

Characterization of Microporous Carbon Materials by Means of a New Gamma-Type Adsorption Isotherm Equation

I. The Optimization Program Based on the Simulated Annealing Algorithm (SA)

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A new numerical procedure, based on the simulated annealing algorithm (SA), for optimizing the parameters of a new recently developed gamma-type adsorption isotherm equation is proposed. This procedure is verified for three modeled adsorption isotherms assuming some arbitrarily chosen shapes of the pore size distribution function (asymmetrical bell-shaped functions possessing one or two points of inflection and decreasing to a zero-hyperbolic-like function). To study the properties of the presented algorithm, several different models of temperature decrease were tested. It is shown that the best results are obtained for the models of temperature decreasing rapidly. Additionally, the SA algorithm provides (in a very short time) values of the optimization parameters that are very close to the global minimum of the fitness function. From the practical point of view, the obtained results are satisfactory and the proposed method can be successfully applied to determining the parameters of the microporous structure of activated carbons. © 2001 Academic Press

Key Words: adsorption; activated carbon; gamma-type isotherm equation; microporosity; pore size distribution; simulated annealing algorithm.

1. INTRODUCTION

It is known that adsorption processes play an important role in various fields of modern technique, such as medicine and analytical chemistry (1–5). The adsorption properties of porous materials (activated carbons, carbon fibers, molecular sieves, and others) strictly depend on the presence of small pores called micropores (diameter of micropores ($2x$) \leq 2 nm according to IUPAC classification (6)) in the internal structure (7). It is generally accepted that slit-shaped micropores are geometrically and energetically nonuniform, i.e., heterogeneous (1–5). Up to now, several methods for evaluating the functions of micropore size distribution (PSD) as well as of energy distribution have

been developed (1–5). Connected together with a so-called “local isotherm equation,” they lead to global adsorption isotherms (GAI). Among the models of local isotherms, those developed from Dubinin’s theory of the volume filling of micropores are the most important and widely applied for describing adsorption in the micropores of activated carbons. Although both the Dubinin–Rhadushkevich (DR) and the Dubinin–Astakhov (DA) equations possess limitations (3, 8–10), they still occupy the leading position in the adsorption field. Moreover, the parameters of the equations, i.e., the total micropore volume and the characteristic energy of adsorption, are regarded as standard values and are quoted in nearly all papers where the characterization of carbon microporosity is discussed (1–5, 11). Although some authors are of the opinion that the DA equation does not adequately represent the adsorption process in a homogeneous microporous structure (and it cannot be used as a local adsorption isotherm in the GAI equation), the experimental results presented recently (12) do not confirm this view. It was shown that the DA equation successfully fits experimental results on nitrogen and benzene adsorption onto series of microporous films with almost homogeneous microporosity (pore size distributions were determined using DFT), and the differences in adsorption enthalpy calculated from the DA equation and measured calorimetrically are mainly due to the phase change of benzene in micropores, where adsorbed molecules are in a quasi-solid state. These results support Stoeckli’s concept; it was he who first proposed applying Dubinin’s equations as kernels in GAI (13, 14). Several methods for solving those unstable integral equations have been suggested and developed (1–5, 10). Some of them assume *a priori* the type of a micropore size distribution function (1–5, 10, 13–19), for example, Gaussian, exponential, Maxwell–Boltzman, Rayleigh-type, and fractal. The recently presented analytical solution of GAI using the DA equation as a kernel and assuming the gamma-type micropore size distribution function (18) seems to be a very interesting one. The proposed equation is very promising because the assumed gamma-type distribution function generates the most common shapes of distributions

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(3, 18, 20). Furthermore, this equation was derived on the basis of a clear physical meaning of the integration range; i.e., the authors used in integration the physical bounds of an adsorption system.

The aim of the present study is to propose and analyze a procedure for fitting the new adsorption isotherm equation to generated adsorption data. This procedure should fulfill three main conditions: it should be easy, should be as fast as possible, and should lead to reliable results as far as the pore size distribution is considered. In the current study we want to analyze the conditions that should be fulfilled to obtain the most reliable pore size distribution functions. Thus, a numerical program, based on the simulated annealing algorithm (21), for evaluating the new gamma-type adsorption isotherm parameters has been developed. Model calculations are presented to test the applicability of this algorithm, and the conditions that lead to the same PSD as assumed in modeled isotherms are defined.

