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REGULAR ARTICLE

Structural and Morphological Properties of Nanoporous Carbon Materials Obtained from Biomass

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The present work investigated the structural and morphological properties of nanoporous carbon materials obtained from biomass, specifically waste coffee grounds, through thermochemical alkaline activation at various temperatures (400-900 °C). The influence of the temperature of chemical activation of plant raw materials on the porosity and structure of the obtained carbon materials was investigated. It is shown that the obtained carbon materials have a specific surface area of 400-1050 m^2/g and a pore volume of 0.23-0.51 cm^3/g, depending on the activation temperature. The study revealed that micropores with sizes ranging from 0.65 to 1.25 nm dominated the porous structure, particularly at higher activation temperatures.It was established that an increase in the obtaining temperature to 600 ºC leads to a decrease in the size of carbon particles, which was attributed to the partial combustion of smaller fragments. In contrast, at temperatures between 700-900 °C, the size of carbon fragments increased from 6.5 nm to 8.5 nm, likely due to the thermal decomposition of lignin and hemicellulose components in the biomass. Furthermore, at temperatures above 800 °C, an increase in the content of sp3 carbon was noted, indicating the transformation of the carbon structure. The results demonstrated that the optimal activation temperature range for obtaining highly porous carbon materials with well-developed surface areas was 800-900 °C. This temperature range facilitated the formation of a microporous structure with a significant fraction of pores below 1.25 nm in diameter. By adjusting the activation temperature, it is possible to obtain carbon materials with controlled morphology and optimized porosity, making them suitable for energy storage applications.

Keywords: Nanoporous carbon material, Thermochemical activation, Specific surface area, Pore size distribution.

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1. INTRODUCTION

The depletion of traditional energy sources and the growing electricity demand are pushing scientists to develop new energy storage technologies. Electrochemical capacitors (EC), as one of the advanced energy storage technologies, promise to solve the problem of instability of renewable energy sources and provide high power density for modern electronic devices [1]. Carbon materials such as graphene, activated carbon, and carbon nanotubes are widely used to make EC electrodes. Nanoporous carbon materials (NCM) obtained from biomass are of particular interest due to the availability and environmental friendliness of the raw materials. The process of chemical activation using active agents that increase porosity allows the creation of materials with a developed porous structure that provides high capacity and effective adsorption of electrolyte ions [2-5]. Pore structure [4-7], electrical conductivity [7], electrolyte wettability [8], electrode material mass [9], binder amount [10], and electrolyte amount [6] are important factors for improving the electrochemical performance of carbon electrodes and ECs in general. Given this, systematic studies of the relationship between the properties mentioned above of the carbon material and the electrochemical characteristics of ECs made on their basis are important.

This work aims to develop a technology for obtaining nanoporous carbon materials from coffee waste and to study the effect of the synthesis conditions on its structural properties.

2. MATERIALS AND METHODS OF RESEARCH

A series of nanoporous carbon materials with different structural and morphological characteristics were obtained from waste coffee grounds by thermochemical activation. The process of obtaining NCM included several stages [11]: 1) drying of raw materials at a temperature of 65-85 °C for 48 hours; 2) mixing dried bio-raw material with an activating agent (potassium

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hydroxide) and distilled water in a ratio of 1:0.5:1; 3) heating and heat treatment for 30 minutes at temperatures of 400-900 °C (in steps of 100 °C); 4) washing to neutral pH and drying. Materials with different porosity characteristics were obtained by changing the activation temperature. The obtained NCM samples were conventionally designated as S400 ÷ S900 (for example, S500 is NCM activated at 500 °C).

The specific surface area of NCM was determined by the Brunauer-Emmet-Teller (BET) method from the analysis of N_2 adsorption isotherms obtained using the Quantachrome Autosorb system (version 2200e) at a temperature of – 196 °C. The *t*-method (proposed by de Boer and Lippens) was used to estimate micropores' specific surface area and volume. All samples were degassed in a vacuum at a temperature of 180 °C for 18 h before measurement. In addition, the distribution of pores by size was analyzed using the density functional theory (DFT) method.

Raman spectra of NCM were obtained on a Horiba Jobin-Yvon T-64000 triple spectrometer. The studied carbon materials were irradiated with a laser (Ar^+/Kr^+) with a wavelength of 488 nm. The power of the laser beam varied from 0.25 to 25 mW. The radiation was recorded in the backscattering geometry. The accuracy of determining the frequency position of the phonon line was less than 0.15 cm^{-1}. Radiation focusing was performed using an Olympus BX41 confocal microscope using a 100× objective lens with a numerical aperture of 0.09.

