THE EFFECT OF THERMAL MODIFICATION ON THE DEVELOPMENT OF CARBON MATERIAL MICROPOROUS STRUCTURE

B.K. Ostafiychuk, I.M. Budzulyak, N.Ya. Ivanichok, B.I. Rachiy, R.P. Lisovsky

Abstract: A research is done to characterize the microporous structure of outgoing and thermally modified (673 K, 180 min) plant-extracted carbon material. The porous system characteristics are worked out by different methods on low temperature (77K) N_2 adsorption-desorption based isotherm. It is stated that thermal modification contributes to the enlargement of specific surface (from 361 m^2/g to 673 m^2/g), an increase in total pore volume (from 0,166 cm^3/g to 0,477 cm^3/g) and an increase in micropore volume (from 0,127 cm^3/g to 0,173 cm^3/g). Most effectively thermal modification is apt to form nanopores with diameters of 0,75; 1,25 and 4 nm.

Keywords: porous carbon material, thermal modification, low temperature porometry, structural and adsorptive characteristics.

1. INTRODUCTION

Porous carbon material (PCM) possesses unique physical and mechanical properties and is widely used – from nanoelectronics and supercapacitors to composite material [26, 5]. Providing carbon material with necessary electrical and physical properties, apart from those which are defining for the material-based electrochemical capacitors, is carried out both in the course of its obtaining and by way of chemical and thermal treatment of carbonized material [4]. Traditional raw materials for the production of quality PCM is hardwood, fruit seeds, coconut peel, coal, and resins with high- content coal and natural micro- and mesoporosity [10].

From the point of view of its practical use the conspicuous characteristics PCM are internal pore volume, the specific surface and volume of micropores. The simplest and most reliable method of measuring these characteristics is gas sorption. Gas sorption measurement is easy to install and use.

The goal of figuring out the specifics of application of N_2 adsorption- desorption to characteristics of PCM porous structure is to assess the impact of its thermal characteristic versions to the carbon material, obtained from apricot pits; and to analyze applicability of different methods of calculation for the characteristics of carbon material porous structure.

2. EXPERIMENT AND DISCUSSION

The object of research is the process of forming carbon material porous structure in the course of its obtaining and further thermal modification. The subject of research is the PCM, obtained by

hydrothermal carbonization of apricot pits-extracted material under the pressure of water vapour $(12-15) \cdot 10^5$ Pa. The temperature range of carbonization activation totalled 873-1273 K. Thermal activation is carried out 3 h at temperature 673 ± 3 K that leads to obtaining the samples, the symbols being listed in Tab. 1.

Temperature carbonating activation, K	Samples after carbonation activation	Samples after thermal activation at 673 K
873	CA- 1	CTA - 1
973	CA - 2	CTA - 2
1073	CA - 3	CTA - 3
1173	CA - 4	CTA - 4
1273	CA - 5	CTA - 5

Tab. 1. Marking of PCM samples

A microscopic research is done by means of the e- microscope Zeiss Supra 40 VP (Carl Zeiss Group Germany) with a field cathode (Field Emission), e-microscope GEMINI and a fully oil-free vacuum system with the mode of operation on low vacuum (VP).

Determination of PCM structural and adsorptive characteristic is carried out by means of Ni sorption at temperature T = 77 K on the automatic sorptometer Quantachrome Autosorb (Nova 2200 e). The samples have been degased at 453 K during 20 hours.

The following methods are employed to calculate the parameters of CA and CTA porous structure : 1) proposed by Brunauer, Emmett, Teller [3] BET method in boxes, with a limited range of relative pressure P/P_0 = 0.05-0.035;   2) the method of Langmuir (method L) [13], which is based on the assumption that the adsorbent saturation limit corresponds to the formation of a monolayer of nitrogen, and 3) the method of BJH, proposed by Barret, Joyner and Halenda [1], and 4) the method of DH, the proposed Dollimore and Heal [7]; 5) t-method [6] and its modification MR method [21] to determine the micropore size distribution; 6) α_s-method [11]; 7) the method of DR- method [8]; 8) HK-method proposed by Horvath and Kawazoe, which calculates the size of the region of small micropores relative pressure adsorption isotherm and is designed for materials, which is dominated by slit-like pores [12]; 9) method SF, developed by Saito and Foley for cylindrical micropores [27]; 10) method DFT (Density functional Theory), which is based on density functional theory [9].

Here are the parameters that characterize carbon material porous structure: S (m^2/g) – specific surface volume; V_Σ (cm^3/g) – the total volume calculated by the volume of adsorbed nitrogen at. $P/P_0 > 0,995$; the volume of micropores V_m (cm^3/g) is calculated by a t-method, external surface area S_{ext} (m^2/g) and micropore surface S_m (m^2/g) by the formula $S_m = S_{BET} - S_{ext}$; d (nm) – an average diameter or width of the pores.