2. THE NEW GAMMA-TYPE ADSORPTION ISOTHERM EQUATION

As proposed by Stoeckli, the GAI with the DA equation as a kernel is defined as (13, 14)

$$W(A) = W_0 \int_{\Omega\left(\frac{1}{E_0^n}\right)} \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] f\left(\frac{1}{E_0^n}\right) d\left(\frac{1}{E_0^n}\right), \quad [1]$$

where W_0 denotes the limiting adsorption of vapor per unit volume in micropores, β is the similarity coefficient that characterizes an adsorbate molecule, E_0 is the characteristic adsorption energy, n is the equation parameter (for the DR equation $n = 2$), and A is the molar Gibbs' enthalpy of adsorption defined by the formula

$$A = RT \ln\left(\frac{p_0}{p}\right), \quad [2]$$

where R is the universal gas constant, T is temperature, p_0 is the saturation vapor pressure of an adsorbate, and p is the equilibrium pressure.

Assuming DA to be a kernel in Eq. [1], the PSD function to be the gamma-type distribution, and the physical boundaries of an adsorption system, the following equation can be derived (18, 22),

$$W(A) = \frac{W_0 \left(\frac{A^n}{\beta^n \rho} + 1\right)^{-(\nu+1)} \left[\gamma\left(\nu + 1, \left(\frac{A^n}{\beta^n} + \rho\right) \zeta x_{\max}^n\right) - \gamma\left(\nu + 1, \left(\frac{A^n}{\beta^n} + \rho\right) \zeta x_{\min}^n\right) \right]}{\left[\gamma\left(\nu + 1, \zeta \rho x_{\max}^n\right) - \gamma\left(\nu + 1, \zeta \rho x_{\min}^n\right) \right]}, \quad [3]$$

which can be rewritten in the integrated form

$$W(A) = W_0 \frac{\left(\frac{A^n}{\beta^n \rho} + 1\right)^{-(\nu+1)} \times \int_{\left(\frac{A^n}{\beta^n} + \rho\right) \zeta x_{\min}^n}^{\left(\frac{A^n}{\beta^n} + \rho\right) \zeta x_{\max}^n} e^{-t} t^\nu dt}{\int_{\zeta \rho x_{\min}^n}^{\zeta \rho x_{\max}^n} e^{-t} t^\nu dt} \quad \text{for } (x_{\min} \leq x \leq x_{\max}), \quad [3a]$$

where ν and ρ are the gamma-type distribution function parameters, x_{\min} and x_{\max} are the lower and upper limits of a micropore system, respectively, and ζ relates E_0 to the micropore dimension x (the half-width) through the equation

$$\zeta = E_0^{-n} x^{-n}. \quad [4]$$

On the basis of Eq. [3], the parameters of the micropore distribution can be obtained using the formula (18)

$$J(x) = \chi x^{n(\nu+1)-1} \exp(-\rho \zeta x^n), \quad [5]$$

where the normalization factor is defined by (18)

$$\chi = \frac{n(\rho \zeta)^{\nu+1}}{\gamma(\nu + 1, \zeta \rho x_{\max}^n) - \gamma(\nu + 1, \zeta \rho x_{\min}^n)}. \quad [6]$$

To estimate the parameters of the gamma-type adsorption isotherm equation, we proposed recently several numerical procedures constructed on the basis of modern heuristic methods (genetic algorithm, evaluation program, and hybrid methods (23)). The proposed algorithms have been used to model adsorption systems.

3. PROBLEM FORMULATION

In the present study a minimization problem for finding the minimal value of the fitness (cost) function in the search space is considered. The fitness function is defined by applying the Gauss-Legendre theorem (the least squares procedure) (23)

$$f(x) \equiv \text{fitness} = \sum_i \left(W_i(A) - x[1] \frac{\left(\frac{A_i^2}{\beta^2 x[2]} + 1\right)^{-(x[3]+1)} \times \int_{\left(\frac{A_i^2}{\beta^2} + x[2]\right) \zeta x_{\min}^2}^{\left(\frac{A_i^2}{\beta^2} + x[2]\right) \zeta x_{\max}^2} e^{-t} t^{x[3]} dt}{\int_{x[2] \zeta x_{\min}^2}^{x[2] \zeta x_{\max}^2} e^{-t} t^{x[3]} dt}} \right)^2 \quad \text{for } (x_{\min} \leq x \leq x_{\max}), \quad [7]$$

where $x[1] = W_0$, $x[2] = \rho$, and $x[3] = \nu$. We assume that the task is to minimize $f(x)$ within the search space $D \subseteq R^3$, where $D = \prod_{k=1}^3 \langle \text{left}_k, \text{right}_k \rangle$; i.e., each variable x_k was restricted to a given interval $\langle \text{left}_k, \text{right}_k \rangle$.

