

Steam-Carbon Gasification Catalyzed by Calcium: Assessment of the Porous Structure of Active Carbons from Plum Stones and Synthetic Active Carbons

A. DĄBROWSKI, Z. FEKNER, R. LEBODA AND J. GOWOREK

Department of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

Received March 19, 1996; Revised September 24, 1996; Accepted October 9, 1996

Abstract. A need for an elaboration of the methods for synthesis and characterization of activated carbons with a requisite porous structure has existed for a long time. One of the methods giving possibility for creating controlled mesopore and micropore structures deals with the steam gasification of various carbon materials. In this work the effects of calcium catalyst on the catalytic steam gasification of active carbons from plum stones and porous polymers are presented. Determination of micropores capacity and specific adsorption in mesopores have been performed by means of the α_s method, but adsorption on the heterogeneous solids was described by the integral equation with various local isotherms. This equation has been solved by the regularization method. Based on this method the changes in structural parameters of active carbons depending on the amount of calcium catalyst were estimated.

Keywords: natural active carbons, synthetic active carbons, porous structure, pore size distribution, modification of active carbons

Introduction

Activated carbons are mainly used in adsorption processes both from the gas and liquid phases and their behavior as adsorbents strongly depends on their porous structure (Jankowska et al., 1991; Belyakov, 1991; Wigmans, 1986; Rodriguez-Reinoso, 1986; Linares-Solano, 1986; Capelle and de Vooy, 1983; Mattson and Mark, 1971; Matisova and Skrabakova, 1995). For various purposes, less (Matisova and Skrabakova, 1995; Rudziński et al., 1995; Unger, 1983; Vissers et al., 1988) or more (Jankowska et al., 1991; Belyakov, 1991; Wigmans, 1986; Mattson and Mark, 1971; Matisova and Skrabakova, 1995; Rundling, 1987; Matisova et al., 1995) microporous carbon adsorbents are required. Therefore, it is necessary to work out the conditions to prepare the adsorbents of desired porous structure (Jankowska et al., 1991; Wigmans, 1986; Matisova and Skrabakova, 1995; Unger, 1983;

Vissers et al., 1988; Matisova et al., 1995; Leboda and Dąbrowski, 1996) or the methods of modification of commercial active carbons enabling creation of a controlled structure in them (Wigmans, 1986; Leboda et al., 1993).

One of the methods enabling development of a mesoporous system in the porous structure of carbon adsorbents is the partial gasification of carbon materials by means of water vapor in the presence of various catalysts (Czechowski et al., 1993; Leboda et al., 1990; Leboda et al., 1993).

Carbon gasification reactions catalyzed by calcium compounds were reported in several interesting papers (e.g., Cazarola-Amorós et al., 1993; Cazarola-Amorós et al., 1994; Pérez-Florindo et al., 1993; Linares-Solano et al., 1990).

In these papers the factors influencing the catalytic activity of calcium in the carbon-gas reactions were investigated, e.g., the effect of the heating rate, the

mechanism of calcium sintering during the gasification process and the effect of the chemical state of calcium on the sintering rate.

On the other hand, the mechanism for describing calcium catalysis behavior was proposed when spent activated carbon experiences oxidation by steam and CO₂ (Canon et al., 1994).

As these problems are not the subject of our paper, we will use the term "calcium catalyst" in further considerations, not going into a question of carbon gasification reactions.

This paper presents the results of studies on the influence of the calcium catalyst amount deposited on the active carbon surface on the effects of its porous structure modification during the partial gasification with water vapor.

Using calcium as a catalyst of active carbon gasification reaction proved effective creating a mesopore system. Contrary to other catalysts developing a mesopore system, e.g., ZnCl₂ (Wigmans, 1986), this catalyst is not hazardous for the natural environment and proves to be effective even in small quantities.

The studies were carried out using the carbons obtained from various raw materials. Original structure of initial raw materials, their texture and porosity can play a significant part in the gasification process and finally in creation of new porous structure of modified material. Therefore the active carbon prepared from the natural raw material, i.e., from plum stones (PSAC) and the synthetic active carbon (SAC) prepared from the synthetic polymers were used in our studies. Preparation of active carbons from fruit stones and their modification were the subject of many papers (Lussier et al., 1994; Rodriguez-Reinoso, 1986; Leboda and Dąbrowski, 1996; Leboda et al., 1993; Iley et al., 1973; Marsh et al., 1975; Lopez-Gonzales et al., 1980). Application of such adsorbents in practice was described, among others, in the papers (Rodriguez-Reinoso, 1986; Leboda and Dąbrowski, 1996; Leboda and Lodyga, 1991; Leboda et al., 1990).

The synthetic active carbons have some advantages over other types of carbon adsorbents owing to some properties, characteristic for this type of carbons like: high mechanical strength and sorption capacity as well as a regular spherical shape of granules (Kartel et al., 1991; Puziy, 1995; Puziy et al., 1995). So far, very few papers have been published on modification of porous structure of this type of adsorbents.

Experimental

Initial Adsorbents

Two active carbons of similar porous structure parameters were chosen for our studies. They have similar sizes of specific surface area calculated formally using the BET method (S_{BET}), slightly different sorption capacities of pores (V_p), and also similar means of pore diameters, \bar{r} (Table 1). Mean pore radii were calculated assuming their cylindrical shape by means of the formula: $\bar{r} = 2V_p/S_{\text{BET}}$.

