

## Fractal Structure of Nanoporous Carbon Obtained by Hydrothermal Carbonization of Plant Raw Materials

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The fractal structure of porous carbon materials (PCMs) obtained by hydrothermal carbonization of plant raw materials in the temperature range of 600 ÷ 1100 °C is investigated using the low-temperature porometry method. It is set that materials with a developed microporous structure and a surface fractal dimension of 2.58 are formed at carbonization temperatures of 600 ÷ 800 °C. At higher carbonization temperatures, the value of the fractal dimension of the surface decreases to 2.17, which indicates the formation of an almost smooth surface due to the intensive removal of carbon atoms from the surface layers of the material particles, a decrease in the number of micropores with their transition to mesopores, the combination of small carbon clusters in larger and the formation of microparticles of non-porous carbon material.

**Keywords:** Porous carbon, Low-temperature porometry, Specific surface, Fractal structure.

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### 1. INTRODUCTION

The newest method of fractal analysis in recent decades has become a powerful tool for describing the geometric and structural properties of fractal surfaces and porous structures [1-3]. The fractal dimension is a number that characterizes the given properties of a substance. As a rule, there are two traditional definitions for describing the fractality of a porous material, i.e., the fractal dimension of pores  $D_v$  [4, 5] and the fractal dimension of the surface  $D_s$  [6, 7].

The first fractal dimension indicates an irregularity in the distribution of pores. A larger value of the fractal dimension of pores indicates a narrower size distribution of pores, the behavior of which is described by a power law. The value of the fractal dimension of pores 2 and 3 corresponds, respectively, to a porous material that has a homogeneous pore size distribution and to a material that contains pores of almost the same size. On the other hand, the second fractal dimension characterizes the irregularity of the pore surface, i.e., the pore surface is more ununiform and rough when the value of the surface fractal dimension is larger. A material with a perfectly flat surface has a value of surface fractal dimension 2, and the value of surface fractal dimension 3 corresponds to a very rough pore surface.

Since the geometry and structure of the pore surface are closely related to the surface area, which is electroactive to the electrolyte and plays a key role in increasing the capacity of materials used as electrodes for supercapacitors [8-10] or lithium power sources [11, 12], then there is a necessity for a more detailed study of the structural and morphological properties of such materials and analysis of the effect of various technological factors on them. These factors include the production temperature, heating rate, various types of treatment and activation [13-16]. One of the simplest and most reliable methods that can be used for the specified purposes is the method of gas sorption, for

example, nitrogen [17]. When using this method, adsorbate molecules interact only with the surface of the material accessible to them. As a result, it is possible to obtain information about the presence and the number of open pores in the material and the fractal dimension of their surface.

Therefore, the purpose of this work is to study the fractal structure of hydrothermally carbonized PCMs using the method of low-temperature porometry and establish the peculiarities of its change with increasing carbonization temperature.

### 2. EXPERIMENTAL DETAILS

The initial raw material for carbonization was mechanically crushed apricot kernels, which were placed in an autoclave with distilled water. The autoclave was placed in the oven, where the PCM was obtained for 1 h at a constant temperature. Hydrothermal carbonization of raw materials was carried out in the temperature range  $t = 600-1100^\circ\text{C}$  with a step of 100 °C at a water vapor pressure of  $(6-8) \cdot 10^5$  Pa. The material obtained after the carbonization process was subjected to mechanical grinding twice.

The sorption isotherms of PCMs have been determined using the nitrogen adsorption-desorption isotherms recorded at 77.4 K using a Quantachrome Autosorb Nova 2200e adsorption analyzer. Before measurements, the samples were heated at 180 °C for 24 h for degassing. The specific surface area  $S_{BET}$  was calculated according to the standard Brunauer-Emmett-Teller (BET) method. The specific surface of micropores  $S_{micro}$  was evaluated using the  $t$ -method, the surface of mesopores  $S_{meso}$  was calculated as the difference between the total surface of pores and micropores. The total pore volume  $V$  was evaluated from the nitrogen adsorption at  $p/p_0 \approx 0.99$ , where  $p$  and  $p_0$  denote the equilibrium and saturation pressures of nitrogen at 77.4 K, respectively [17].