4. PROBLEM SOLUTION

Simulated annealing (SA), also known as Monte Carlo annealing, statistical cooling, probabilistic hill-climbing, stochastic relaxation, and probabilistic exchange, is the heart of the proposed procedure. The main idea of SA is presented in Fig. 1 (21). As one can see, SA is based on an analogy taken from classical thermodynamics. To grow a crystal, one starts by heating a row of materials to a molten state. Then one reduces the temperature until the crystal structure is frozen in. This goes wrong if the cooling is done too quickly; in particular, some irregularities are located in the crystal structure and the trapped energy level is much higher than that in a perfectly structured crystal. As one can notice, for high temperatures, SA behaves as a purely random search. With the gradual fall of temperature, SA becomes similar to a classical hill-climbing method. Thus, the temperature decrease model, applied during the calculations,

Procedure simulated annealing

begin

$t \leftarrow 0$

initialize Temperature

select a current point v_c at random

evaluate v_c

repeat

repeat

select a new point v_n in the neighbourhood of v_c

if $\text{fitness}(v_c) < \text{fitness}(v_n)$

then $v_c \leftarrow v_n$

else if $\text{random}[0,1) < e^{-\frac{\text{fitness}(v_c) - \text{fitness}(v_n)}{\text{Temperature}}}$

then $v_c \leftarrow v_n$

until (termination-condition)

Temperature $\leftarrow g(t, \text{Temperature})$

$T \leftarrow T+1$

until (halting-criterion)

end

FIG. 1. The structure of simulated annealing.