3. RESULTS AND DISCUSSION

The electrochemical characteristics of ECs largely depend on the structural and morphological parameters of the electrode materials used in their manufacture [12]. With an unchanged ratio of potassium hydroxide and raw materials in the production of carbon material, the temperature of thermochemical activation is an important factor that affects the morphology and porous structure of the obtained material.

Nitrogen adsorption/desorption isotherms made it possible to calculate the parameters of the porous structure of carbon materials: the specific surface area according to the BET (S_{BET}) and DFT (S_{DFT}) methods, the specific surface area of meso- (S_{meso}) and micropores (S_{micro}), the total volume of pores (V_{total}) and the volume of micropores (V_{micro}) (Table 1). It can be seen from the table that the activation temperature in the range of 800-900 °C is optimal for obtaining a carbon material with a highly developed surface area. The change in the microporous structure of NCM due to thermochemical activation at different temperatures was studied using the DFT method (Fig. 1).

In the DFT method, fundamental molecular parameters characterizing the gas-gas (gas-liquid) and gas-solid interaction in the adsorption system are used for calculation, assuming that all pores have a slit-like shape.

Following the genesis of the porous structure of carbon materials as a result of different activation temperatures, it can be noted that the microporous structure begins to form at temperatures of 500 °C (Fig. 1, S500) since the material obtained at 400 °C (Fig. 1, S400)

Table 1 – Parameters of the porous structure of nanoporous carbon materials

Sample	S_{BET}, m^2/g	S_{DFT}, m^2/g	S_{meso}, m^2/g	S_{micro}, m^2/g	V_{total}, cm^3/g	V_{micro}, cm^3/g
S400	31	23	30	–	0.092	–
S500	172	193	44	80	0.161	0.038
S600	374	309	27	319	0.228	0.132
S700	446	478	27	402	0.237	0.162
S800	703	632	22	671	0.331	0.272
S900	1056	1170	45	996	0.507	0.398

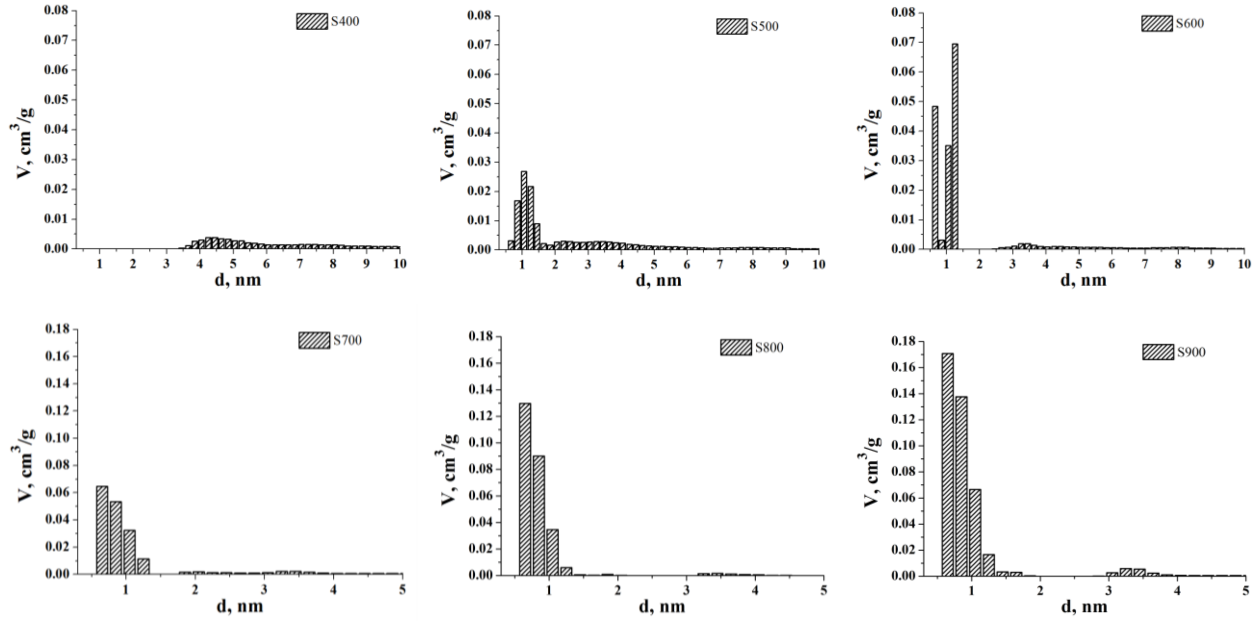

Fig. 1 – The distribution of the pore volume by size is simulated by the DFT method for NCM obtained at different temperatures of thermochemical activation