The initial active carbon (PSAC) was obtained from the Wood Dry Distillation Works in Hajnówka, Poland. This active carbon has been prepared by granulation, carbonization at elevated temperatures (823–873 K) and activation (1173–1273 K) with water vapor as a basic activating agent.

Surface contaminations with mineral matter and, where necessary, poorly carbonized parts of the particles were removed from the commercial active carbon by the process described previously (Leboda and Lodyga, 1991). In this method an appropriate mixture of a mineral acid and an organic solvent was used. Such adsorbent was the initial material for subsequent studies. Synthetic active carbon (SAC) applied in the present study was prepared from porous copolymers of vinylpyridine and styrene with divinylbenzene by carbonization at 1173 K followed by water vapor activation (973 K) (Puziy et al., 1995).

Impregnation with the Catalyst

Catalytic gasification of the initial active carbons was undertaken as described previously (Leboda et al., 1993). The adsorbent surface was impregnated with 0.25, 0.5, 1.0, 1.5, 2.0, 2.5% w/w of calcium catalyst. The percent in the weight concentration of calcium catalyst (% w/w) indicate the percent contribution of the calcium Ca(II) catalyst with reference to the

Table 1. Essential information about active carbons studied.

Adsorbent	S_{BET} m ² /g	V_p cm ³ /g	\bar{r} nm	Source
PSAC	1138	0.68	1.2	Plum stones
SAC	1126	0.74	1.3	Porous copolymer of styrene-divinylbenzene

weight of active carbon samples. An aqueous solution of $\text{Ca}(\text{CH}_3\text{COO})_2$ from POCh Gliwice, Poland, was used. Excess moisture was removed by drying under mild conditions.

Adsorbent Activation

Activation of initial active carbons and those with the calcium catalyst was carried out in the quartz fluid reactor at 1073 K for 1.5 h. The quartz reactor was placed in the electric oven enabling the temperature control. In the reactor 10g of adsorbent was placed which was then heated in the stream of deoxidized nitrogen (flow rate $200 \text{ cm}^3/\text{min}$) till the conditions of isothermal activation (1073 K) were reached. Then the nitrogen flow was stopped and water vapor was passed through the reactor. Water was provided into the reactor through the boiler proper at 573 K using a pump of MASTERFLEX type (Cole-Parmer Instrument Company, USA). The rate of water bathing was $0.6 \text{ cm}^3/\text{min}$. After the isothermal activation the reactor was cooled in the stream of deoxidized nitrogen.

Adsorbent Testing

After gasification, calcium catalyst was removed from the prepared samples of active carbons using 6% HCl in the extraction columns. The calcium $\text{Ca}(\text{II})$ content in the filtrate was analyzed using an atomic absorption spectroscopy ASA-3 (Carl Zeiss-Jena, Germany) with a hollow-cathode lamp.

Nitrogen adsorption and desorption were studied on all adsorbents, using the Sorptomat 1900 (Carlo-Erba Co., Milan, Italy). The surface areas, S_{BET} , were calculated according to the BET method, using 0.162 nm^2 as the coverage area per nitrogen molecule.

Results

Parameters of porous structure of carbon adsorbents under investigation were estimated from low-temperature (77 K) adsorption isotherms of the nitrogen. The most characteristic adsorption-desorption experimental isotherms are presented in Figs. 1–4. The isotherms for the initial adsorbents (PSAC—Fig. 1; SAC—Fig. 3) are of type H4 according to the classification of hysteresis loops recommended by IUPAC (Sing et al., 1985). The other isotherms (Figs. 2 and 4) are similar, but closer to type H3. These adsorption

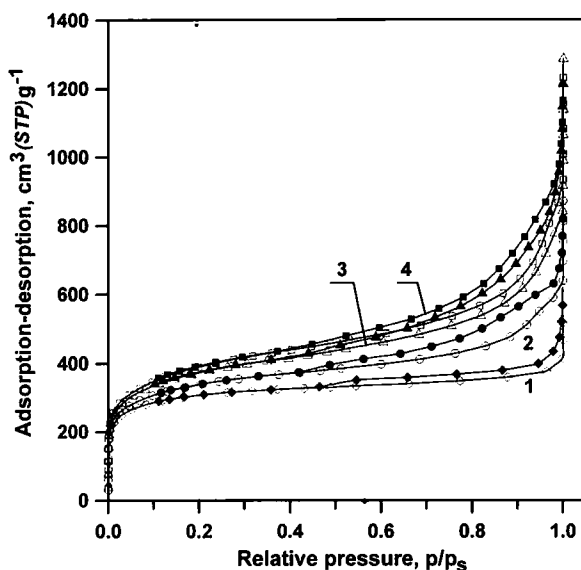


Figure 1. Low-temperature adsorption-desorption isotherms of nitrogen determined for the following adsorbents: PSAC initial (1), PSAC-0.5% (2), PSAC-2.0% (3), PSAC-2.5% (4) (see Table 2).