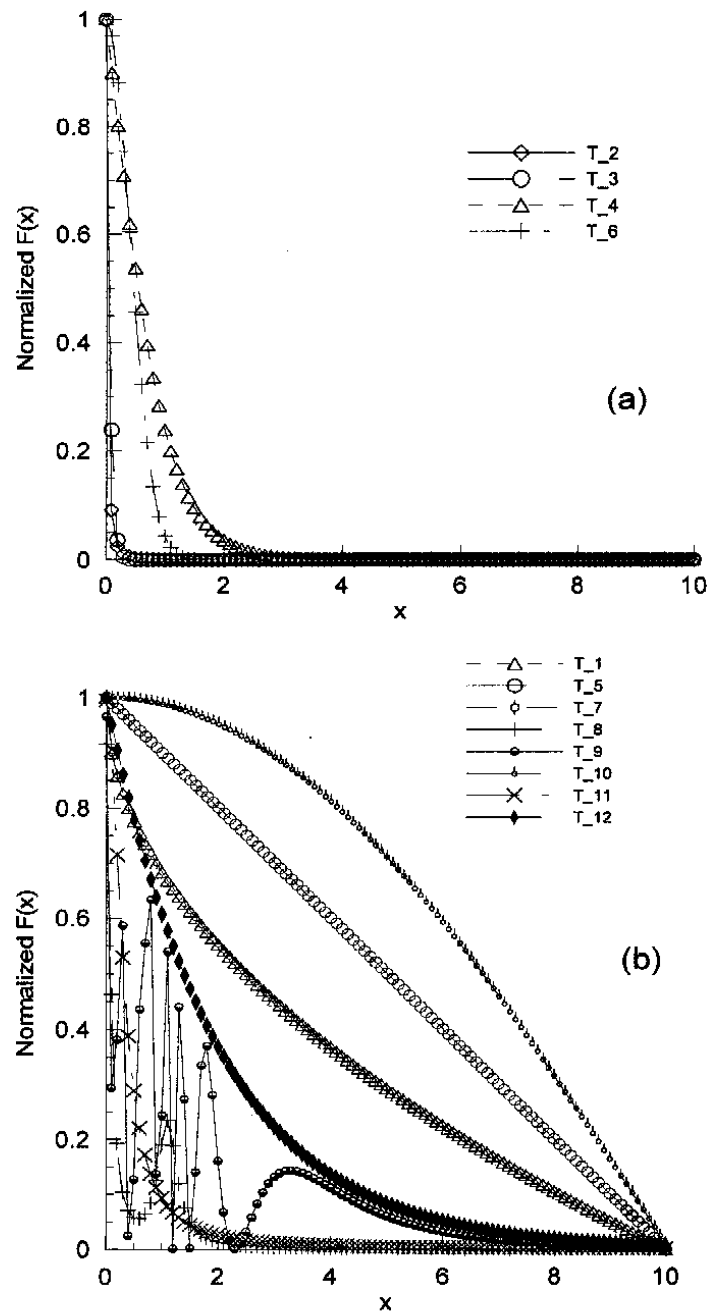


FIG. 2. The models of temperature reduction used in the SA program.

seems to be essential for affecting the values of the parameters of PSD obtained from the fitting of the experimental isotherm using Eq. [3a].

To check the behavior of the proposed procedure as well as to find the effect of the temperature decrease model on the obtained PSD functions, we used the following conditions:

- The starting temperature was equal to 100.
- Twelve functions of temperature decrease were tested. Their plots are shown in Fig. 2. Because some of them seem to generate almost identical plots (for example, T₆ and T₁₁), in Table 1 we include the mathematical formulas describing each model,

TABLE 1

The Model of Temperature Functions Used in the SA Algorithm (All Projected Functions Are Normalized to Unity for x Varying between 0 and 10)

Temperature model code	Equation
T.1	$\frac{1}{x^2 + 1}$
T.2	$\frac{1}{1000x^2 + 1}$
T.3	$\frac{2}{\exp(20x) + 1}$
T.4	$\frac{x + 2}{\exp(2x) + 1}$
T.5	$1 - \frac{x}{10}$
T.6	$\frac{1}{0.398945\sqrt{2\pi}} \exp\left(-\frac{x^2}{0.318314}\right)$
T.7	$1 - \sqrt{\frac{x}{10}}$
T.8	$\frac{1}{x^2 + 0.01} + \frac{1}{(x - 1.1)^2 + 0.04}$ 110
T.9	$1 + \sin\left(\frac{1}{(0.2x + 0.0001)^2}\right)$ $2 \exp(0.55x)$
T.10	$\cos\left(\frac{x}{6.4}\right)$
T.11	$\frac{0.32}{\pi(x^2 + 0.32^2)}$
T.12	$\frac{2.50659}{\sqrt{2\pi}} \exp\left(-\frac{x}{2}\right)$

• A new point v_n was generated in the neighborhood of current points v_c by means of the formula (so-called Gauss mutation (24))

$$v_c = v_n + N(0, \sigma), \tag{8}$$

TABLE 2

The Values of the Gamma-Type Adsorption Isotherm Parameters for All Generated Adsorption Isotherms

Isotherm code	Variable	Value of the variable
Iso.1	$x[1]$	0.2
	$x[2]$	333.2
	$x[3]$	0.7
Iso.2	$x[1]$	0.4
	$x[2]$	331.2
	$x[3]$	2.6
Iso.3	$x[1]$	0.8
	$x[2]$	120
	$x[3]$	-2.6

where $N(0, \sigma)$ is a random Gaussian number with mean zero and with standard deviation σ .

5. RESULTS AND CONCLUSIONS

By using Eq. [3a] and the parameters from Table 2, we modeled three adsorption isotherms (in the range of relative pressure from 1×10^{-7} up to 1). The main idea was to generate different (arbitrarily chosen) pore size distribution shapes (solid lines in Figs. 3 and 4), i.e., the asymmetrical bell-shaped functions possessing one (Figs. 3a and 4a) or two (Figs. 3b and 4b) points of inflection and decreasing to a zero-hyperbolic-like function (Figs. 3c and 4c). It should be emphasized that some of the presented cases were analyzed in Ref. (18), where the new adsorption isotherm equation was developed and compared with other isotherm equations (18). To check the procedure proposed in the current study, the modeled isotherms were fitted by using the SA algorithm. In Table 3 the proposed SA program provides

