Prediction of the micropore structure parameters and adsorption properties of activated carbons

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A regularity govering variations of volume and linear size of micropores in carbon adsorbents during their vapor-gas activation was found. A parameter was proposed that characterizes the degree of development of the micropore system in activating carbons and an initial carbonized material. The parameter is defined as the number (or surface area) of micropores in the volume unit of the micropore zones. This parameter allows one to rationalize the choice of carbonized materials for the preparation of activated carbons with specified adsorption properties and to establish the range of activation beyond which the structure of the micropores loses stability. Furthermore, the parameter serves to predict how activation affects micropore structure parameters and adsorption properties of carbons. This in turn indicates the optimal degrees of microporosity of carbons needed to attain required adsorption properties.

Key words: activation, activated carbons, micropores, specific surface area, adsorption.

To develop adsorbents with desired adsorption properties, it is necessary to know the features of the micropore structure formation. In particular, a mathematic model is necessary to predict a change in the geometric characteristics of micropores and adsorption properties of carbon adsorbents upon vapor-gas carbon activation.

A model describing development of microporosity during the activation of carbon adsorbents

A character of microporosity of activated carbons (AC) is due to the structural features of carbon crystals that have a layered texture. Each layer of these crystals is formed by a net of the six-membered carbon rings. Micropores are voids between the layers and resemble parallel slits in their form. Let us consider a model of an infinite slit-like micropore.

In the microporous zone of a carbon adsorbent we can distinguish an unit volume formed by the walls of the micropore (Fig. 1). According to the model of slit-like micropores, the volume (W_0/cm^2 g^{-1}) and specific surface area (S/cm^2 g^{-1}) of the parallel slit-like micropores with a width H/nm are related as $S = 2W_0/H$. It can be expected that the S and W_0 values would increase with the increasing pore size. However, when the above parameters are attributed to the volume unit of the microporous zone rather than to the weight unit, then an increase in the pore widths would only proportionally increase the volume fraction of micropores determined as

$$W_0/(W_0 + 1/\rho),$$

where ρ/g cm^{-3} is the density of the carbon material. The surface area S' and the number of micropores in the unit volume remain constant (see Fig. 1). The relaitionship between S'(cm^2 cm^{-3}) and the number of micropores N (1/cm) per the length unit of the model sorbent in the direction normal to the pore walls is determined as $S' = 2N$.

Hence, the number of micropores and their surface area in the volume unit of microporous zones remain constant during the activation of a carbonized material, and that permits the elucidation of the relationship between the parameters of micropore structure of different AC.[1]

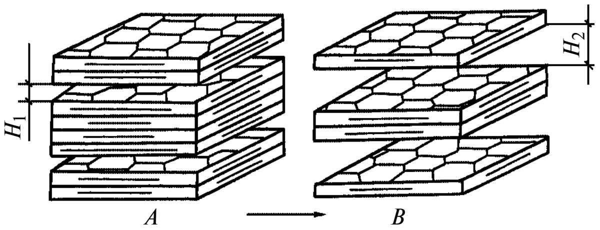

Fig. 1. A change in the micropore volume during activation of carbons (*A*, *B* are two successive steps of activation).

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$$S'_1 = S'_2 = ... = S'_i = \frac{2W_{0(i)}}{(W_{0(i)} + 1/\rho)H_i} = \text{const}, \quad (1)$$

where indices 1, 2, ..., i correspond to the micropore structure parameters of adsorbents with different extent of activation.

In the general case, an increase in the micropore size alone can not account for development of the micropore structure on activating carbon sorbents. In a carbonized material and weakly activated carbons, the micropores exist, which are inaccessible to adsorptives, when their dimensions exceed the apertures of pores. It has been found experimentally,[2—6] that an increase in accessibility of these pores can be achieved by a minor combustion of carbon, when a change in the apparent density is not noticeable in fact. Therefore, the pore volume inaccessible to an adsorptive (Δv/cm^3 g^{-1}) can be determined as a difference

$$\Delta v = (1/d) - (1/\rho), \quad (2)$$

where d is the density of the adsorbent found with the use of an adsorptive as a picnometric substance.