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### 3. RESULTS AND DISCUSSION

According to the data of low-temperature porometry for PCMs obtained at the indicated temperatures of hydrothermal carbonization, nitrogen adsorption/desorption isotherms are qualitatively similar (Fig. 1). A detailed analysis, based on a quantitative comparison of the amount of nitrogen adsorbed by the samples and the appearance of the adsorption curves, gives grounds for asserting that the adsorption isotherms for PCMs obtained in the carbonization temperature range of  $600 \div 900$  °C belong to type I according to the IUPAC classification [17]. Isotherms of this type are characteristic of microporous solids that have a relatively small external surface (zeolites, activated carbons, metal organic lattices). At higher carbonation temperatures, adsorption isotherms of PCMs belong to type II, which is typical for non-porous adsorbents.

All isotherms are also characterized by the divergence of the adsorption and desorption curves, especially in the low-pressure region, which is called low-pressure hysteresis. According to [17], the main reason for this behavior may be the presence of long and narrow pores with narrow necks close in size to the nitrogen molecules. Other reasons that can also cause the appearance of low-pressure hysteresis are the irreversible chemical interaction of the adsorbate with the adsorbent and the swelling of the spatial high-molecular framework of the adsorbent.

Using the data of low-temperature porometry, it is possible to establish what changes the fractal structure of PCMs undergoes in the process of carbonization of plant raw materials. In particular, the surface fractal dimension  $D_s$  of PCMs can be determined by rearranging the nitrogen adsorption isotherm according to the equation [18]:

$$\ln(V/V_{mono}) = const + A \left[ \ln(\ln(p_0/p)) \right], \quad (1)$$

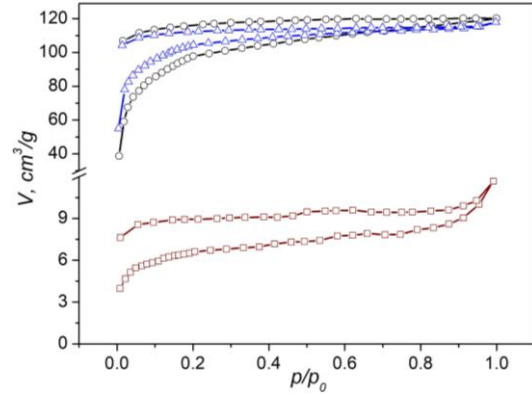
where  $V$  is the volume of adsorbed gas,  $V_{mono}$  is the volume of adsorbed gas that covers the surface of the sample with a monolayer;  $A$  is a degree indicator that depends on  $D_s$ ,  $p_0/p$  is the relative pressure. The volume of the monolayer coating  $V_{mono}$  was calculated according to the BET method [17]:

$$\frac{1}{W \left[ \left( \frac{p_0}{p} \right) - 1 \right]} = \frac{1}{W_{mono} \cdot C} + \frac{C-1}{W_{mono} \cdot C} \cdot \left( \frac{p}{p_0} \right), \quad (2)$$

where  $W$  is the mass of gas adsorbed at the relative pressure  $p/p_0$ ,  $W_{mono}$  is the mass of the adsorbed substance forming a monolayer that covers the entire surface,  $C$  is the BET constant, which characterizes the adsorption energy in the first adsorption layer and is an indicator of the magnitude of the adsorbent/adsorbate interaction.

At the initial stage of nitrogen adsorption, Van der Waals forces prevail during the interaction of PCM and gas, while surface tension forces at the liquid-gas interface can be neglected. In this case, the relationship between parameters  $A$  and  $D_s$  is given by the equality:

$$A = \frac{D_s - 3}{3}. \quad (3)$$



**Fig. 1** – Nitrogen sorption isotherms for PCMs obtained at different carbonization temperatures: 600 °C (-○-), 800 °C (-Δ-), 1100 °C (-□-)

During further adsorption, the forces of surface tension between the gas and the liquid begin to prevail, so the following ratio is fulfilled:

$$A = D_s - 3. \quad (4)$$

It follows from equations (3) and (4) that the surface fractal dimension of PCMs can be determined based on the equation required for a particular case. The limit that determines the dominance of surface tension forces or Van der Waals ones is given by the equation [19]:

$$\alpha = 3(1 + A) - 2. \quad (5)$$

Surface tension forces prevail when  $\alpha < 0$ . If  $\alpha \geq 0$ , then Van der Waals forces prevail.