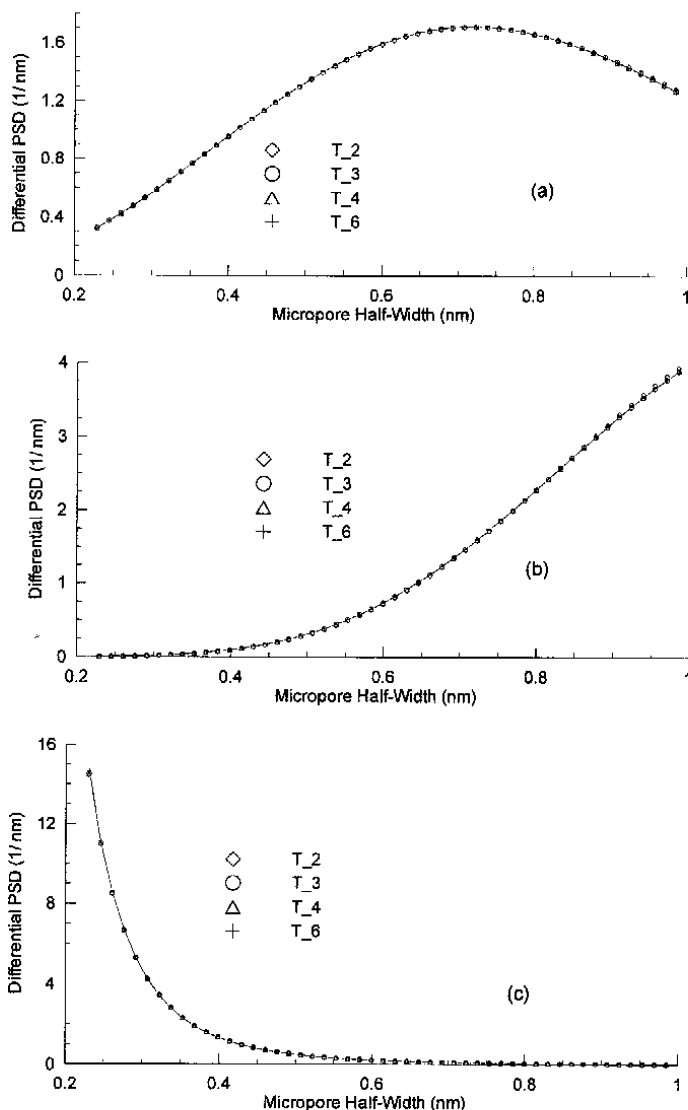


FIG. 3. Micropore size distribution obtained by using the SA program for Iso.1 (a), Iso.2 (b), Iso.3 (c) (solid line: PSD assumed during modeling).