In the study of PCM structural properties important is the shape and size of micro- and nanopores formed in the material as a result of technological operations in the course of their obtaining and further treatment. In Fig. 1 is a SEM-image of BK-3 carbon material surface at different scales. When considering the PCM surface (Fig. 1) one can see surface microgaps, round and oval transport pores, which in most cases are filled with fragments of coal fractures. The entire surface observes white inclusions which are the main source of metal, oxygen , and the remnants of burnt cinder [24].
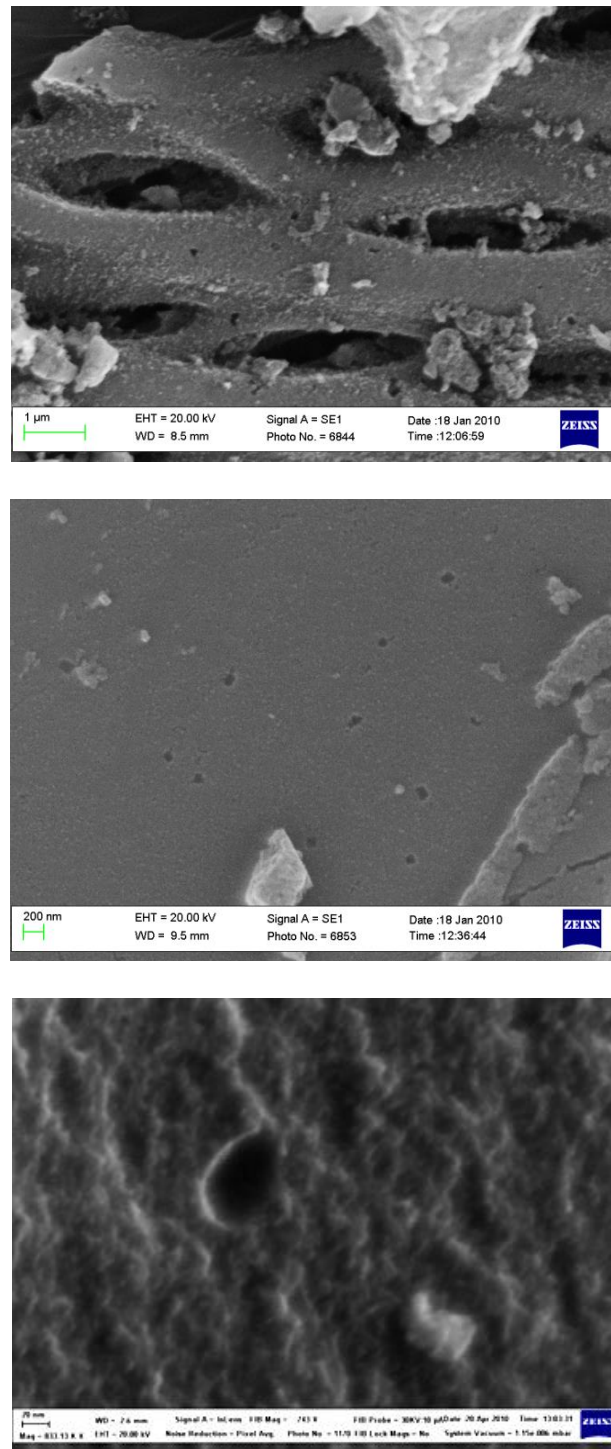
Fig. 1. The microstructure of the surface of carbonated PCM

For uncovering internal pores and making new ones thermal activation of carbonized carbon material is done at temperature (673 K, 180 min), followed by the opening of porous structure (Fig. 2) which has been invisible before treatment in contrast to the outgoing material surface with separate outputs of pores. The reason for this structure is that organic substance of the material surface is burned in the course of obtaining carbon from a plant-extracted material, but the remnants rise along the channels (pores) from grains onto the surface under vapour pressure. Thus, thermal activation makes it possible to cleanse coal surface from organic and adsorbed remnants that result in new pores and an increase of porosity.
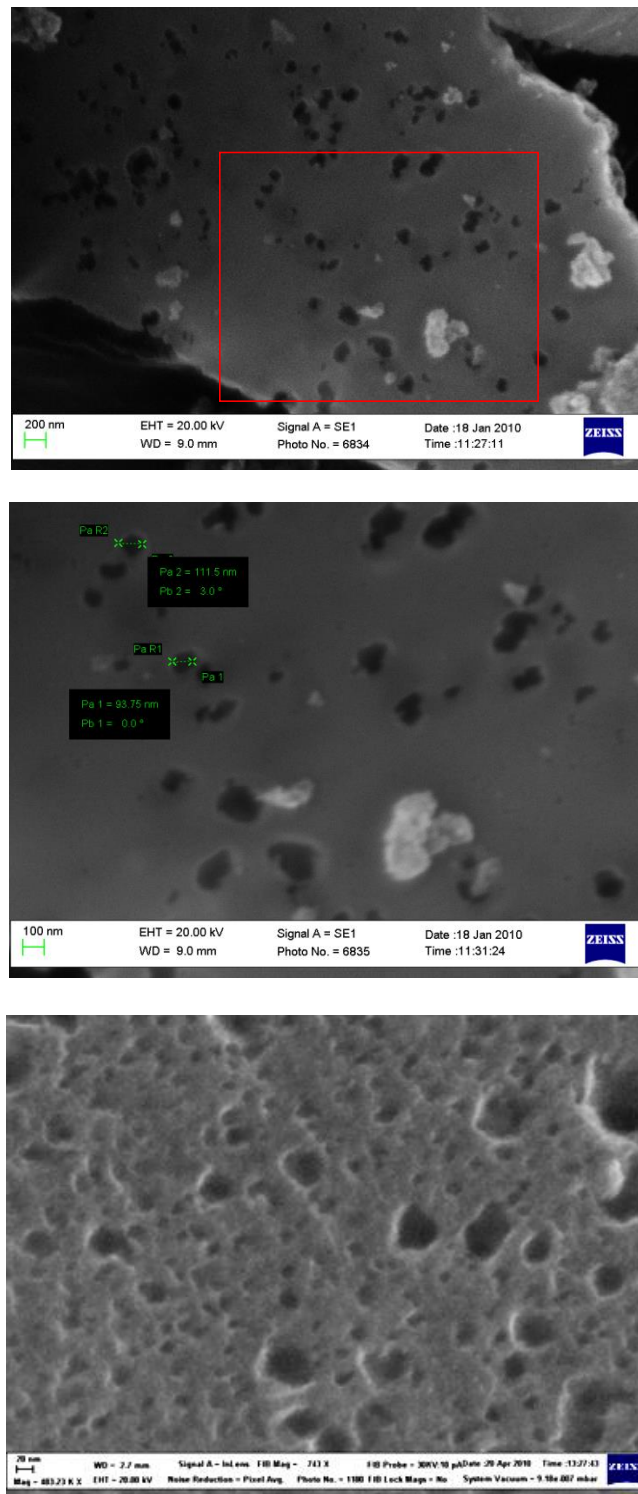
Fig. 2. SEM-surface image of CTA-3 samples