Presentation of adsorption isotherms of the studied materials in coordinates  $\ln(V/V_{mono}) = f\{\ln[\ln(p_0/p)]\}$  allows to determine the value of the constant  $A$  according to the slope of the curve. Then, depending on  $\alpha$  parameter, one can estimate the surface fractal dimension  $D_s$  of PCMs according to equations (3) and (4). For all PCMs, there is a linear relationship between  $\ln(V/V_{mono})$  and  $\ln[\ln(p_0/p)]$  (Fig. 2), which indicates the large-scale properties of the surface of the materials.

Analysis of dependences (Fig. 2) indicates the presence of at least 2-3 linear sections with different slopes due to differences in scale properties. However, the more adsorption layers are formed on the surface of the material, the smoother the interface between the adsorbent and the adsorbate becomes. So, in this case, the surface fractal dimension  $D_s$  no longer describes the surface of the solid/gas interface but characterizes adsorbed agglomerates of molecules. Therefore, for the correct determination of the surface fractal dimension  $D_s$  of PCMs, the first linear section was chosen.

According to the calculations, parameter  $\alpha < 0$ , which gives grounds to use formula (3) to determine  $D_s$ . An increase in the temperature of hydrothermal carbonization of plant raw materials leads to a decrease in the fractal dimension of the surface to values close to 2, which indicates the formation of an almost smooth surface (Table 1).