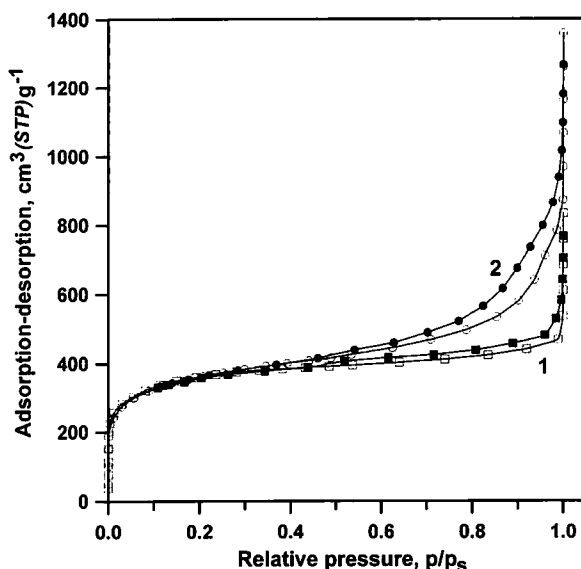


Figure 2. Low-temperature adsorption-desorption isotherms of nitrogen determined for the following adsorbents: PSAC-0% (1), PSAC-1.5% (2) (see Table 2).

isotherms are typical for microporous adsorbents. In all cases, adsorption hysteresis which is always reproducible was observed. It is known (Sing et al., 1985) that H3 loop is observed with aggregates of plate-like particles giving rise to slit-shaped pores, but H4 hysteresis loop is associated with narrow slit-like pores.

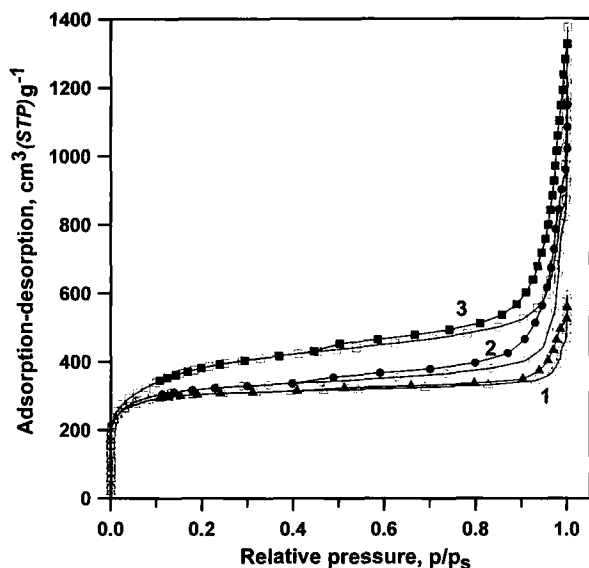


Figure 3. Low-temperature adsorption-desorption isotherms of nitrogen determined for the following adsorbents: SAC-initial (1), SAC-1.5% (2), SAC-2.5% (3) (see Table 3).

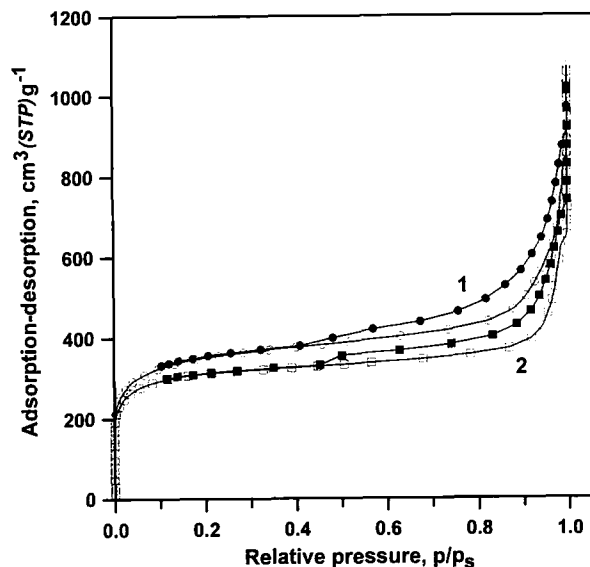


Figure 4. Low-temperature adsorption-desorption isotherms of nitrogen determined for the following adsorbents: SAC-0.25% (1), PSAC-1.0% (2) (see Table 3).

Computation Procedure

The main characteristics of the carbon porous structure, which defines its adsorption properties are the adsorption capacity and size of micropores as well as the surface area of mesopores. The model of slit-shaped

micropores was used in the present study and the size of micropores has been determined from the half-width of the slits. Because of highly disordered structure of the microporous carbons, they are best characterized by a distribution of the half-widths. The main parameters of the distribution function are the average half-width (\bar{x}) and its variance (σ_x^2).

Determination of the adsorption capacity of micropores and the surface area of mesopores from nitrogen adsorption isotherms was performed using the α_s method (Gregg and Sing, 1982). Adsorption on the heterogeneous microporous solids was described by the common integral equation (Jaroniec and Madey, 1988; Rudziński and Everett, 1992):

$$\Theta_{\text{mi}}(p, T) = \int_{x_{\text{min}}}^{x_{\text{max}}} \theta(x, p, T) F(x) dx \quad (1)$$

where $\Theta_{\text{mi}}(p, T)$ is the relative filling of the micropores at a given adsorptive pressure p and temperature T (77 K); $\theta(x, p, T)$ is the local relative filling of micropores with a half-width x , as described by Dubinin-Astakhov equation (Dubinin et al., 1979); x_{min} and x_{max} are the minimum and maximum half-widths of micropores and $F(x)$ is the normalized distribution function of the half-width. We used $x_{\text{min}} = 0.24$ nm and $x_{\text{max}} = 2.64$ nm, because these limits are determined by the dimension of the N_2 molecule (0.225 nm) and transition of the volume-filling mechanism in the micropores to the layer-by-layer adsorption mechanism in the mesopores at $p/p_s > 0.4$ for nitrogen adsorption (Dubinin, 1979). Equation (1) was solved by the regularization method (Tichonov et al., 1990; Puziy et al., 1995).