has a mesoporous structure with a surface area of 23 m^2/g (Table 1, DFT method). The mesopore volume is also minimal (Fig. 1, S400). In materials obtained at temperatures of 500-700 °C, micropores with a size of 0.65-1.45 nm are formed (Fig. 1). At higher temperatures, there is an increase in the number of pores with a range of 0.65-1.25 nm, which make up to 80 % of the total volume of pores.

Establishing the nature of the carbon material and studying the intramolecular interaction was carried out by the Raman spectroscopy method. This method makes it possible to detect minimal changes in the structure of the material caused by different activation temperatures, as it is highly sensitive to symmetric non-covalent bonds with no or small dipole moment. This criterion is for C-C bonds. First-order Raman spectra for thermochemically activated carbon materials in the frequency range 500-1900 cm^{-1} are presented in Fig. 2.

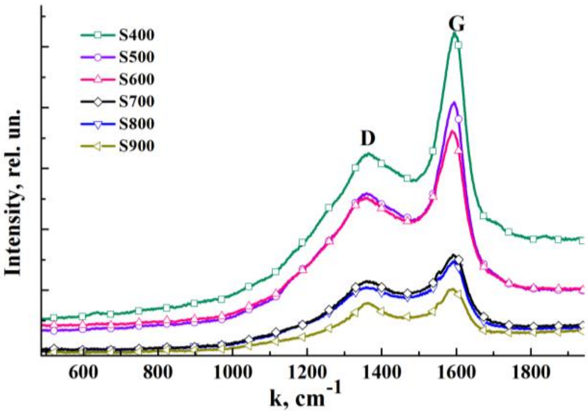

Fig. 2 – Raman spectra for NCM obtained at different temperatures of thermochemical activation

The Raman spectra (Fig. 2) are typical for disordered graphite and they contain two rather sharp modes. *G* peak is for graphite domains, doubly degenerate deformation vibration of the hexagonal ring around 1580-1600 cm^{-1}, and *D* peak is for disordered carbon (due to the final crystal size, the A$_{1g}$ mode of the lattice becomes Raman active) around 1350 cm^{-1}. The phonon modes present in the spectra are usually attributed to phonons of the E$_{2g}$ symmetry zone center and A$_{1g}$ symmetry phonons, respectively. There is no *D* peak in ideal highly ordered graphite. This peak begins to appear in the presence of a disordered structure.

When studying the effect of grinding on the change in the crystal structure of natural graphite, additional bands appear on the Raman spectra. As a result of grinding natural graphite, in addition to a single band at 1580 cm^{-1}, two more signals appear on the Raman spectra centered around 1360 and 1620 cm^{-1}, which are responsible for the presence of disordered carbon with structural defects [14].

Possessing high sensitivity to changes in transsymmetry, this method can distinguish several types of carbon (graphite, glassy carbon, diamond), as well as the ratio of these components in the carbon material. Information on the change in the crystal structure and average crystallite sizes of graphite (L_a) of nanoporous carbon materials depending on the temperature of thermochemical activation was obtained from Raman spectra (Fig. 2) by approximating the *D* and *G* bands with Lorentzians (Fig. 3) and numerical values are given in Table 2. When modeling Raman spectra with Lorentzians, the coefficient of determination was $R^2 \approx 0.99$.