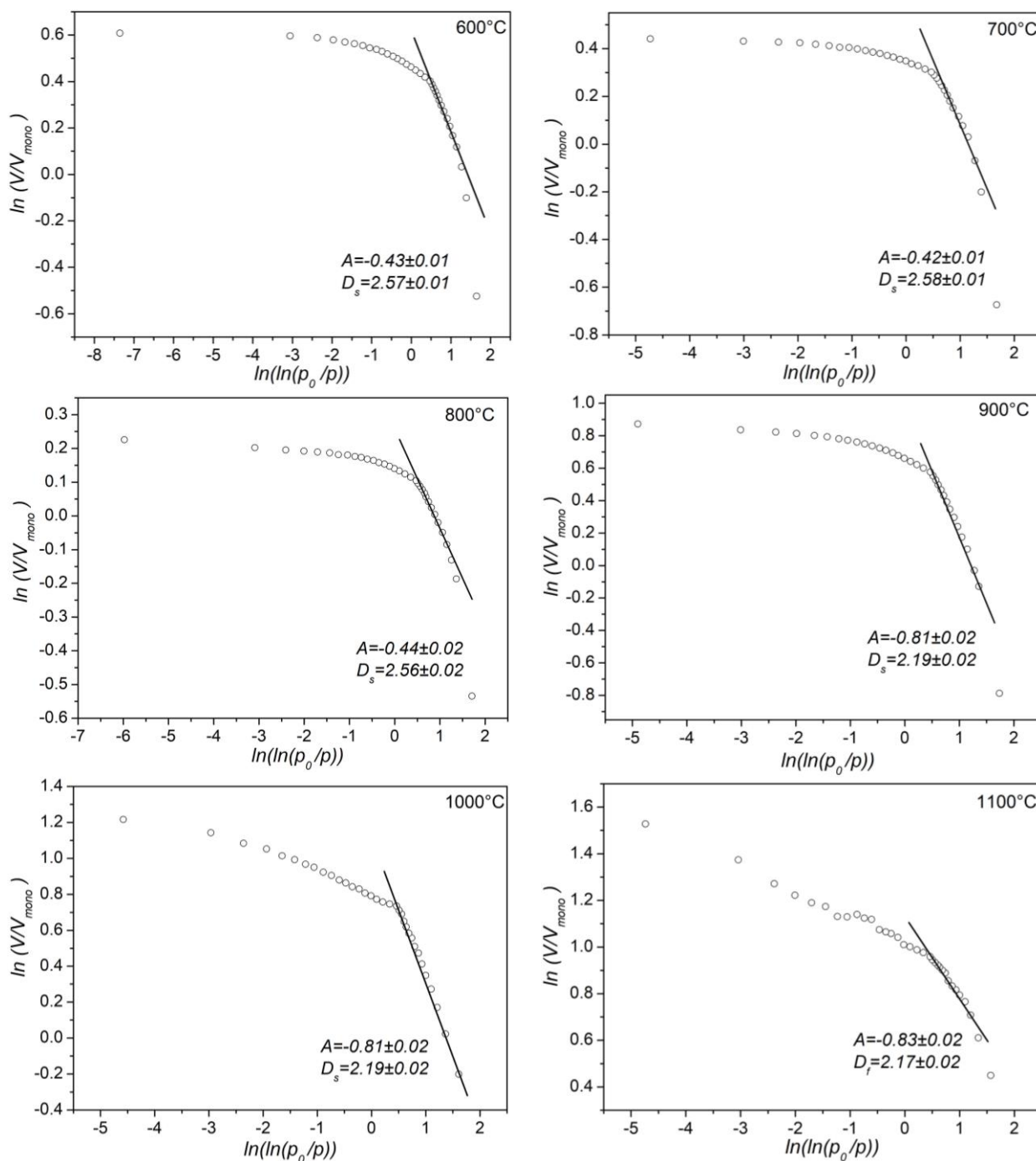


Fig. 2 – Dependences  $\ln(V/V_{mono}) = f\{\ln[\ln(p_0/p)]\}$  rebuilt on the basis of nitrogen adsorption isotherms of PCMs obtained at different carbonization temperatures

Table 1 – Parameters of the porous structure of carbon materials

$t$ , °C	$S_{BET}$ , m <sup>2</sup> /g	$S_{micro}$ , m <sup>2</sup> /g	$S_{meso}$ , m <sup>2</sup> /g	$V$ , cm <sup>3</sup> /g	$A$	$\alpha$	$D_s$
600	357	282	75	0.186	$-0.43 \pm 0.01$	-0.29	$2.57 \pm 0.01$
700	374	338	36	0.174	$-0.42 \pm 0.01$	-0.26	$2.58 \pm 0.01$
800	382	338	44	0.182	$-0.42 \pm 0.01$	-0.26	$2.58 \pm 0.01$
900	265	185	80	0.151	$-0.81 \pm 0.02$	-1.43	$2.19 \pm 0.02$
1000	45	34	11	0.031	$-0.81 \pm 0.02$	-1.43	$2.19 \pm 0.02$
1100	12	9	3	0.011	$-0.83 \pm 0.02$	-1.49	$2.17 \pm 0.02$

Since the use of water vapor significantly increases the yield of volatile components of the raw material, the obtained result is due to the more intense extraction of carbon atoms from the near-surface layers of the carbon framework during the transition from the stage of polycondensation of aromatic molecules to the stage of the first carbonization, which is accompanied by the formation of carbon layers and the primary nuclei of graphite [20]. The removal of volatile components at the stage of cyclization, aromatization, and polycondensation leads to the formation of materials with a developed microporous structure and a weakly expressed outer surface  $S_{ext}$  (Table 1). When the carbonization temperature increases, there is a decrease in the number of micropores, their merging with the transition to mesopores, densification of the material structure due to the formation of carbon layers at higher carbonization temperatures ( $t = 1000 \div 1100^\circ\text{C}$ ), the merging of small carbon clusters into larger ones

and the formation of non-porous carbon material microparticles.

#### 4. CONCLUSIONS

The possibility of using the low-temperature porometry method for studying the fractal structure of PCMs obtained at different temperatures of hydrothermal carbonization of plant raw materials is shown. It was found that the surface fractal dimension of materials changes from 2.58 to 2.17 in the studied range of carbonization temperatures ( $600 \div 1100^\circ\text{C}$ ) due to the removal of carbon atoms from the near-surface layers of material particles, which leads to a decrease in the specific surface area of micropores, an increase in the relative content mesopores, which have a smoother surface, the gradual merging of small carbon clusters into larger ones, and the formation of microparticles of a non-porous carbon material.