Preliminary computations show, that the use of Dubinin-Radushkevich equation (Dubinin, 1979) for the kernel in Eq. (1) leads to significant deviation of calculated isotherms from the experimental in their initial part. Minimum deviations were obtained at $n = 3$. This value of exponent in the Dubinin-Astakhov equation was used in all computations. In this equation the half-width of the micropore is connected with energy constant E_0 as $x = k/E_0$, where the constant $k = 12$ kJ nm mole⁻¹ for the N_2 adsorption. The relative limit of the validity of experimental point on the adsorption isotherm, $S_1 = 0.01$, was employed in calculation of the distribution curves by the regularization method.

The mesopore size distributions in terms of their radii were calculated using the model of the cylindrical pores and the method developed by Dollimore and Heal (Dollimore and Heal, 1970).

Table 2. Basic characteristics of porous structure of PSAC active carbon.

Adsorbent calcium catalyst (%)	V_{mic} cm ³ /g	V_p cm ³ /g	$V_p - V_{mic}$ cm ³ /g	S_{mes} m ² /g	S_{mic} m ² /g	$\frac{V_{mic}}{V_p}$ %
PSAC initial	0.46	0.68	0.21	86	885	67.6
PSAC-0%	0.55	0.81	0.26	110	1038	67.9
PSAC-0.25%	0.45	0.86	0.41	225	833	52.3
PSAC-0.5%	0.42	0.98	0.56	289	764	42.8
PSAC-1.0%	0.41	1.15	0.74	380	732	35.6
PSAC-1.5%	0.40	1.36	0.96	427	784	29.4
PSAC-2.0%	0.43	1.37	0.94	424	741	31.4
PSAC-2.5%	0.44	1.43	0.99	461	733	30.8

Table 2 presents the basic characteristics of porous structure of active carbon prepared from plum stones (PSAC). From the analysis of the data in Table 2 it follows that gasification of the initial PSAC without a catalyst causes the increase of the total sorption capacity of pores, V_p , by about 19%. This increase is caused mainly by development of a microporous system in the modified adsorbent. However, the global microporosity of the adsorbent expressed by the quotient V_{mic}/V_p (%) does not change due to simultaneous small development of mesopores which is smaller than creation of micropores. It follows from the comparison of the suitable values of S_{mes} and S_{mic} (see Table 2). The S_{mic} values were calculated using the following formula (Stoeckli et al., 1989):

$$S_{mic} = 2V_{mic}/d \quad (2)$$

where d is the width of slit-like micropores expressed in nm, but V_{mic} is the total volume of micropores accessible to the adsorbate.

Appearance of the calcium catalyst on the surface of the modified adsorbent changes the direction of porous structure development during its gasification. First of all, the mesopore surface area, S_{mes} increases which is accompanied by the increase in the total sorption capacity, V_p . At the minimum amount of the catalyst used for the gasification reaction, i.e., in the range 0–0.25%, the volume V_{mic} does not change practically, but S_{mes} increases over two and half times compared with S_{mes} of the initial active carbon. Therefore microporosity of the obtained product decreases to 52.3%. The increase of catalyst amount in the range 0.5–2.5% does not cause essential changes in the sorption capacity of gasified carbon micropores. However, the increase of catalyst amount over 0.25% causes from 3

Table 3. Basic characteristics of porous structure of SAC active carbon.

Adsorbent calcium catalyst (%)	V_{mic} cm ³ /g	V_p cm ³ /g	$V_p - V_{mic}$ cm ³ /g	S_{mes} m ² /g	S_{mic} m ² /g	$\frac{V_{mic}}{V_p}$ %
SAC initial	0.46	0.74	0.28	56	1045	62.2
SAC-0%	0.53	0.82	0.29	60	1039	64.6
SAC-0.25%	0.40	1.27	0.87	318	755	31.5
SAC-0.5%	0.45	0.88	0.43	109	1000	51.1
SAC-1.0%	0.42	1.04	0.62	156	913	40.4
SAC-1.5%	0.43	1.30	0.87	164	843	33.1
SAC-2.0%	0.46	1.26	0.80	128	868	36.5
SAC-2.5%	0.54	1.55	1.01	234	806	34.8

to over 5 times increase of mesoporous system share in the global porous structure of the modified material. A systematic increase of V_p and decrease of microporosity of individual samples are observed (Table 2).

Table 3 presents the effects of initial synthetic active carbon (SAC) gasification and those of the adsorbent impregnated with the calcium catalyst. This adsorbent behaves similarly to PSAC, though a careful analysis of the data in Table 3 indicates some differences. This can be seen comparing the characteristics of the carbons impregnated with 0.25% w/w catalyst. Greater changes in the porous structure parameters are observed for the synthetic active carbon than for the PSAC adsorbent. A greater decrease of V_{mic} and increase of V_p and S_{mes} results in a significant drop in microporosity. The application of twice as large amount of the calcium catalyst, i.e., 0.5% causes even the increase of the gasified product microporosity (Table 3, SAC-0.5%). However, with the further increase of the deposited catalyst (1–2.0% w/w), the extent of microporosity decreases in comparison with the initial material, but practically within the individual samples (SAC-1.0; 1.5; 2.0 w/w catalyst) it changes slightly. The other structural parameters (V_{mic} , V_p , S_{mes} , S_{mic}) behave in a similar way. Using a large amount of the catalyst (2.5% w/w) in a gasification reaction causes great changes of porous structure parameters (V_{mic} , V_p , S_{mes}) whose values increase. Proper changes in the micro- and mesopore system develop distinctly during the catalytic gasification.