Information about these characteristics was obtained by analyzing the position of the maximum of the *G* and *D* bands, the full width of the band at half height (ω), and the integrated intensity of the I_G and I_D bands of the combination scattering. Analyzing the Raman spectra (Fig. 3), it is possible to distinguish groups of materials with almost the same intensity (S500-S600

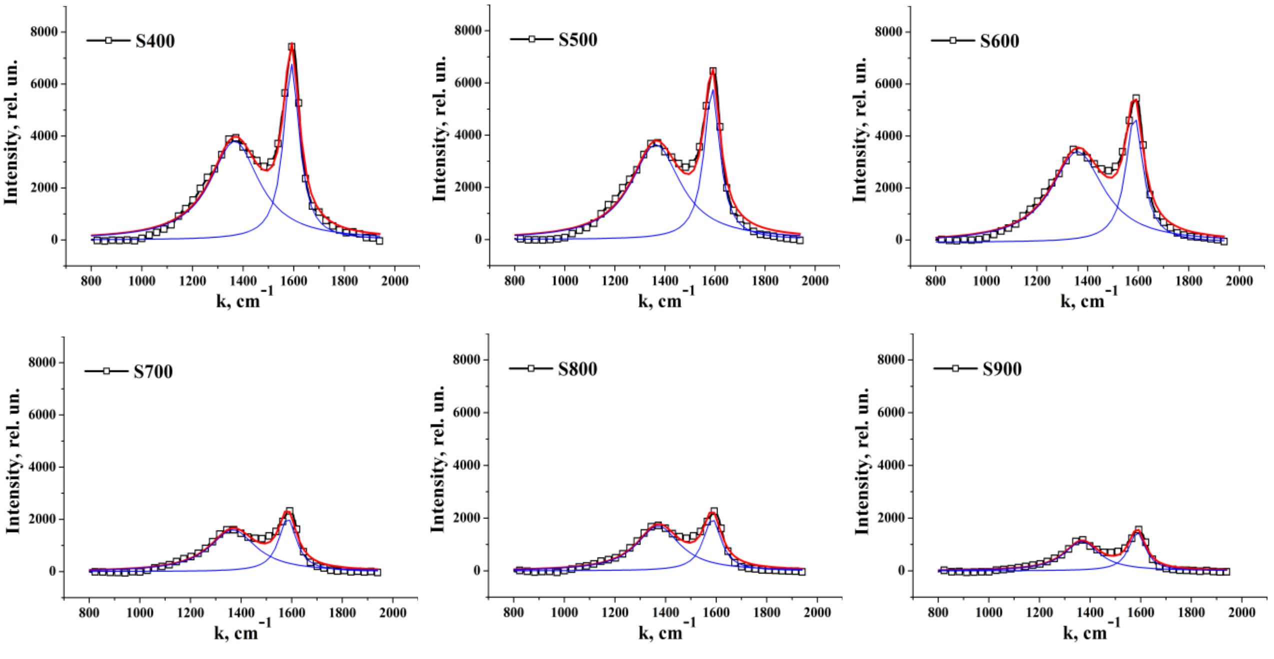

Fig. 3 – Approximation of Raman spectra of NCM obtained at different temperatures of thermochemical activation

Table 2 – Parameters of modeled curves obtained for approximation of Raman spectra of NCM

Sample	S400	S500	S600	S700	S800	S900
D, cm $^{-1}$	1366.58	1363.56	1360.45	1364.37	1368.74	1370.90
ΔD, cm $^{-1}$	0.91	1.06	0.93	1.29	1.11	0.87
$\omega(D)$, cm $^{-1}$	235.75	241.22	251.72	223.19	206.80	167.78
$\Delta\omega(D)$, cm $^{-1}$	2.83	3.29	2.87	4.04	3.47	2.78
$I(D)$	1408000	1379932	1381811	561238	554456	295608
$\Delta I(D)$	13431	15070	12943	8285	7547	3751
G, cm $^{-1}$	1590.85	1587.72	1584.96	1583.59	1584.10	1585.60
ΔG, cm $^{-1}$	0.25	0.32	0.32	0.54	0.54	0.42
$\omega(G)$, cm $^{-1}$	76.13	76.04	83.24	84.58	85.58	79.55
$\Delta\omega(G)$, cm $^{-1}$	0.86	1.10	1.13	1.85	1.85	1.41
$I(G)$	810737	696830	634569	273157	265894	182936
$\Delta I(G)$	7967	8857	7844	5334	5043	2622

and S700-S800). An increase in the activation temperature leads to a decrease in the intensity of the spectra and blurring of the *G* and *D* peaks. The *G* and *D* peaks of different intensities, positions, and widths continue to dominate the Raman scattering spectra of nanocrystalline and amorphous carbon [13].

Analyzing the data in Table 2, it is possible to trace the shift of the *D* and *G* peaks towards lower frequencies by 8-10 cm $^{-1}$ with an increase in the obtaining temperature to 600-700 ºC. A further increase in the temperature over 700 ºC leads to a shift of these peaks in the opposite direction (Fig. 4).