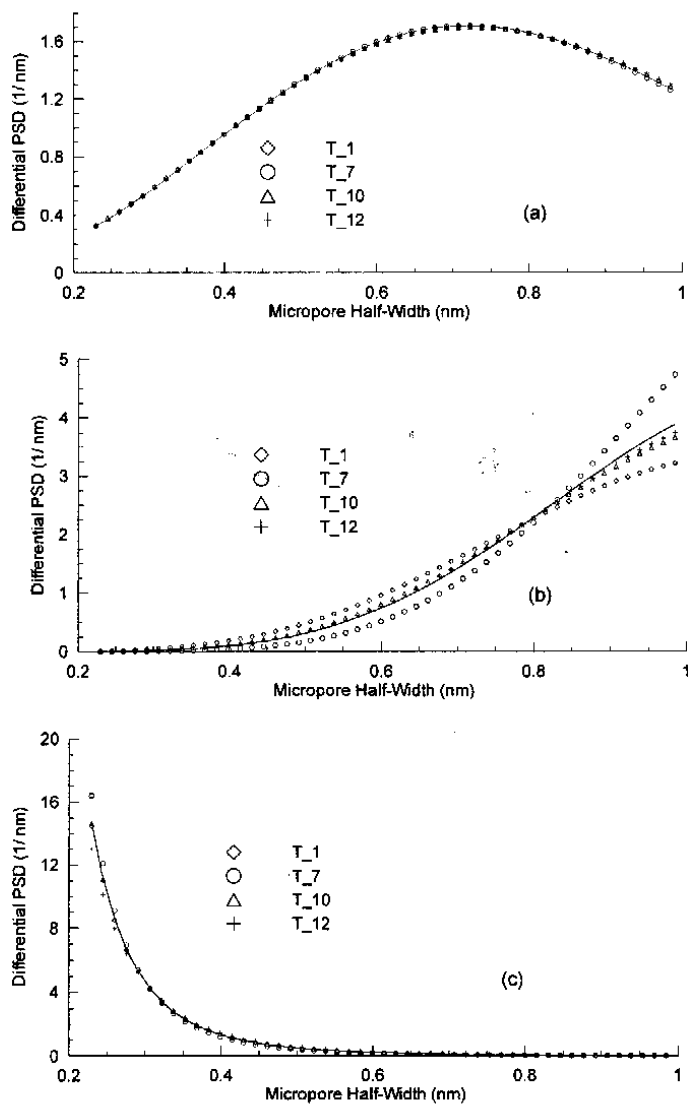


FIG. 4. Micropore size distribution obtained by using the SA program for Iso_1 (a), Iso_2 (b), Iso_3 (c) (solid line: PSD assumed during modeling).

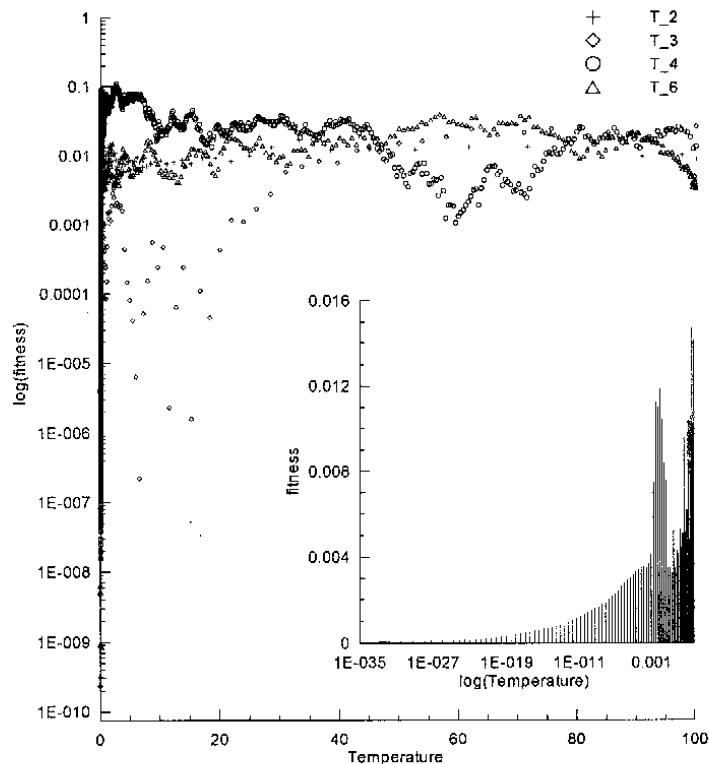


FIG. 5. The behavior of the fitness function during an optimization process for quick temperature reduction models.

optimized parameters that are very close to the optimal value (i.e., a very small value of the fitness function is obtained). It can be noted that the proposed SA algorithm leads to exactly the same shape of PSD as that modeled; however, (which is very important) the goodness of the fit strictly depends on the choice of the temperature model. First of all, the best results (Fig. 3) are obtained for fast decreasing hyperbolic-like temperature reduction models (T₂–4 and T₆; Fig. 2a, Table 1). In these cases the progress of the optimization process was observed for temperatures lower than 0.1 (see Fig. 5). In this area

TABLE 3
The Parameters of the Gamma-Type Adsorption Isotherm Obtained by Using the SA Algorithm for All Temperature Models