Thus, when a fraction of the micropore volume is inaccessible to an adsorptive, the total pore volume is greater than the experimentally determined value of W_0 by the Δv value. Accordingly, the expression

$$S'_1 = S'_2 = ... = S'_i = 2N_i = \\ = 2\frac{W_{0(i)} + \Delta v_i}{(W_{0(i)} + \Delta v_i + 1/\rho)H_i} = \text{const}, \quad (3)$$

that relates micropore volumes and sizes of carbons with different extent of activation is commonly valid.

A relationship between the micropore width H and characteristic adsorption energy E has been studied earlier.[7,8] In this work, a relationship deduced for a slit-like micropore formed by parallel infinite planes will be used

$$H = 10.8 \cdot \beta^{2/3} \cdot E^{-2/3}, \quad (4)$$

where H/nm is the pore width; E/kJ mol^{-1} is the characteristic adsorption energy; 10.8/nm $\cdot$ (kJ mol^{-1})$^{2/3}$ is a numerical coefficient; a similarity constant β relates the energies of this adsorptive E and the standard adsorptive (benzene) E_0: $E_0 - E = \beta E_0$. It is approximated by the parachors ratio of the corresponding liquids.

Equation (4) was obtained by the quantitative comparison of two opposite effects influencing the adsorbate density in micropores.[9] The first effect, a decrease in the density the adsorbate compared to that of the bulk liquid adsorbed at saturation, is due to steric constraints, which prevent the adsorbed molecules from forming the same molecular arrangemnet as in the bulk liquid. Compression of adsorbed species in the micropore volume to attain the pressure proportional to the characteristic adsorption energy[10] results in the opposite effect, an increase in the adsorbate density. The method of evaluation of the shape and size of the micropores has been developed on the basis of comparison of these two effects.[11] The application of this method to carbon sorbents makes it possible to conclude that micropores in carbons have a slit-like shape and their widths, according to Eq. (4), are inversely proportional to the characteristic adsorption energy in the 2/3 power.

The above process of the microporosity development is more complex in fact, and the model proposed includes some assumptions. First, the H values characterize the average width of all micropores, whereas with adsorption data the size of those micropores can be determined that are accessible to the adsorptive. This can result in substantial errors in S_i (or N) of poorly activated carbons in which the volume of micropores unavailable to the adsorptive (Δv) is significant. For carbons with different burn-offs, $\Delta v \ll W_0$ and one can accept $\Delta v = 0$ ($d = \rho$). Examination of the experimental data results in the empirical relation between Δv and the volume of the micropores, which can be opened up during activation

$$\Delta v_i = \Delta v_0[1 - (W_{0(i)} - W_0)^{1/4}], \quad (5)$$

where Δv_0, W_0 and Δv_i, $W_{0(i)}$ are the characteristics of the pore volume of the studied (basic) and predicted adsorbents, respectively.

Second, one should expect that the S' (or N) values should decrease during very strong activation. The reason may lie either in the increasing fraction of mineral matter (ash) or in the fact that the finest packets of carbon nets with the highest surface area are preferentially incorporated in burning the pore walls. The average width of the pore walls Z can be obtained by considering that the N (or S') parameters are the same for both micropores and the forming walls. Then, according to the above model,

$$Z = H\frac{1/\rho}{W_{0(i)} + \Delta v_i}. \quad (6)$$

The estimation of a change in the width of the micropore walls is necessary to find the limiting activation conditions above which further gasification would lead to a collapse of the pore structure rather than to an increase in the micropore volume.

Results and Discussion

Table 1 presents the results of calculations of the Eq. (3) parameters for 31 activated carbons divided into seven series according to the nature of the initial material.