Fig. 3 shows typical isotherms of N_2 adsorption for CA-3 and CTA-3 samples which belong to the isotherms of type II and can be observed in polymolecular adsorption [20]. It is hysteresis that is observed in CTA-3 samples (type H4 by IUPAC classification [11]) which is usually associated with capillary condensation in mesopores. The point of branching adsorption and desorption curve is observed at $p/p_0 \approx 0.42$, where p and p_0 – vapour pressure of N_2 adsorbate and pressure of its saturated pore at 77 K, respectively. Hysteresis as wells as another phenomenon can be observed in CA-3 samples which is manifested as the discrepancy between the branches of adsorption and desorption in a relatively low pressure and is called the hysteresis of low pressure. There are several possible reasons

for its manifestation: swelling of spatial highly molecular frame of adsorbent, permanent retention of adsorbent molecules in pores, the size of which is close to adsorbate molecules; permanent chemical interaction of adsorbate and adsorbent [11].
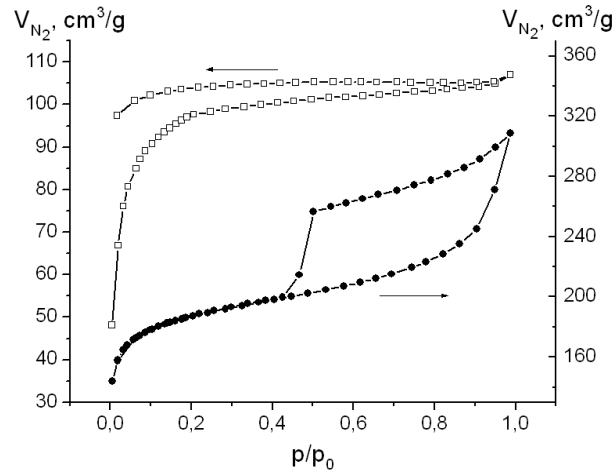

Fig. 3. Isotherms of N₂ sorption (77 K) for CA-3 (–□–) and CTA-3 (–●–)

As the isotherms of carbonized PCM adsorption -desorption samples (samples CA) are similar, they are not shown in this work.

Fig. 4 shows the isotherms of carbon material N_2 adsorption after its thermal activation (samples CTA). For all the samples the isotherms belong to those that are characterized by the presence of hysteresis loops. The analysis of the isotherms makes it possible to trace the impact of thermal activation on the development of activated carbon porous structure.
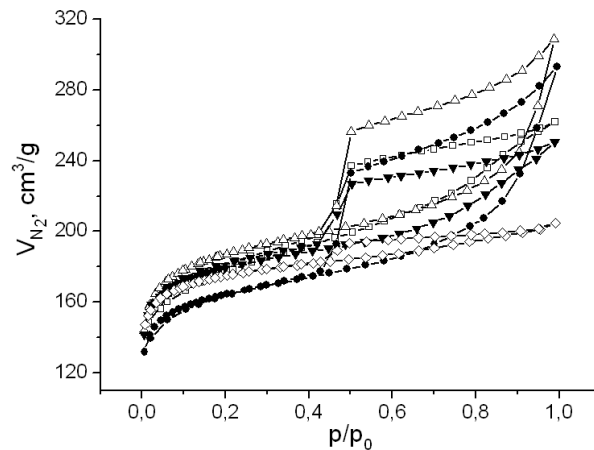

Fig. 4. A N₂ sorption isotherm (77) for thermally modified
PCM: –□– CTA-1; –●– CTA-2; – Δ – CTA-3; –▼– CTA-4; –◊– CTA-5

As a quantitative measure of hysteresis (ΔV_H) the difference of N_2 adsorbed volume is taken from isotherms of desorption (V_{de}) and adsorption (V_{ad}) at $p/p_0 = 0.7$: $\Delta V_H = V_{de}-V_{ad}$. Estimates of low pressure hysteresis (ΔV_{LPH}) held at $p/p_0 = 0.2$: $\Delta V_{LPH} = V_{de}-V_{ad}$.

