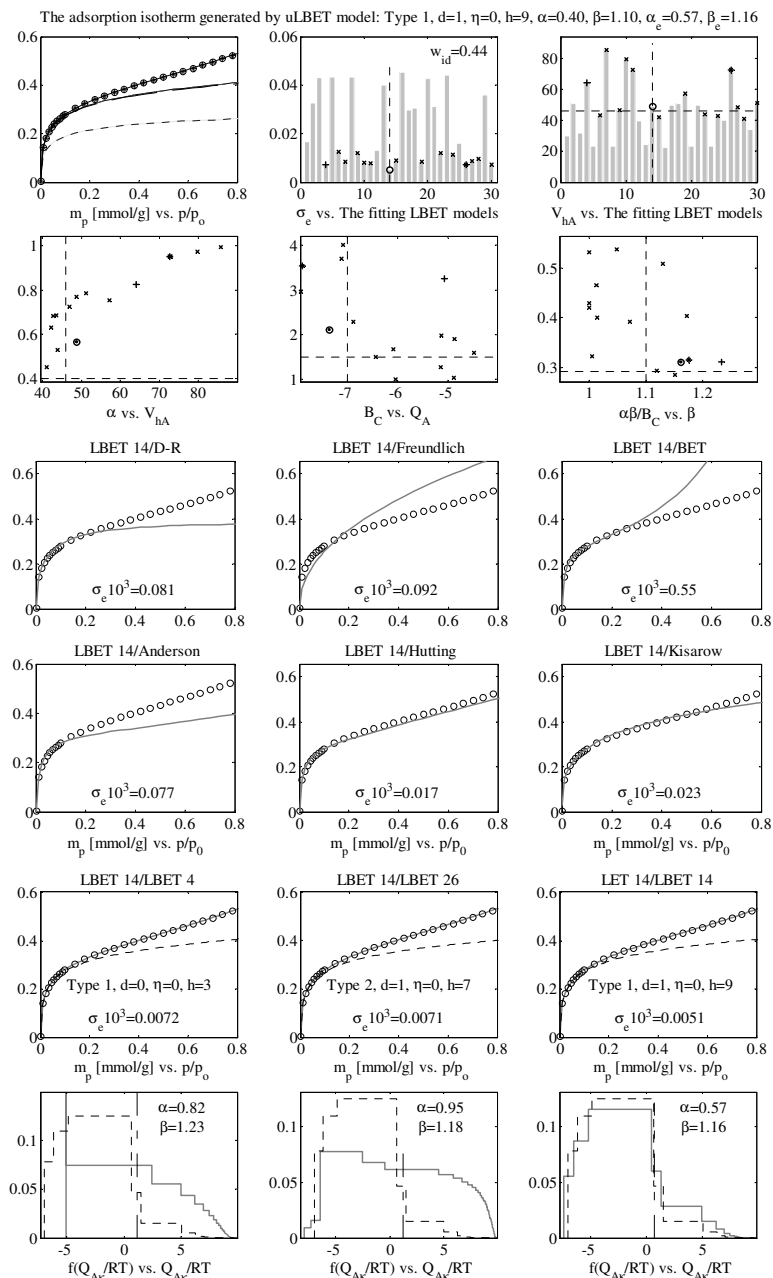


Fig. 7. The multivariate identification results for a single isotherm generated by  $uLBET$  models in realistic case of the surface energy mapping and fitted by chosen classical equation and  $LET$  formulas with five parameters.