As seen in Table 1, the N and S' values for each series of AC remain constant in the whole region of variation in the micropore volume. Therefore, these parameters characterize the development of the micropore system in carbonized materials and AC. Somewhat lower N and S' values are found for the adsorbents with the largest micropore volume, and this is explained by

Table 1. A change in the parameters of the micropore structure during activation of carbon adsorbents

Raw material for AC	W_0 /cm^3 g^{-1}	E_0 /kJ mol^{-1}	H /nm	$N \cdot 10^{-6}$, cm^{-1}	S' /m^2 cm^{-3}
Birch wood[12]	0.26	25.3	1.25	2.85	570
	0.29	23.0	1.33	2.87	574
	0.31	21.9	1.38	2.91	582
	0.37	18.1	1.57	2.83	566
	0.46	15.7	1.72	2.89	578
Beech wood[13]	0.35	26.5	1.22	3.50	701
	0.44	21.8	1.38	3.51	702
	0.53	18.7	1.53	3.48	695
	0.61	16.6	1.66	3.42	684
Hydrate-cellulose fiber[14]	0.28	21.6	1.39	3.21	642
	0.39	17.7	1.59	3.15	630
	0.44	17.1	1.63	3.16	632
	0.62	13.8	1.87	3.13	627
Liquid and solid products of wood pyrolysis[15]	0.18	31.6	1.08	3.26	652
	0.22	28.1	1.17	3.26	652
	0.32	22.1	1.37	3.26	652
	0.37	19.1	1.47	3.22	644
Copolymer of 2-methyl-5-vinyl-pyridine and divinyl benzene[16]	0.29	26.6	1.21	3.39	678
	0.46	18.8	1.53	3.36	672
	0.66	15.2	1.76	3.39	678
Furfural (ground carbon)	0.330	28.9	1.15	3.84	768
	0.43	24.2	1.29	3.83	766
	0.52	20.8	1.43	3.73	747
	0.70	18.0	1.58	3.83	767
	0.79	16.5	1.67	3.78	757
	0.86	14.8	1.79	3.62	724
Furfural (spheric carbon)	0.27	30.8	1.10	3.66	732
	0.35	27.3	1.19	3.66	732
	0.58	19.4	1.50	3.72	744
	0.90	15.1	1.77	3.73	746
	1.29	12.1	2.05	3.59	718

incorporation of the thinest micropore wall in burning. In particular, when the adsorption volume of the carbons of the latter series increases from 0.90 to 1.29 cm^3 g^{-1}, the S' parameter decreases from 746 to 718 m^2 cm^{-3}) with a decrease in Z from 0.91 to 0.74 nm. The width of the wall equal to 0.74 nm corresponds to the distance between two carbon nets, and this value can likely be accepted as a critical limit of the micropore volume. Further activation would lead to a progressive degradation of the micropore structure.

The validity of relation (3) serves to evaluate the dynamics of changes in the micropore structure parameters and adsorption properties of AC upon activation. The evaluation includes calculation

— spheric surface area of the S' parameter for the series of carbons under study from the characteristics of one (basic) sample found experimentally;

— of the micropore width H for the predicted adsorbent from Eq. (3) at the specified micropore volume W_0;

— of the characteristic adsorption energy for the standard adsorptive (benzene) E_0 from Eq. (4).

A knowledge of the W_0 and E_0 parameters is sufficient to determine the amounts of various substances adsorbed at specified pressure and temperature from the Dubinin—Radushkevich equation known from the theory of the volume filling of micropores (TVFM)[17]

$$av = W_0\exp[-(A/E_0\beta)^2], \tag{7}$$

here a is the amount adsorbed, v is the molar volume of the adsorbate, A is the differential molar work of adsorption.