In Fig. 5 is the dependence of hysteresis temperature on PCM temperature obtained. It can be seen in the Figure that carbonized coal material structural properties responsible for hysteresis phenomenon all over the range of temperatures, and in the interval 973-1073 K do not substantially change ($\Delta V_{LPH} \approx 6$ cm³/g, $\Delta V_H \approx 3$ cm³/g). Hysteresis in low pressure for CTA samples is actually not manifested, and values of ΔV_{LPH} are to close to nil. Hysteresis in high relative pressure ($p/p_0 = 0.42$-1.0) is manifested for all the samples, but value ΔV_H for CTA samples is lower than for CA samples.

Besides, the ΔV_H parameter for CTA samples rapidly changes with a temperature rise maximum at ~973 K that testifies to the maximum development of mesopores at this temperature (Tab. 2).

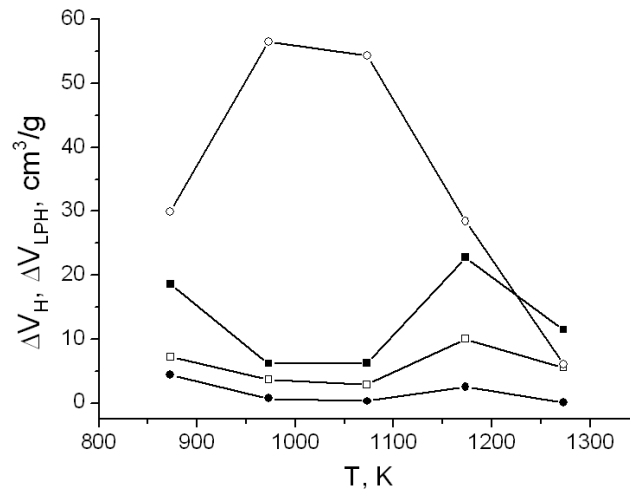*Fig. 5. Dependence of hysteresis effect for PCM on obtained temperature:*
ΔV_{LPH} for CA (–■–); ΔV_H for CA (–□–); ΔV_{LPH} for CTA (–●–); ΔV_H for CTA (–○–)

As is seen in Tab.2, with temperature rise up to 1073 K the specific surface of S_{BET} increases both for CA samples and CTA ones and reaches 673 m²/g (*CTA-3*). At this value of specific surface of micropores S_{micro} equals 406 m²/g and their relative V_{micro}/V_Σ content makes up 36% of the total volume of pores. For thermally activated material obtained at temperatures 1173-1273 K, the specific surface of S_{BET} decreases to 626 m²/g.

Parameters	Sample	Temperature, K				
		873 *(1)*	973 *(2)*	1073 *(3)*	1173 *(4)*	1273 *(5)*
S_{BET}, m²/g	CA	337	342	361	206	46
	CTA	535	592	673	646	626
S_{micro}, m²/g	CA	274	271	314	131	31
	CTA	307	327	406	460	535
S_{meso}, m²/g	CA	83	42	43	75	15
	CTA	228	265	261	186	91
V_Σ, cm³/g	CA	0.186	0.149	0.166	0.122	0.033
	CTA	0.405	0.454	0.477	0.388	0.317
V_{micro}, cm³/g	CA	0.114	0.112	0.127	0.056	0.016
	CTA	0.176	0.137	0.173	0.195	0.227
V_{micro}/V_Σ, %	CA	61	75	77	46	49
	CTA	44	30	36	50	71

Tab. 2. Parameters of carbon material porous structure

In Fig. 6 is the distribution of pores by the size for CTA samples calculated in the therms of desorption with the BJH method. The distribution curves show that for all the thermo modified samples the major share in the total volume of pores is made up of pores with the radius 1.8-2.0 nm.
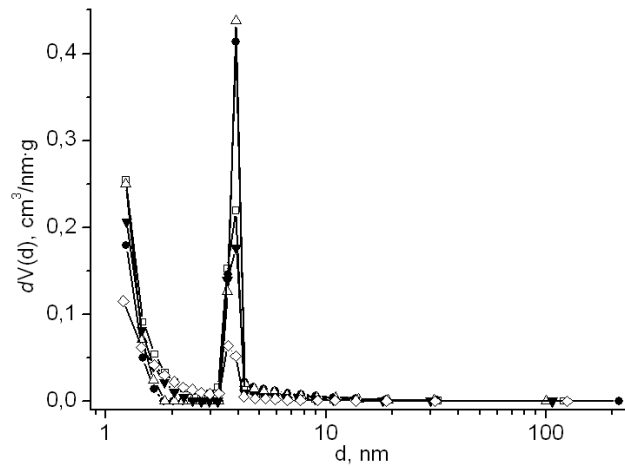
Fig. 6. The distribution of pore volume by the size for thermally activated PCM: –□– CTA-1; –●– CTA-2; – ∆ – CTA-3; –▼ – CTA-4; –◊– CTA-5

For these studies, to compare the parameters of porous structure and their influence on the specific characteristics of PCM have been selected samples of CA-3 and CTA-3.

The outgoing experimental basis for all theoretical calculations and interpretation is a sorption isotherm (Fig. 3) of samples of a given mass, i.e. the dependence of the number of evenly sorbed by the sample N_2 (under normal conditions) on the relative pressure of gaseous N_2 p/p_0. The characteristics of carbon material porous structure are defined by these isotherms, the values of which are calculated through different methods (Tab. 3).