Structure of Mesopores

Figure 5 presents the distribution curves of the mesopores radii for the carbon samples included in Table 2.

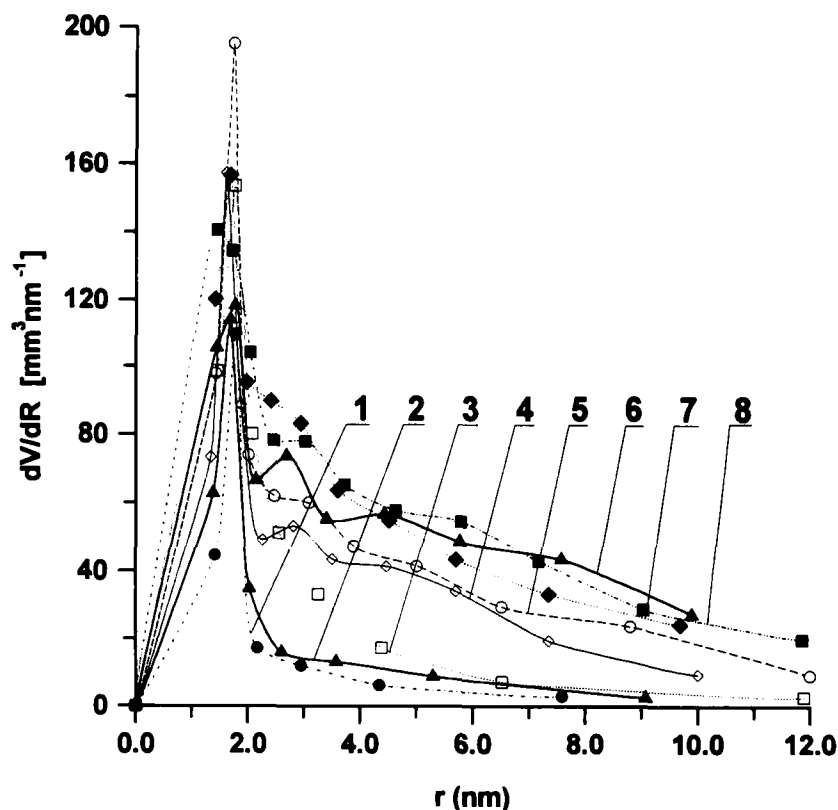


Figure 5. Mesopore size distributions for the following adsorbents: PSAC initial (1), PSAC-0% (2), PSAC-0.25% (3), PSAC-0.5% (4), PSAC-1.0% (5), PSAC-1.5% (6), PSAC-2.0% (7), PSAC-2.5% (8) (see Table 2).

As can be seen the radii of the pores corresponding to the maximum of curves for all samples have similar values ($r_{\max} \approx 2$ nm). However, individual curves differ in shape, showing different asymmetry which is connected with the geometric structure of formed mesopores.

The changes of the values of the areas below the individual curves are well correlated with the changes of S_{mes} of individual samples (Table 2). Asymmetry of differential curves (Fig. 5) indicates geometrical heterogeneity of mesopore sizes. The initial PSAC and the same adsorbent partially gasified in the absence of a catalyst possess a uniform mesoporous structure. Generally speaking, gasification of PSAC in the presence of a catalyst causes creation of additional mesopores of differentiated sizes. The larger amount of the calcium catalyst was used in the gasification reaction, the more mesopores were created and the more geometrically heterogeneous they were.

Another situation is presented by the distribution curves of mesopores radii for the initial synthetic

active carbon and the products of its gasification (Fig. 6). All samples of these adsorbents (Table 3) are characterized by smaller geometrical heterogeneity of mesopores than the corresponding samples included in Table 2. The gasification process of SAC both in the presence and absence of the catalyst causes both the increase of the amount of mesopores of a dominant radius (value r in the maximum of distribution curve) in the initial sample as well as development of new mesopores of the radius greater than the dominant one.

Structure of Micropores

Table 4 presents the parameters of microporous structure of PSAC active carbons obtained from the numerical analysis of nitrogen adsorption isotherms by means of the regularization method (Tichonov et al., 1990; Puziy et al., 1995). The calculated micropore distribution curves possess one maximum characterized by a practically constant value $x_1 = 0.32$ nm for all the