The efficient parameters of micropores of the basic sample, calculated ignoring adsorption on the micropore surface, are best suited for the calculation of the structure parameters and related adsorption properties of AC.[17] This obviates a necessity for taking into account the changes in the mesopore structure. In addition, the accuracy of the description of the adsorption isotherms with Eq. (7) decreases for strongly activated carbons (E_0 < 19 kJ mol^{-1}).[18] In these cases, the two-term TVMF equation has been used[17]

$$W = W_{01}\exp[-(A/E_{01})^2] + W_{02}\exp[-(A/E_{02})^2], \tag{8}$$

which reflects a superposition of two microporous structures with the W_{01} and E_1 parameters for conventional micropores as well as W_{02} and E_{02} for larger micropores, supermicropores.

On going from Eq. (7) to Eq. (8) in the description of the adsorption isotherms, one should take into account that the total micropore volume W_0 of supermicroporous adsorbents is the sum of W_{01} and W_{02}, and the characteristic adsorption energy determined with Eq. (4), is the weighted average value:

$$E_0 = \frac{E_{01} + \alpha E_{02}}{1 + \alpha}, \tag{9}$$

where $\alpha = W_{02}/W_{01}$.

In these cases (E_0 < 19 kJ mol^{-1}), the parameters of Eq. (8) are determined[1] from the expressions

$$1/(1 + \alpha) = 5.16 \cdot 10^{-2} \cdot E_0 - 0.24, \tag{10}$$

$$E_{02}/E_{01} = 9.72 \cdot 10^{-2} \cdot \alpha^{-1} + 0.375. \tag{11}$$

Table 2 presents the predicted parameters of carbons derived from furfural and calculated by Eqs. (1)—(5) and compares these parameters with those obtained by processing the experimental adsorption isotherms for benzene vapor.

One can conclude from the findings of Table 2 that the experimental and predicted parameters for carbons coincide satisfactorily. The difference between adsorption isotherms for benzene vapor calculated from the TVFM equations using the predicted parameters of the microporous structure and the experimentally obtained adsorption isotherms does not exceed 3%.

Table 2. Parameters of microporous structure of spheric AC from furfural predicted and calculated from experiment

Prediction or Experiment	W_{01}	W_{02}	E_{01}	E_{02}	E_0	H /nm	S' /m^2 cm^{-3}	Δv /cm^3 g^{-1}
	cm^3 g^{-1}		kJ mol^{-1}					
Experiment	0.29	0	32.9	0	32.9	1.05	736	0.097
				Basic Sample				
Experiment	0.34	0.04	27.0	22.2	26.5	1.22	750	0.011
Prediction	0.37	0	25.3	0	25.3	1.25	736	0.020
Experiment	0.58	0.07	19.3	17.4	19.1	1.51	774	0.009
Prediction	0.44	0.21	20.5	11.8	17.7	1.59	736	0.010
Experiment	0.59	0.47	18.3	8.6	14.0	1.86	749	0.004
Prediction	0.49	0.57	19.2	8.8	13.7	1.89	736	0.003
Experiment	0.49	0.94	19.4	8.2	12.0	2.06	731	0
Prediction	0.55	0.88	18.5	8.0	12.1	2.05	736	0

The possibility of predicting the dynamics of a change in the adsorption properties of AC during their progressive gasification enables adsorbents with desired adsorption properties to be developed. Figure 2 shows adsorption of carbon disulfide (β = 0.7) on the activated carbons with S' = 500 and 700 m^2 cm^{-3} as a function of the micropore volume developed on activating the carbonized material.