Parameter	PCM	Method of calculation									
		BET	L	BJH	DH	t–method	α_s–method	DR	DA	HK	SF
S, m²/g	CA-3	361	442	–	–	–	–	–	–	–	–
	CTA-3	673	829	–	–	–	–	–	–	–	–
S_{micro}, m²/g	CA-3	–	–	–	–	318	–	452	–	–	–
	CTA-3	–	–	–	–	413	–	835	–	–	–
S_{ext}, m²/g	CA-3	–	–	1.98	2.16	43.1	–	–	–	–	–
	CTA-3	–	–	232	237	261	–	–	–	–	–
V_Σ, cm³/g	CA-3	0.166	–	0.005	0.005	–	–	–	–	–	–
	CTA-3	0.477	–	0.286	0.279	–	–	–	–	–	–
V_{micro}, cm³/g	CA-3	–	–	–	–	0.127	0.130	0.161	0.162	0.148	0.148
	CTA-3	–	–	–	–	0.173	0.188	0.297	0.322	0.284	0.285
V_{micro}/V_Σ, %	CA-3	–	–	–	–	77	78	97	98	89	89
	CTA-3	–	–	–	–	36	39	62	68	60	60
d, nm	CA-3	1.84	–	3.22	3.22	–	–	2.55	1.74	0.37	0.45
	CTA-3	2.84	–	3.89	3.89	–	–	1.86	1.22	0.37	0.45

Tab. 3. The parameters of porous structure in CA and CTA samples, calculated by different methods

The specific surface area of S calculated by means of multipoint BET in the linear schedule of dependence *1/[W(p₀/p)-1]* on *p₀/p* in the range of an adsorption isotherm for the relationship *p₀/p* within 0.05-0.35 equals 361 m²/g and 673 m²/g for CA-3 and CTA-3 samples, respectively. In CTA-3 sample the magnitude of the surface area and the total volume of pores is about 3 times greater than the corresponding values CTA-3 (0.477 cm³/g and 0.166 cm³/g, calculated under *p/p₀ = 0.99* in assumption

that all the pores have been filled with liquid adsorbate). From the data obtained one can conclude that the porous structure of CTA-3 is developed better than that of CA-3.

The researches [14, 19, 22, 23] read that it is incorrect to apply the BET method for the study of microporous samples as its use is limited while defining the specific surface of pores of the sample under study, micropores are taken out of account. This is why in commercial devices (Autosorb-type and other analogues) L-, DR-, t-, and α_s-methods are widely used in the investigation of micropore-content objects, in particular, in defining the surface area of microporous material the L-method is applied which in contrast to the BET method gives for CA-3 and CTA-3 samples higher values of the specific area of surface (~440 m^2/g and 820 m^2/g , respectively).

To assess the volume of micropores in the presence of meso-, and macropores the t-method is oftener applied, in which the outgoing sorption isotherm is rebuilt as the function of a new variable t. The latter value is called the statistical thickness of the adsorption film and is determined by the following expression: $t = (W/W_{mono})\sigma$, where W – amount of adsorbed vapor, depending on the relative pressure p/p_0; W_{mono} – the capacity of a monolayer on the surface of the sample; σ –monomolecular thickness adsorption film (for nitrogen at T = 77 K is assumed to be 0.354 nm [11]). Calculated like this values for t. are a good match even to the samples different by the chemical nature of the surface [17, 18]. For carbon adsorbents, first of all, soot, the authors [18] recommend to make use of an equation for the statistical thickness of adsorbed film proposed in ASTM D-6556-01 [28] standards.

For microporous samples a dependence plot of the volume of gas absorbed in normal conditions on t is a straight line which cuts off the segment of the vertical axis for calculation of micropore volume V_{micro}. According to the slope of the line calculated value of the external specific surface area of the sample S_{ext} (Fig. 7).

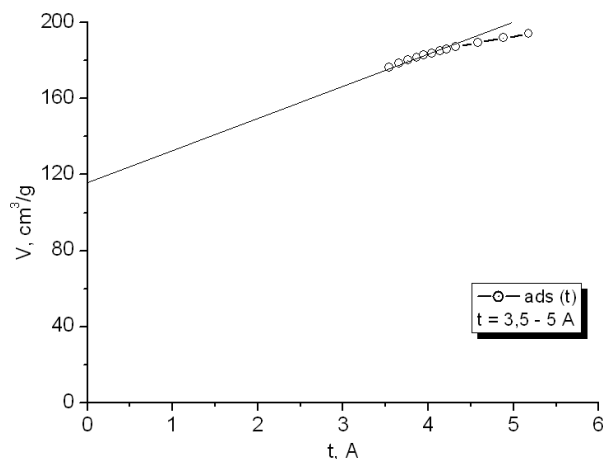*Fig. 7. t-method for N_2 adsorption in CTA-3 sample*

The volume filling of micropores is completely neglected in the theory of t-method, as it is assumed that it happens at considerably smaller relative pressures of gaseous N_2 on condition the statistical thickness of adsorptive layer remains small. To check the correctness of applying the t-method, the data obtained are compared with the results received from α_s -method, and the DR-method which is based on the theory of volume filling of micropores [8].

The comparison of different methods for porous structure parameters is carried out for thermally activated carbon CTA-3 sample. Defined by BET-, DR-, DFT- and t-methods the specific surface values are pretty close and are in the interval S = 609-674 m^2/g, which means these methods can be applied for defining the surface area of plant-extracted activated carbon.