Isotherm code	Variable	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_10	T_11	T_12
Iso_1	x[1]	0.2000	0.2000	0.2000	0.1999	0.1999	0.1999	0.2000	0.2004	0.2003	0.2005	0.1999	0.2002
	x[2]	325.68	324.41	332.53	335.24	330.90	337.58	337.58	326.80	316.37	319.80	323.91	317.33
	x[3]	0.6815	0.6777	0.6983	0.7043	0.6975	0.7106	0.7070	0.6916	0.6619	0.6636	0.6740	0.6644
	fitness	1.79e-8	2.60e-8	2.3e-10	4.84e-9	6.18e-7	5.31e-9	1.06e-6	8.07e-7	2.59e-7	4.61e-6	1.60e-7	2.18e-7
Iso_2	x[1]	0.3883	0.4006	0.4000	0.4000	0.4069	0.4000	0.4131	0.4016	0.3954	0.3964	0.4017	0.3974
	x[2]	315.07	334.79	330.51	321.24	312.81	330.42	332.44	337.10	338.54	330.42	319.16	328.08
	x[3]	2.0755	2.6550	2.5975	2.5628	2.8405	2.5971	3.1760	2.6943	2.4809	2.4468	2.6126	2.4914
	fitness	1.50e-3	1.07e-5	2.1e-10	1.85e-8	4.42e-4	1.8e-10	1.32e-3	2.69e-5	1.27e-4	1.30e-4	1.80e-5	5.28e-5
Iso_3	x[1]	0.8025	0.8005	0.8003	0.8002	0.8025	0.8002	0.7907	0.7999	0.8006	0.8004	0.8039	0.8099
	x[2]	112.13	120.96	120.56	130.20	112.79	129.46	127.42	120.30	112.60	127.38	120.79	110.31
	x[3]	-2.5649	-2.5571	-2.5668	-2.5564	-2.5511	-2.5570	-2.7876	-2.5710	-2.5706	-2.5737	-2.4966	-2.3887
	fitness	1.20e-4	6.26e-6	1.17e-6	8.91e-7	7.40e-5	9.11e-7	1.71e-3	2.70e-6	2.40e-6	3.54e-5	2.12e-4	1.69e-3

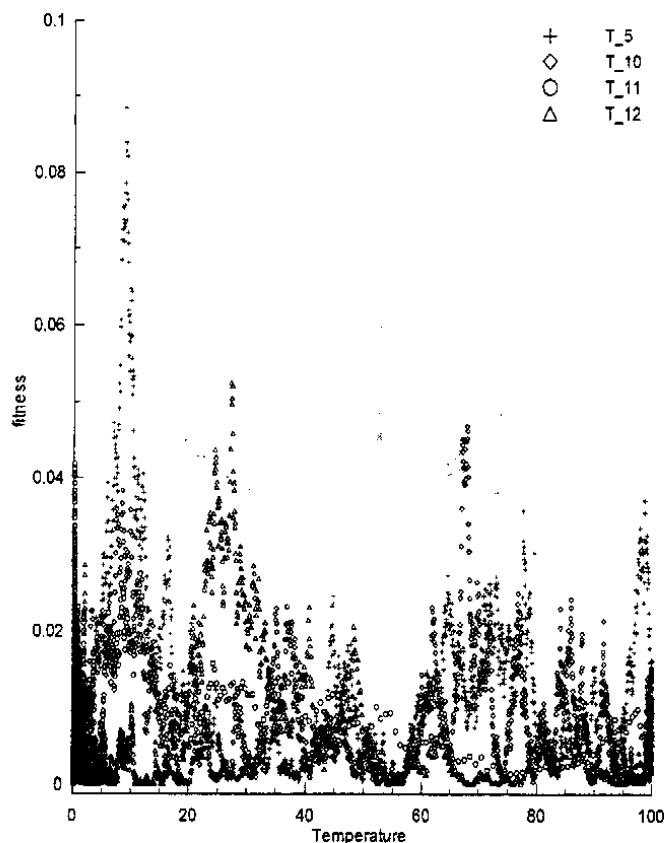


FIG. 6. The behavior of the fitness function during the optimization process for the remaining temperature models.

the SA program behaves as a hill-climbing algorithm. It should be stressed once more that in such a case an optimization process gives very similar shapes of micropore size distributions for all tested adsorption isotherms. For all the remaining models (for example, linear, slow-decreasing hyperbolic-like, non-monotonic, and others, Fig. 2b) of temperature reduction, an optimization process is very similar to a classical random search algorithm (see Fig. 6). Consequently, for these models of temperature reduction, the obtained results are poor and the obtained PSDs differ from the modeled ones, especially for the case of the asymmetrical bell-shaped function possessing two points of inflection.

Considering the obtained results, we want to emphasize that the SA program can be successfully applied to characterizing microporous carbons; however, attention should be paid to applying a proper cooling temperature function. The reproducibility of the assumed pore size distribution is very good, and the proposed procedure for numerically solving Eq. [3] is a very powerful optimization tool.

The application of the SA program to the description of experimental adsorption data and the simplification of the

gamma-type adsorption isotherm will be the subject of next papers.

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