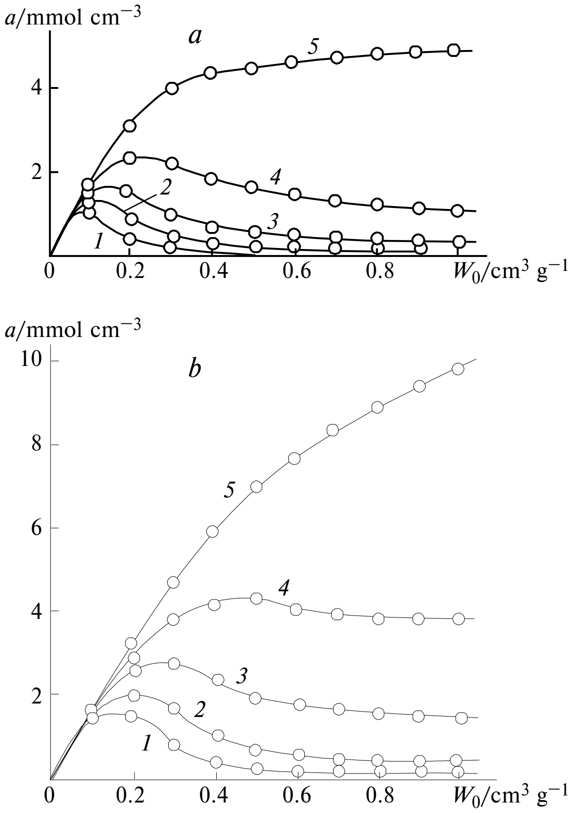

Fig. 2. Predicted adsorption properties of AC as a function of the volume of micropores formed during activation of carbonized material: S' = 500 (*a*) and 700 m^2 cm^{-3} (*b*). Adsorptive is carbon disulfide, $p/p_s = 1 \cdot 10^{-5}$ (*1*), $1 \cdot 10^{-4}$ (*2*), $1 \cdot 10^{-3}$ (*3*), $1 \cdot 10^{-2}$ (*4*), and $1 \cdot 10^{-1}$ (*5*).

It follows from the above data that at moderate and specifically at low relative pressures, the curves $a_{p/p_s} = f(W_0)$ are characterized by clear maxima whose positions determine the optimal micropore volume and adsorption achievable at this volume. The expected potential of any carbonized material to give AC with specified adsorption properties can be evaluated in this way.

The problems of achieving the highest adsorption by the volume unit of the adsorbent layer rather than by the weight unit are not rare in the adsorption practice. Noteworthy, the AC bulk density Δ (g cm^{-3} of a layer) decreases upon activation because the adsorption capacity of the layer volume is determined by the product $a\Delta$ (mmol cm^{-3} of a layer). The Δ value is the weight m of the adsorbent layer of the V volume, which includes the carbon volume m/ρ, the volumes of micro-, meso-, and macropores, as well as the volume of voids between granules in the layer, $\Delta V\varepsilon$. Designating $\Delta(V_{me} + V_{ma}) = \varepsilon'$ as the volume fraction of meso- and macropores in the layer, and $\Delta V\varepsilon = \varepsilon_0$ as the layer porosity, we obtain after transformation

$$\Delta = m/V = \frac{1-(\varepsilon'+\varepsilon_0)}{1/\rho + W_0}. \qquad (12)$$

As is known, the porosity remains nearly constant during activation. One can also accept that the volume fraction of the meso- and macropores remains unchanged in a wide range of the activiation conditions because these pores have a specific surface area that is by several orders of magnitude lower than the surface area of micropores. Therefore, when the activation occurs in the kinetic region, the developed structure is mainly microporous. Hence, $1 - (\varepsilon_0 + \varepsilon') = \text{const}$ and

$$\Delta = K\left(\frac{1}{\rho} + W_0\right)^{-1}. \qquad (13)$$

Figure 3 shows how the microporosity development changes the adsorption properties of the volume unit of the carbon layer. In the calculation of the Δ value by