There is a good for microporous materials co-ordination of the parameters of standard t-method with BET-method that has also been observed for CTA-3 sample under study, for one of the known ways to define external surfaces in microporous samples lies in the initial filling of some substance with the following definition of the sample specific surface by BET-method [11]. Quite different are the results obtained after correction of sorption isotherms on the volume of micropores calvulated according to DR-method. These isotherms by the shape markedly deviate from classical, and BET is not

a straight line in the coordinates; and the values of specific surface differ considerably (Tab. 3) from the values of external specific surface defined by the t-method or BET-method.

The values of specific area defined by BJH- and DH methods are smaller because a micropore area is not counted in calculation and the methods are used in defining the volume of meso- and macropores with their distribution by the size.

A similar pattern is observed when determining the total volume of pores and the volume of micropores. BJH-, and DH methods give a lower value V_Σ (0.286-0.279 cm^3/g), than the value of the total pore volume calculated at $p/p_0 = 0.99$ (Tab. 3). Methods HK and SF give a close value $V_{micro} \approx 0.28$ cm^3/g though the former provides the presence in the material of Z-shaped pores, and the SF-method cylindrical. This value is close to the volume of micropores defined by DR- and DA-methods (Tab. 3). The proportion of micropores defined by DR-, DA-, HK- and SF-methods is 60-68% of the total volume of pores V_Σ. The ratio V_{micro}/V_Σ for the value V_{micro} obtained by t- and α_s-method give lower results. It should be noted that the listed methods are often applied for defining the parameters of activated carbon materials porous system and carbon nanotubes [15, 16].

The obtained difference in micropore volumes for one and the same sample by t-method (α_s-method) and DR (DA)-method is probably that in addition to micropores, mesopores also contribute to the defined volume by DR-method increasing the obtained value V_{micro}. A similar pattern is described in the works by the authors [2, 15, 25] who conduct a comparison of micropore volumes obtained by different methods for several samples of activated coal. For most coal volume value of micropores defined by t- and α_s-method exceeds the corresponding magnitudes calculated by the DR-method. These samples contain micropores but do not have mesopores. At the same time there is a reverse ratio for PCM with both micropores and mesopores: the volume of micropores, defined by the DR-method, is larger than the values calculated by t- and α_s-method and are observed for our PCM samples. This can be explained by the fact that the DR-method takes into account both micropores and mesopores.

The average diameter of pores for CTA-samples defined by BJH and DH methods is the same and equal to 3.89 nm, though the diameter obtained by the DR-method has substantially less value (1.86 nm). The HK method leads to low values (d = 0.3 nm) which by metric order approach to the defects of three-dimensional structure of solids, vacancies, in particular. The SF method gives average values of the diameter which are smaller than those for ultra micropores (d ≤ 1.4 nm). However, it is unlikely that the porous system of our samples has only represented those pores.

Thermal activation significantly changes the dependence character of the total volume of pores on the diameter of pores (Fig. 8) calculated by the isotherms of desorption through the BJH method which is usually used for estimation of pore distribution by the size [16]. Thermal activation of the original raw material contributes to the increase in the volume of pores of all sizes and develops the pore diameter in the vicinity of 4 nm.
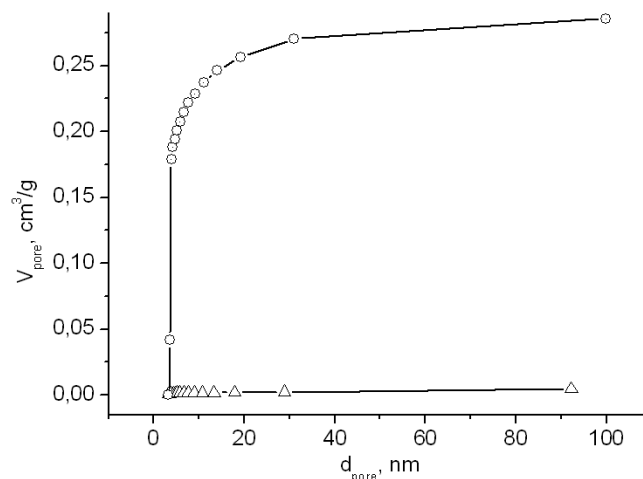

Fig. 8. Dependence of pore volume on their diameter
(BJH method) for samples: 1 - outgoing (CA-3); 2 - thermally activated (CTA-3)

The investigation of micropore distribution by the size was carried according to MP- and DFT methods. One can conclude from the MP method of distribution that thermal modification initiates formation of diameter pores < 2 nm with maximum in the vicinity of 0.75 nm (Fig. 9).
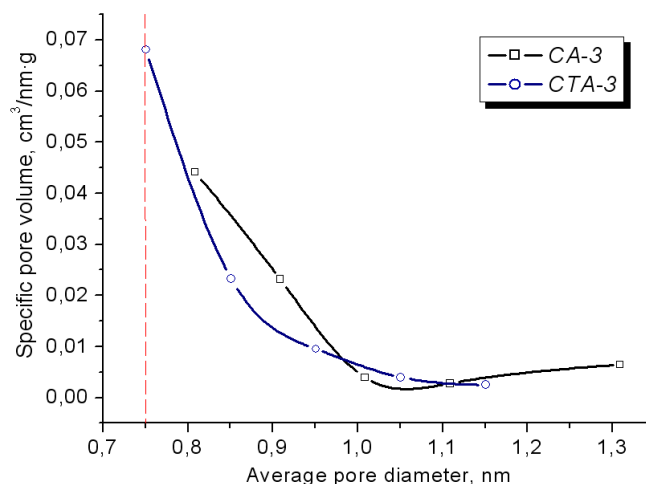