#### REFERENCES

1. L.A. Browning, W. Watterson, E. Happe, S. Silva, R.A. Valenzuela, J. Smith, M.P. Dierkes, R.P. Taylor, N.O.V. Plank, C.A. Marlow, *Nanomaterials* **11**, 636 (2021).
2. H. Yue, V. Reguero, E. Senokos, A. Monreal-Bernal, B. Mas, J.P. Fernández-Blázquez, R. Marcella, J.J. Vilatel, *Carbon* **122**, 47 (2017).
3. B.K. Ostafiychuk, V.I. Mandzyuk, Yu.O. Kulyk, N.I. Nagirna, *Nanoscale Res. Lett.* **9** No 1, 160 (2014).
4. N.Ya. Ivanichok, O.M. Ivanichok, P.I. Kolkovskiy, B.I. Rachiy, S.-V.S. Sklepova, Yu.O. Kulyk, V.V. Bachuk, *Phys. Chem. Solid State* **23** No 1, 172 (2022).
5. A.P. Terzyk, P.A. Gauden, G. Rychlicki, R. Wojsz, *Coll. Surf. A* **152** No 3, 293 (1999).
6. Z.Z. Zhang, *Adv. Mater. Sci. Eng.* 1-6, 468370 (2015).
7. S.I. Pyun, C.K. Rhee, *Electrochim. Acta* **49** No 24, 4171 (2004).
8. P.R. Choi, S.-G. Kim, J.C. Jung, M.-S. Kim, *Carbon Lett.* **22**, 70 (2017).
9. V.I. Mandzyuk, I.F. Myronyuk, V.M. Sachko, I.M. Mykytyn, *Surf. Eng. Appl. Electrochem.* **56** No 1, 93 (2020).
10. N.Ya. Ivanichok, I.M. Budzuliak, M.I. Moiseienko, R.P. Lisovskiy, B.I. Rachiy, A.M. Gamarnyk, L.V. Turovska, S.A. Lisovska, *Phys. Chem. Solid State* **21** No 1, 35 (2020).
11. A. Pozio, M. Di Carli, A. Aurora, M. Falconieri, L.D. Seta, P.P. Prossini, *Nanomaterials* **12**, 1349 (2022).
12. V.I. Mandzyuk, N.I. Nagirna, R.P. Lisovskyy, *J. Nano-Electron. Phys.* **6** No 1, 01017 (2014).
13. J.E. Park, G.B. Lee, S.Y. Hwang, *J. Electrochem. Sci. Technol.* **12** No 3, 339 (2021).
14. B.I. Rachiy, B.K. Ostafiychuk, I.M. Budzulyak, N.Ya. Ivanichok, *J. Nano- Electron. Phys.* **7** No 4, 04077 (2015).
15. I.F. Myronyuk, V.I. Mandzyuk, V.M. Sachko, R.P. Lisovsky, B.I. Rachiy, *J. Nano- Electron. Phys.* **8** No 4, 04006 (2016).
16. X. Luo, S. Chen, T. Hu, Y. Chen, F. Li, *SusMat.* **1** No 2, 211 (2021).
17. S.J. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity* (Academic Press: 1982).
18. P. Pfeifer, K.-Y. Liu, *Stud. Surf. Sci. Catal.* **104**, 625 (1997).
19. I.M.K. Ismail, P. Pfeifer, *Langmuir* **10** No 5, 1532 (1994).
20. M. Inagaki, *Structure and Texture of Carbon Materials in Carbons for Electrochemical Energy Storage Systems* (Eds. by F. Beguin, E. Frackowiak) (CRC Press – Taylor and Francis Group, Boca Raton-New York: 2002).

### Фрактальна структура нанопористого вуглецю, отриманого гідротермальною карбонізацією рослинної сировини

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Методом низькотемпературної порометрії досліджено фрактальну структуру пористих вуглецевих матеріалів, отриманих гідротермальною карбонізацією рослинної сировини в діапазоні температур  $600 \div 1100^\circ\text{C}$ . Встановлено, що за температур карбонізації  $600 \div 800^\circ\text{C}$  формуються матеріали з розвиненою мікропористою структурою, поверхнева фрактальна розмірність яких становить 2,58. За вищих температур карбонізації значення фрактальної розмірності поверхні зменшується до значення 2,17, що свідчить про формування майже гладкої поверхні за рахунок інтенсивного видалення атомів карбону з приповерхневих шарів частинок матеріалу, зменшення кількості мікропор з їх переходом у мезопори, об'єднання дрібних вуглецевих кластерів в більш крупніші та формування мікрочастинок непористого вуглецевого матеріалу.

**Ключові слова:** Пористий вуглець, Низькотемпературна порометрія, Питома поверхня, Фрактальна структура.