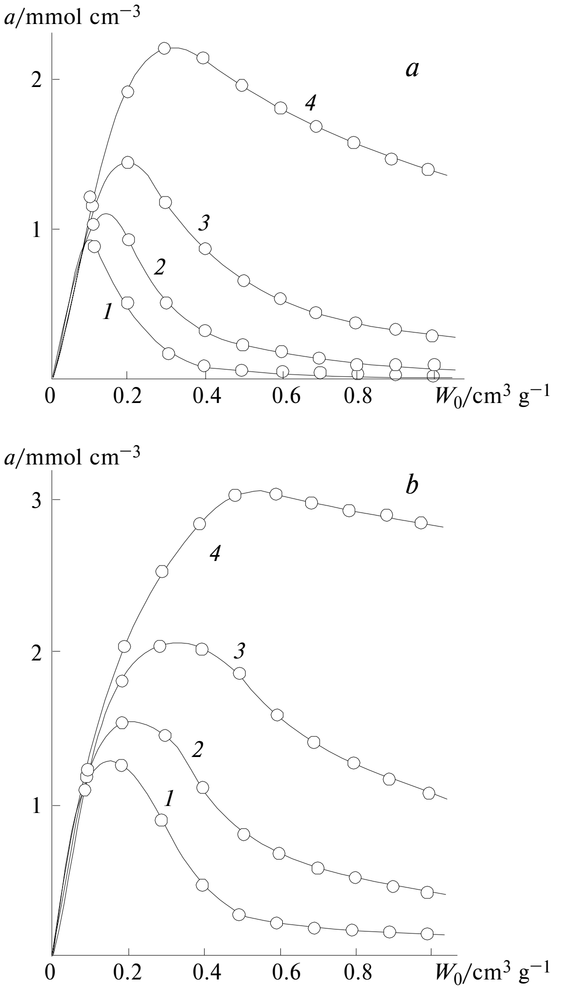

Fig. 3. Predicted adsorption properties of the volume unit of activated carbons as a function of the volume of micropores formed upon activation of the carbonized material: $S' = 500$ (*a*) and 700 m^2 cm^{-3} (*b*). Adsorptive is carbon disulfide, $p/p_s = 1 \cdot 10^{-4}$ (*1*), $1 \cdot 10^{-3}$ (*2*), $1 \cdot 10^{-2}$ (*3*), and $1 \cdot 10^{-1}$ (*4*).

Eq. (13), the $K = 0.41$ was taken from the reference data[19] for granulated AC.

It is seen that unlike the curves $a_{p/p_s} = f(W_0)$, the curves $(a\Delta_{p/p_s}) = f(W_0)$ are characterized by significantly more clearly pronounced maxima. An increase in the S' parameter from 500 to 700 m^2 cm^{-3} results in a shift of the maxima to larger micropores, indicating an increase in the adsorption capacity with the increasing micropore volume.

Thus, the activation of carbonized materials with a developed system of micropores should produce more active carbon adsorbents.

As can be seen in Table 3, the S' and N' parameters, which characterize the degree of microporosity, depend substantially on the nature of the initial material and can differ more than two times. Relatively low values of S' and N are typical of the AC obtained from most abundant raw materials: peat, lignite, coal, and anthracite. The S' and N values for different charcoals increase in the following sequence: birch and pine AC < fruit stone AC < coconut shell AC. The AC from thermoreactive polymers (phenol-formaldehyde, furyl resins, furfural, *etc.*) and polyvinylidene chloride are characterized by the most developed micropore structure.

Table 3. Parameters characterizing the degree of microporosity of AC obtained from different raw material

Raw material	S' /m^2 cm^{-3}	$N \cdot 10^{-6}$ /cm^{-1}
Peat	380—540	1.9—2.7
Lignite	420—480	2.1—2.4
Coal	440—540	2.2—2.7
Anthracite	480—530	2.4—2.7
Lignin	585—640	2.9—3.2
Dry residue of sulfate liquor	480—500	2.4—2.5
Birch and pine wood	520—620	2.6—3.1
Fruit stones	600—660	3.0—3.3
Beech wood	770	3.5
Coconut shell	680—740	3.4—3.7
Petroleum pitch	620—690	3.1—3.5
Thermoreactive polymers	670—790	3.3—4.0
Polyvinylidene chloride	800—840	4.0—4.2

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