Fig. 9. Distribution of micropores by the size (MP method)

Classical theories such as DR and DA and half empirical approaches, HK and SF in particular, do not fully describe the filling of micropores and narrow mesopores. This leads to an understatement of the true size and error in calculation.A modern approach to the description of adsorption isotherms and pore distribution by the size for microporous materials is based on quantum-mechanical calculation. The essense of the approach is to construct theoretical isotherms for different pores of microporous adsorbent-adsorbate. Calculation is carried out according to the Density Functional Theory (DFT). The DFT method was used to get the distribution of PCM micro- and mesopores. The method takes into account the fundamental molecular parameters that characterize the interaction of gas-gas and gas-solid in the adsorptive system. The results obtained are presented as a set of bar charts in Fig. 10.

The DFT method makes it possible to determine the specific surface , the total pore volume, and their distribution both by the size and by the volume (Tab. 4). The obtained data (Fig. 10, Tab. 4) show that for CA-3 sample the contribution to the specific surface area and total pore volume is made only by micropores. Thermal activation of the CA-3 sample contributes to the development of micropore diameter ~ 1.25 nm and pore diameter ~ 4 nm.
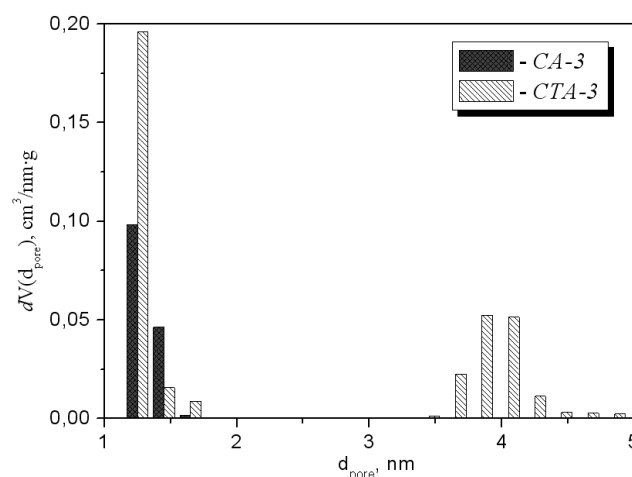

Fig. 10. Distribution of pores by the size (DFT method)

Parameter	CA-3	CTA-3
Specific surface area, m²/g	295	609
Total pore volume, cm³/g	0.146	0.426
Micropore volume (d < 2 nm), cm³/g	0.146	0.221
Surface area of micropores (d < 2 nm), m²/g	295	522
Average pore diameter, nm	1.29	3.97

Tab. 4. Structural and adsorptive characteristics of carbon material (DFT method)

Obtained by the methods MP (Fig. 9) and DFT (Fig. 10) dependencies for CA-3 and CTA-3 samples are quantitatively different due to differences in the physical models assigned at the core of these methods. But qualitatively both methods confirm that thermal activation contributes to the development of pores of a certain size.

3. CONCLUSIONS

Thus the temperature of synthesis is an important control of porosity that allows you to receive PCM with adjustable porous structure. Hydrothermal carbonization of apricot pits and further thermal activation of origin raw material forms a high specific surface and porous structure of carbon material. The optimal temperature synthesis of PCM from the enlarged area of micro- and mesopores is 1073 K. Under the conditions of thermal versions of origin raw material enlarges the specific surface area and porous structure of activated carbon, so do the diameter pores up to 5 nm. The most noticeable effect is observed for pores with diameters of 0.75, 1.25 and 4 nm.

To determine the specific surface of plant-extracted porous carbon material the BET-, t- and α_s - methods are most correct. The DR method gives inflated values of the specific surface of micropores as compared to the t- and α_s - methods. A possible reason for it that the DR method takes into account both micropores and mesopores.

REFERENCES

[1] Barret E.P., Joyner L.C., Halenda P.P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.*, **73** (1) (1951), 373-380. doi: 10.1021/ja01145a126

[2] Bauvan L.A., Tsyba N.N., Tamarkina Y.V., Kucharenko V.A. The effect of potassium hydroxide to the porous system of solid thermolysis products of lignite. *Chemistry and Chemical Engineering. Donetsk: Donetsk National Technical University*, **152** (2009), 99-105. (in Ukrainian)

[3] Brunauer S., Emmett P.H., Teller E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, **60** (2) (1938), 309-319. doi: 10.1021/ja01269a023

[4] Burchell T.D. *Carbon Materials for Advanced Technologies*. Pergamon, Amsterdam, 1999.

[5] Butyrin G.M. *Highly porous materials*. Chemistry, Moscow, 1976. (in Russian)

[6] de Boer J.H., Lippens B.C., Lippens B.G., Broekhoff J.C.P., van der Heuvel A., Osinga Th. J. The t-curve of multimolecular N₂-adsorption. *J. Colloid Interface Sci.*, **21** (4) (1966), 405-414.

[7] Dollimore D., Heal G.R. Pore size distribution in a system considered as an ordered packing of spherical particles. *Journal of Applied Chemistry of the USSR*, **14** (1) (1964), 109.