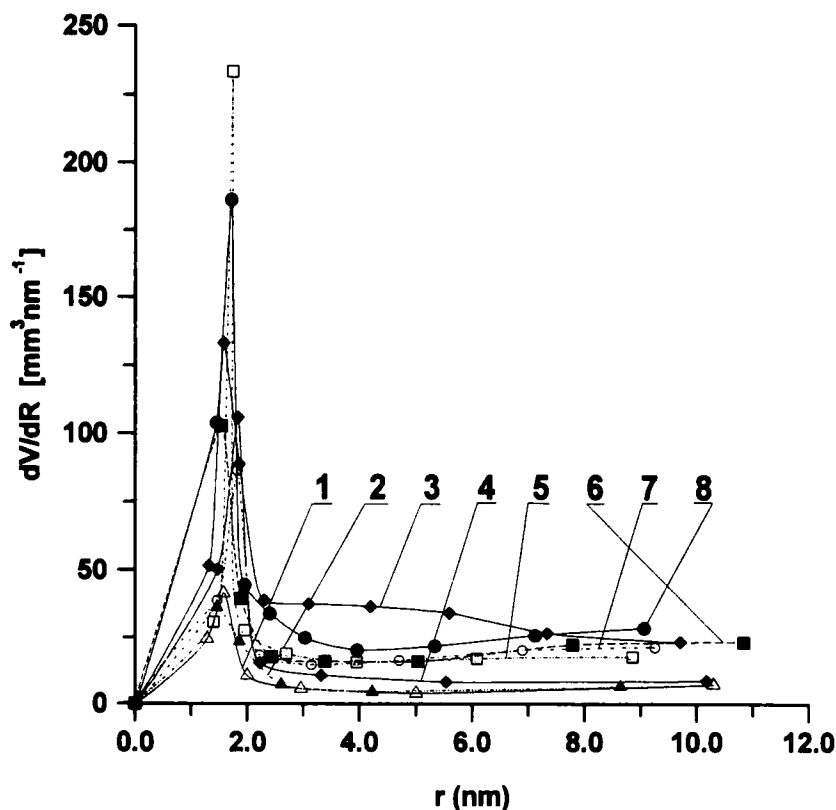


Figure 6. Mesopore size distributions for the following adsorbents: SAC initial (1), SAC-0% (2), SAC-0.25% (3), SAC-0.5% (4), SAC-1.0% (5), SAC-1.5% (6), SAC-2.0% (7), SAC-2.5% (8) (see Table 3).

studied samples. The parameter σ_x^2 characterizes structural heterogeneity of micropores and shows the scatter of the size x . As follows from the analysis of the values of this parameter presented in Table 4, modification of the porous structure of the initial PSAC active carbon carried out both in the presence and absence of the catalyst causes the increase of the micropore geometrical heterogeneity (except the sample PSAC-1.0%), the evidence of which are the quantities \bar{x} which differ significantly from the corresponding quantities x_1 .

The parameters of microporous structure for the initial and modified SAC active carbons analogous to those discussed above are presented in Table 5. The analysis of these data indicates main differences in the effects of microporous structure modification compared with the PSAC adsorbent. Generally speaking, the calculated curves of pore size distribution for the SAC samples (except SAC-2.5% w/w catalyst) are characterized by a smaller scatter of x (smaller σ_x^2) and the smaller average micropore size \bar{x} . That means that gasification of SAC prepared from the porous

Table 4. Microporous structural parameters of PSAC active carbon computed by means of regularization method.

Adsorbent calcium catalyst (%)	\bar{x} nm	σ_x^2 nm ²	x_1 nm
	$S_1 = 1 \cdot 10^{-2}$		
PSAC initial	0.60	0.145	0.32
PSAC-0%	0.66	0.190	0.32
PSAC-0.25%	0.61	0.151	0.32
PSAC-0.5%	0.64	0.183	0.32
PSAC-1.0%	0.61	0.127	0.35
PSAC-1.5%	0.64	0.152	0.32
PSAC-2.0%	0.67	0.160	0.32
PSAC-2.5%	0.67	0.186	0.32

polymer in the presence of the calcium catalyst provides the samples possessing a homogeneous microporous structure. The optimal amounts of a catalyst to obtain such adsorbents are in the range 0.5–2.0% w/w (Table 2). However, for the active carbon from plum

Table 5. Microporous structural parameters of SAC active carbon computed by means of regularization method.

Adsorbent calcium catalyst (%)	\bar{x} nm	σ_x^2 nm ²	x_1 nm
	$S_1 = 1 \cdot 10^{-2}$		
SAC initial	0.44	0.069	0.32
SAC-0%	0.56	0.103	0.32
SAC-0.25%	0.56	0.105	0.33
SAC-0.5%	0.48	0.070	0.32
SAC-1.0%	0.51	0.079	0.32
SAC-1.5%	0.57	0.079	0.35
SAC-2.0%	0.54	0.060	0.35
SAC-2.5%	0.77	0.252	0.32

stones (PSAC) this amount equals to 1.0% w/w of the catalyst.

Conclusions

The final porous structure of the carbon adsorbent depends on the initial material used for production of active carbons. Effectiveness of porous structure changes in the studied active carbons depends on carbon matter reactivity. Active carbons produced from vegetable materials are well gasified. In the crystallographically heterogeneous structure of such carbons, besides disordered structures, more or less ordered graphite structures are found (Jankowska et al., 1991; Wigmans, 1986; Rodriguez-Reinoso, 1986).

Active carbon gasification reactions are of a topochemical character. Therefore morphology of gasified carbon grains plays an important part in their porosity creation. Disordered structures are most active in the activation process and they undergo gasification as the first. The modified active carbon becomes "enriched" in graphite-like phases which are less reactive (Leboda et al., 1993). Morphology of the SAC adsorbent studied by us is more homogeneous which results from the controlled and more explicitly determined chemical mechanism of preparation of the initial raw material, i.e., porous polymer used for synthetic carbon production than in the case of carbonization of carbons prepared using agriculture by-products. Owing to such homogeneous morphology of synthetic active carbon, more homogeneous geometric structures of micro- and mesopores were obtained than in the case of carbon from plum stones.