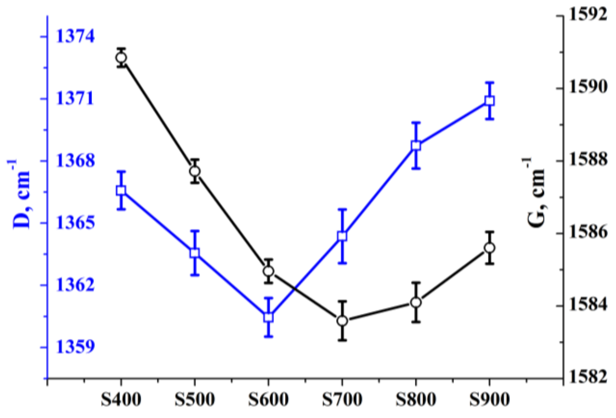

Fig. 4 – The positions of the *G* and *D* bands of the Raman spectra of NCM

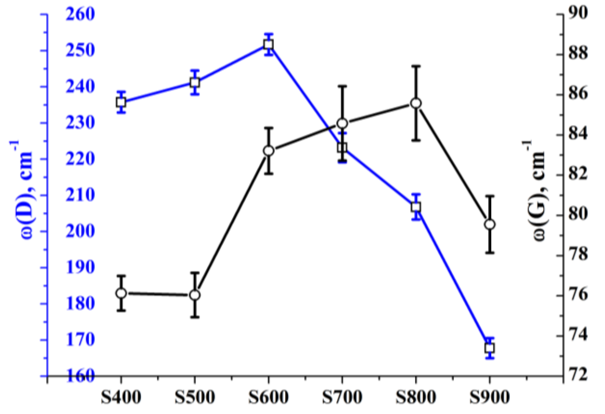

Fig. 5 – The value of the full width of the *G* and *D* bands at half-height

An increase in the obtaining temperature of NCM above 700 ºC leads to a decrease in the value of the full line width at half height for *G* and *D* bands, which indicates an increase in the ordering of graphite crystallites during heat treatment at high temperatures (Fig. 5, Table 2).

At temperatures higher than 800 ºC, there is an increase in the position of the *G* peak (Fig. 4), a decrease in the intensity ratio of I_D/I_G combination scattering (Fig. 7), as well as a decrease in the value of the full width at half the height of the *G* band (Fig. 6), which indicates on the growth of the *sp*3 carbon content [13]. An increase in the obtaining temperature to 600 ºC leads to a decrease in the size of the NCM graphite crystallites (Fig. 6), which is probably related to their burning. It is assumed that these carbon fragments are formed from cellulose and to some extent from hemicellulose, which has a lower destruction temperature compared to lignin [16, 17].

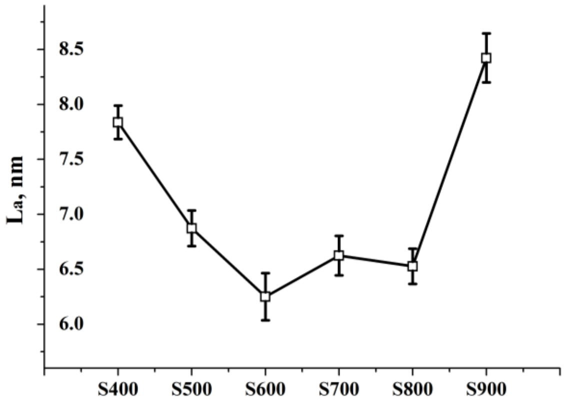

Fig. 6 – Average sizes of graphite crystallites in NCM

Hemicellulose has the lowest decomposition temperature of 220-320 °C, and cellulose has a slightly higher decomposition temperature of about 320 °C [17]. The next temperature ranges of NCM obtaining (700-900 °C) is characterized by an increase in the size of carbon fragments from 6.5 nm to 8.5 nm, probably related to the thermal decomposition of lignin and hemicellulose. An increase in the obtaining temperature leads to the formation of primary agglomerated spherical particles with an average size of 10 to 100 nm, depending on the formation mechanism. Spherical carbon particles contain graphite and amorphous parts.

Graphite-like domains usually consist of 3-4 turbostratically stacked carbon polyaromatic layers with average lateral dimensions up to 3 nm and interlayer distances of approximately 0.35 nm [18].