[8] Dubinin M.M., Radushkevich L.V. On the equation of the characteristic curve for the active carbon. *Reports of the USSR*, **55** (4) (1947), 331-334. (in Russian)

[9] Evans R., Marconi U.M.B., Tarazona P.J. Capillary condensation and adsorption in cylindrical and slit-like pores. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, **82** (1986), 1763-1787.

[10] Fenelonov V.B. *Porous carbon*. Institute of Catalysis SB RAS, Novosibirsk, 1995. (in Russian)

[11] Greg S., Sing K. *Adsorption, Surface Adsorption, Surface, Porosity*. Mir, Moscow, 1984. (in Russian)

[12] Horvath G., Kawazoe K. Method for the calculation of effective pore size distribution in molecular sieve carbon. *J. Chem. Eng. Jpn*., **16** (5) (1983), 470-475. doi: 10.1252/jcej.16.470

[13] Jacobs P., Tompkins F. *Chemistry of the solid state*. Foreign Literature Publishing House, Moscow, 1961. (in Russian)

[14] Karnaukhov A.P. *Supported metal catalysts converting carbon hydrogens*. Novosibirsk, Institute of Catalysis, 1978. (in Russian)

[15] Knerelman E.I., Zvereva G.I., Kislov M.B. Characterization of the products on the basis of single-walled carbon nanotubes by nitrogen adsorption. *Russian Nanotechnology*, **5** (11) (2010), 80-87. (in Russian)

[16] Kurosaki F., Koyanaka H., Tsujimoto M., Imamura Y. Shape-controlled multi-porous carbon with hierarchical micro-meso-macro pores synthesized by flash heating of wood biomass. *Carbon*, **46** (6) (2008), 850–856. doi: 10.1016/j.carbon.2008.02.014

[17] Lippens B.C., de Boer J. H. Studies on pore systems in catalysts: V. The t method. *Journal of Catalysis*, **4** (3) (1965), 319-323. doi: 10.1016/0021-9517(65)90307-6

[18] Lowell S., Shields J. E., Thomas M. A., Thommes M. *Characterization of porous solids and powders: surface area, pore size, and density*. Springer, Dordrecht, Netherlands, 2006.

[19] Lundquist E., Parker G., Rohm Jr. Engineered carbons for ultracapacitor applications. Proceedings of the 14-th International Seminar on Double Layer Capacitors and Similar Energy Storage Devices. Deerfield Beach, Florida (USA) 2004, 14, 69–83.

[20] Marsh H. *Activated Carbon*. Amsterdam, Eslevier, 2006.

[21] Mikhail R.S., Brunauer S., Bodor E.E. Investigations of a complete pore structure analysis: i. Analysis of micropores. *J. Colloid Interface Sci*., **26** (1) (1968), 45-53. doi: 10.1016/0021-9797(68)90270-1

[22] Neymark I.E. *Adsorption and Porosity*. Nauka, Moscow, 1976. (in Russian)

[23] NOVA operating manual, «Quantachrome Instruments», 2010.

[24] Rachiy B.I. Morphology and electrochemical properties of thermally modified nanoporous carbon: published summary of the dissertation on competition of a scientific degree of Candidate of Physical and Mathematical Sciences: specialty 01.04.18 "Physics and Surface Chemistry", Ivano-Frankivsk, 2010.

[25] Rodrigues-Reinoso F. An overview of methods for the characterization of activated carbons. *Pure Appl. Chem.*, **81** (11) (1989), 1859-1866. doi: 10.1351/pac198961111859

[26] Saito R., Dresselhaus M.S., Dresselhaus G. *Physical properties of carbon nanotubes*. World Scientific, New-York, 1998.

[27] Saito A., Foley H.C. Curvature and parametric sensitivity in models for adsorption in micropores. *American Institute of Chemical Engineers Journal*, **37** (1991), 429-436. doi: 10.1002/aic.690370312

[28] Standard Test Method for Carbon Black – Total and external surface area by nitrogen adsorption. D-6556-01. ASTM International, West Conshohocken, Pennsylvania.

Address: B.K. Ostafiychuk, I.M. Budzulyak, N.Ya. Ivanichok, B.I. Rachiy, R.P. Lisovsky: Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano-Frankivsk, 76025, Ukraine.

E-mail: bo@pu.if.ua; ivan-budzulyak@rambler.ru; nashata@ukr.net; bogdan_rachiy@ukr.net; lesrom@rambler.ru.

_____

Проведено порівняння характеристик мікропористої структури вихідного та термічно модифікованого (673 K, 180 хв) вуглецевого матеріалу із сировини рослинного походження. Дані характеристики пористої системи розраховані різними методами на підставі ізотерм низькотемпературної (77 K) адсорбції-десорбції азоту. Встановлено, що термічна модифікація сприяє розвитку питомої поверхні (з 361 м²/г до 673 м²/г), збільшенню загального об'єму пор (з 0,166 см³/г до 0,477 см³/г) і об'єму мікропор (з 0,127 см³/г до 0,173 см³/г). Найбільш ефективно термічна модифікація сприяє утворенню нанопор діаметром 0,75; 1,25 і 4 нм.

Ключові слова: пористий вуглецевий матеріал, термічна модифікація, низькотемпературна порометрія, структурно-адсорбційні характеристики.