Application in the gasification reaction of small amounts (up to 2.5% w/w) of a calcium catalyst made it possible to develop the mesoporous system in both types of active carbons and to increase pore sorption volume as well as to decrease microporosity. Catalytic gasification of synthetic active carbon (SAC) in the presence of calcium catalyst gives smaller changes of S_{mes} , V_p and microporosity compared with the active carbon obtained from plum stones (PSAC); however, modified carbon samples possess more homogeneous micro- and mesoporous structure than the samples of gasified carbon from plum stones. The differences in the porous structure modification of the active carbons studied result probably from their distinct original structure which is more homogeneous in the case of the synthetic active carbon. Another important factor, determining these differences, can be different topography of the calcium catalyst on the surface of both modified carbons. This results from the fact that despite the approximate quantities of the parameters $S_{BET}V_p$, and \bar{r} (Table 1) both initial carbons differ in micro- and mesoporous structure parameters significantly (Tables 4, 5 and also curve 1 and Figs. 5 and 6).

Considering the advantages of synthetic active carbons like hardness, controlled porosity and spherical shape of grains, further studies of such adsorbents are advisable.

Nomenclature

d	width of slit-like micropore
$F(x)$	distribution function of the half-width
p	vapor pressure of sorbate
p/p_s	relative pressure
PSAC	Plum Stone Active Carbon
\bar{r}	average pore radius, nm
S_1	relative limit of the validity of experimental point on the adsorption isotherm in the computations by means of regularization method
SAC	Synthetic Active Carbon
S_{BET}	specific surface area calculated by means of BET method, m ² /g
S_{mes}	mesopore surface area, m ² /g
S_{mic}	micropore surface area, m ² /g
T	absolute temperature, K
V_{mes}	sorption capacity of mesopores, cm ³ /g
V_{mic}	sorption capacity of micropores, cm ³ /g
V_p	sorption capacity of pores, cm ³ /g
w/w	weight in weight concentration

x	half-width of slit-like micropore, nm
x_1	maximum of half-width of micropore slit, nm
\bar{x}	average half-width of slit-like micropore, nm
x_{\min}, x_{\max}	integration limits of the x

Greek Letters

σ_x^2	variance of average half-width of slit-like micropore, nm ²
θ	local relative filling of micropores
Θ_{mi}	total relative filling of micropores