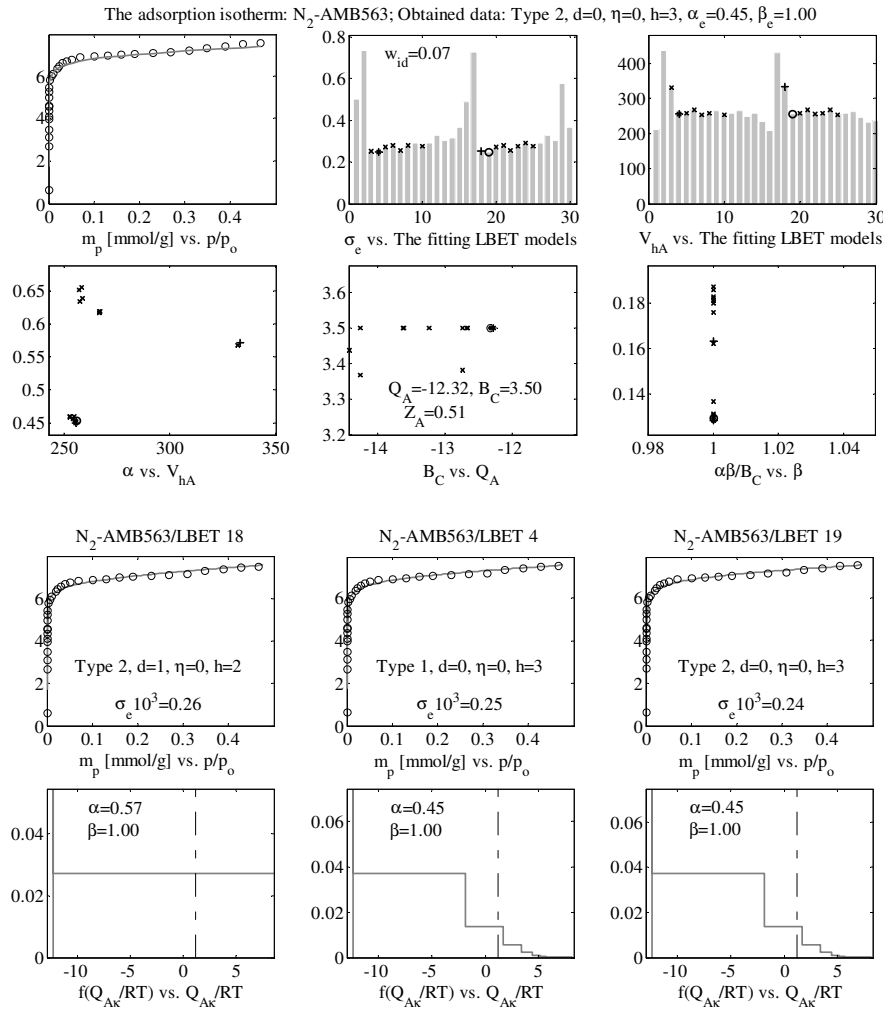


Fig. 8. The results of application of the *LBET* models to examination  $N_2$  isotherm on the active carbon AMB563.

The results presented in Figure 8 show that the active carbon AMB563 [26] have a relatively large fraction of pores with sizes close to a nitrogen molecule with almost homogeneous surface. The remaining pores contain adsorption sites with a large spectrum of energy. Relatively low value of  $w_{id}$  coefficient point out that the obtained energy distribution may vary from the real ones. However this distribution is likely to have a wide range of energy.

#### 4. CONCLUSIONS

The simplified *LBET* formulas are accurate enough to be used in identification procedures instead of their rigorous counterparts – *uLBET* models. It reduces radically the identification computing time. An important advantage of the *uLBET/LBET* formulas is that they may be reliably identified with a low pressure data and then used to predict adsorption isotherms at much higher pressures.

The *LBET* formula, may be recommended to be used directly in the adsorption system identification procedures. Fitting of the *LBET* models provides information on properties of adsorbate clusters deposited in the material. It makes possible to deduce the pore structure properties. The *LBET* based multivariant identification of adsorption systems, with a surface energy distribution structure being presumed in each variant, makes possible to avoid numerical problems caused by a large number of the system parameters to be evaluated. Final analysis of a number of the best fitted variants provides complementary information on adsorption mechanisms, thus enabling for more reliable evaluation of a studied pore structure.

The above results show that the *LBET* models give better insight into the adsorption mechanisms and structure of pores than classical equations. They may be well fitted to different adsorption data in wide pressure range, providing relatively accurate evaluation of the monolayer adsorption capacity. The models give also semiquantitative information on pore structure, adsorbate aggregation mechanisms, and surface energy distribution.

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