The formed domains are often called "Basic Structural Units", which are more or less concentrically oriented around an amorphous core, this arrangement of carbon layers is responsible for the "onion-like" nanostructure. Amorphous particles dominate the core and sometimes form the shell of the primary particle [18].

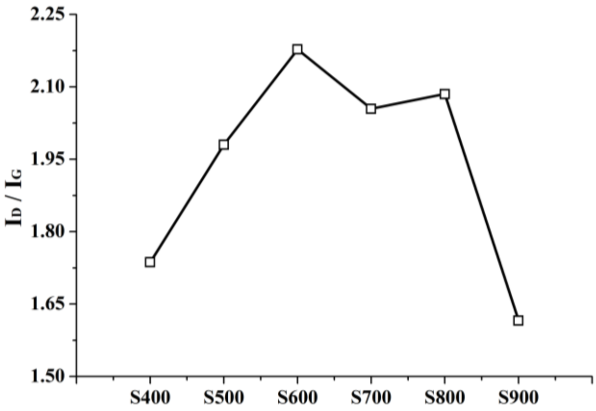

Fig. 7 – I_D/I_G ratio for NCM

Using the obtained data, it is possible to describe to some extent the genesis of the porous structure of the carbon material obtained with thermochemical activation of waste coffee grounds with potassium hydroxide at different final temperatures.

4. CONCLUSIONS

The method of obtaining nanoporous carbon material from biomass using thermochemical alkaline activation to form an optimal pore size ratio is described. It revealed a clear correlation between the pore volume, the specific surface pore area, and the temperature of thermochemical activation. It was established that changing the temperature of thermochemical activation of carbon materials is an effective tool for regulating their porous structure, which makes it possible to obtain samples with a predetermined morphology.

It is shown that the obtained carbon materials have a specific surface area of 400-1050 m^2/g and a pore volume of 0.23-0.51 cm^3/g, depending on the activation temperature. Most pores have sizes of 0.65-1.25 nm in the obtained nanoporous carbon materials.

The analysis of the experimental Raman spectra of NCM showed that an increase in the obtaining temperature up to 600 ºC leads to a decrease in the size of carbon particles, which is probably related to their burning. The temperature ranges of 700-900 °C is characterized by an increase in the size of carbon fragments from 6.5 nm to 8.5 nm, which is probably related to the thermal decomposition of the raw material, and at temperatures higher than 800 °C, an increase in the sp^3 carbon content is observed.

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Структурно-морфологічні властивості нанопористих вуглецевих матеріалів, отриманих з біомаси

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У даній роботі досліджено структурно-морфологічні властивості нанопористих вуглецевих матеріалів, отриманих з біомаси, зокрема відходів кавової гущі, шляхом термохімічної лужної активації в діапазоні температур (400-900 °C). Досліджено вплив температури хімічної активації рослинної сировини на пористість і структуру отриманих вуглецевих матеріалів. Показано, що отримані вуглецеві матеріали мають питому поверхню 400-1050 м^2/г та об'єм пор 0,23-0,51 см^3/г залежно від температури активації. Встановлено, що мікропори розміром від 0,65 до 1,25 нм переважають у пористій структурі, особливо при вищих температурах активації. Показано, що підвищення температури отримання до 600 °C призводить до зменшення розміру частинок вуглецю, що пояснюється частковим згорянням більш дрібних фрагментів. Навпаки, при температурах між 700-900 °C розмір фрагментів вуглецю збільшується з 6,5 нм до 8,5 нм, ймовірно, внаслідок термічного розкладання компонентів лігніну та геміцелюлози в біомасі. Крім того, при температурах вище 800 °C спостерігається збільшення вмісту sp^3 вуглецю, що свідчить про трансформацію його структури. Результати досліджень показали, що оптимальний діапазон температур активації для отримання нанопористих вуглецевих матеріалів з високорозвиненою поверхнею становить 800-900 °C. Даний температурний діапазон сприяє утворенню мікропористої структури зі значною часткою пор діаметром менше 1,25 нм. Регулюючи температуру активації, можна отримати вуглецеві матеріали з контрольованою морфологією та оптимізованою пористістю, що робить їх придатними для застосування в системах зберігання енергії.

Ключові слова: Нанопористий вуглецевий матеріал, Термохімічна активація, Питома площа поверхні, Розподіл пор за розміром.