References

- Belyakov, N.A., *Enterosorption*, Center of the Sorption Technologies, Sankt Petersburg, 1991.
- Canon, F.S., V.L. Snoeyink, R.G. Lee, and G. Dagois, "Reaction Mechanism of Calcium-Catalyzed Thermal Regeneration on Spent Granular Activated Carbon," *Carbon*, **32**, 1285–1301 (1994).
- Capelle, A. and F. de Voors (Eds.), *Activated Carbon ... a Fascinating Material*, Amersfort, The Netherlands, 1983.
- Cazarola-Amorós, D., A. Linares-Solano, C. Salinas-Martínez de Lecea, and F. Kapteijn, "Assessment of the CO₂-Carbon Gasification Catalyzed by Calcium. A Transient Isotopic Study," *Carbon*, **32**, 423–430 (1994).
- Cazarola-Amorós, D., A. Linares-Solano, C. Salinas-Martínez de Lecea, H. Yamashita, T. Kyotani, and A. Tomita, "XAFS and Thermogravimetry Study of the Sintering of Calcium Supported on carbon," *Energy and Fuels*, **7**, 139–145 (1993).
- Czechowski, F., R. Lebeda, and A. Łodyga, Polish Patent No. 288161, (1993).
- Dollimore, D. and G.R. Heal, "Pore-Size Distribution in Typical Adsorbent Systems," *J. Colloid Interf. Sci.*, **33**, 508–519 (1970).
- Dubinin, M.M., "Microporous Structures of Carbonaceous Adsorbents," in *Characterizations of Porous Solids*, S.J. Gregg, K.S.W. Sing, and H.F.S. Stoeckli (Eds.), Society of Chemical Industry, London, 1979.
- Gregg S.J. and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, Tokyo, Toronto, 1982.
- Iley, M., H. Marsh, and F. Rodríguez-Reinoso, "The Adsorptive Properties of Carbonised Olive Stones," *Carbon*, **11**, 633–638 (1973).
- Jankowska, H., A. Świątkowski, and J. Choma, *Active Carbon*, Ellis Harwood, Chichester, Warsaw, 1991.
- Jaroniec, M. and E. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam, 1988.
- Kartel, N.T., A.M. Puziy, and V.V. Strelko, "Porous Structure of Synthetic Active Carbons," in *Characterization of Porous Solids II*, F. Rodríguez-Reinoso (Ed.), pp. 439–447, Elsevier, Amsterdam, 1991.
- Lebeda, R. and A. Łodyga, "Studies on the Application of Polish Commercial Active Carbons in Chromatography. Preparation and Properties of Adsorbent for Separation of Low-Boiling Compounds," *Chem. Anal. (Warsaw)*, **36**, 103–110 (1991).
- Lebeda, R. and A. Dąbrowski, "Complex Carbon-Mineral Adsorbents: Preparation, Surface, Properties and Their Modification," in *Adsorption on New and Modified Inorganic Sorbents*, A. Dąbrowski and V.A. Tertykh (Eds.), pp. 115–146, Elsevier, Amsterdam, 1996.
- Lebeda, R., W. Grzegorzczak, A. Łodyga, and A. Dąbrowski, "Effect of Catalytic Gasification of Active Carbon from Plum Stones on its Mesoporous Structure," *Adv. Sci. and Technol.*, **10**, 221–239 (1993).
- Lebeda, R., A. Gierak, and F. Czechowski, "Zastosowanie Krajobych Adsorbentów Węglowych w Analizie Zanieczyszczeń Wody," [in Polish], *Ochrona Środowiska (Wrocław)*, **1/2**, 19–22 (1990).
- Linares-Solano, A., "Textural Characterization of Porous Carbons by Physical Adsorption of Gases," in *Carbon and Coal Gasification*, pp. 137–178, NATO ASI Series, Series E: Applied Sciences-No. 105, Martinus Nijhoff Publishers, 1986.
- Linares-Solano, A., M. Almela-Alarcón, and C. Salinas-Martínez de Lecea, "CO₂ Chemisorption to Characterize Calcium Catalysts in Carbon Gasification Reactions," *J. Catalysis*, **125**, 401–410 (1990).
- Lopez-Gonzalez, de D., J.F. Martínez-Vichez, and F. Rodríguez-Reinoso, "Preparation and Characterization of Active Carbons from Olive Stones," *Carbon*, **18**, 413–418 (1980).
- Lussier, M.G., C. Shull, and D.J. Miller, "Activated Carbon from Cherry Stones," *Carbon*, **32**, 1493–1498 (1994).
- Marsh, H., M. Iley, J. Berger, and T. Siemienińska, "The Adsorptive Properties of Activated Plum Stone," *Carbon*, **13**, 103–109 (1975).
- Matisova, E. and S. Skrabakova, "Carbon Sorbents and Their Utilization for the Preconcentration of Organic Pollutants in Environmental Samples," *J. Chromatogr.*, **A**, **707**, 145–179 (1995).
- Matisova, E., M. Strakova, S. Skrabakova, and J. Novak, "A Novel Porous Carbon and Its Perspectives for the Solid Phase Extraction of Volatile Organic Compounds," *Fresenius J. Anal. Chem.*, **352**, 660–663 (1995).
- Mattson, J.S. and H.B. Mark, Jr., *Activated Carbon, Surface Chemistry and Adsorption from Solution*, Marcel Dekker Inc., New York, 1971.
- Pérez-Florindo, A., D. Cazarola-Amorós, and A. Linares-Solano, "CO₂-Carbon Gasification Catalyzed by Alkaline-Earths: Comparative Study of the Metal-Carbon Interaction and of the Specific Activity," *Carbon*, **31**, 493–500 (1993).
- Puziy, A.M., "Heterogeneity of Synthetic Active Carbons," *Langmuir*, **11**, 543–546 (1995).
- Puziy, A.M., R. Lebeda, V.I. Bogillo, V.P. Shkilev, and A. Łodyga, "Porous Structure and Adsorption Properties of Synthetic Active Carbons," *Adv. Sci. and Technology*, **12**, 267–277 (1995).
- Rodríguez-Reinoso, F., "Preparation and Characterization of Activated Carbons," in *Carbon and Coal Gasification*, pp. 601–642, NATO ASI Series, Series E: Applied Sciences-No. 105, Martinus Nijhoff Publishers, 1986.
- Rudziński, W. and D.H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, London, 1992.
- Rudziński, W., A. Gierak, R. Lebeda and A. Dąbrowski, "Studies of Properties of Complex Carbon-Silica Adsorbents Used in Sorption-Desorption Processes (Solid-Phase Extraction)," *Fresenius J. Anal. Chem.*, **352**, 667 (1995).
- Rundling, J., *Organic Solvent Vapor Analysis of Workplace Air*, Royal Institut of Technology, Stockholm, 1987.
- Setoyama, N.M., R. Rukie, T. Kasu, T. Suzuki, and K. Kaneko, "Surface Characterization of Microporous Solids with the Adsorption and Small Angle X-ray Scattering," *Langmuir*, **9**, 2612 (1993).

- Sing, K.S.W., D.H. Everett, R.A.W. Haul, and L. Moscou, "Reporting Physisorption Properties Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity," *Pure Appl. Chem.*, **57**, 603 (1985).
- Stoeckli, H.F., I. Ballerini, and S. de Bernardini, "On the Evolution of Micropore Widths and Areas in the Course of Activation," *Carbon*, **27**, 501–502 (1989).
- Tichonov, A.N., V. Goucharsky, V.V. Stepanov, and A.G. Jagolz, *Numerical Methods of Solving the Ill-Posed Problems*, Nauka, Moscow, 1990.
- Unger, K.K., "Porous Carbon Packings for Liquid Chromatography," *Anal. Chem.*, **55**, 361A–372A (1983).
- Visser, J.P.R., F.P.M. Merex, S.M.A. Bouwens, V.H.J. de Beer, and R. Prins, "Carbon-Covered Alumina as a Support for Sulfide Catalyst," *J. Catal.*, **114**, 291–302 (1988).
- Wigmans, T., "Fundamentals and Practical Implications of Activated Carbon Production by Partial Gasification of Carbonaceous Materials," in *Carbon and Coal Gasification*, J.L. Figureiro (Ed.), pp. 559–599, NATO ASI Series., Series E: Applied Sciences-No. 105, Martinus Nijhoff Publishers, 1986.