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THERMOCHEMICAL TRANSFORMATION IN THE PROCESS OF OBTAINING AND MODIFICATION OF NANOPOROUS CARBON

M.O. Nykoliuk, B.I. Rachiy, I.M. Budzulyak, L.O. Moroz

Abstract. The paper is devoted to the study of the thermochemical transformation in the process of obtaining and modification of nanoporous carbon. Nanoporous carbon material, which was gotten in carbonization process, is characterized by specific surface area. The thermogravimetric study of materials with linear heating and isothermal aging at a certain temperature were made to study the effect of thermal activation, which was conducted in air and argon atmospheres.

Keywords: nanoporous carbon material, heating, thermogravimetric study, weight loss.

1. INTRODUCTION

The unique ability of carbon atoms to form different valence states of hybridization of atomic orbitals creates conditions for the use of these materials in different areas of production. Nanoporous carbon materials (NVM) have a particular interest, which contain a mixture of nano-sized fragments of sp2 and sp3 - bonds, because these structures are of considerable scientific and practical interest as a material for creating extra large capacity in the capacitor systems and selective sorbents.

High requirements for properties of nanoporous carbon require systematic research on the influence of process parameters and subsequent receipt of chemical and thermal processing on its structure (size and pore volume, pore size distribution, specific surface area), when it is used as an electrode material of electrochemical capacitors (EC). Particularly important is the study of the characteristics of nanoporous carbon directly in the process of obtaining it from biomass (fruit seeds, coconut shell, flax fibers).

Natural raw materials are a composite chemical complex, which mainly consists of structurally bound water and less of non-structural compounds such as ash, protein, soluble sugars, starches, lipo and oils. The main structural compounds of dry plant material are cellulose, hemicellulose and lignin. Hemicellulose has a lower thermal stability than cellulose (Fig. 1), it is the first decomposed by heating biomass temperature range of 220-320°C, more thermostable cellulose starts to decompose around 320°C.

Cellulose and hemicellulose polysaccharides have different thermal stability due to differences in chemical structure. Cellulose is a natural linear polysaccharide, which is built from anhydride of D-glucopyranose, with a polymerization degree in the order of 10,000. Cellulose polymers are combined into crystalline, fibrous structures which ensure thermal stability. Hemicellulose is a branched hetero-

sacharide which consists of complex non-amyloid and non-cellulose polysaccharides. The degree of polymerization of hemicellulose is quite low, so it is amorphous.

2. MATERIALS AND METHODS

Lignin is a irregular branched polymer with macromolecules, which are held by ethereal and C-C bonds. Lignin is characterized by a slow process of thermal decomposition, covering the temperature range from 160 to 900°C. Different content from chemicals leads to differences in the behavior of biomass in the process of carbonization. To study the carbonization plant material are used differential-thermal (DTA) and thermogravimetric (TG) analysis.
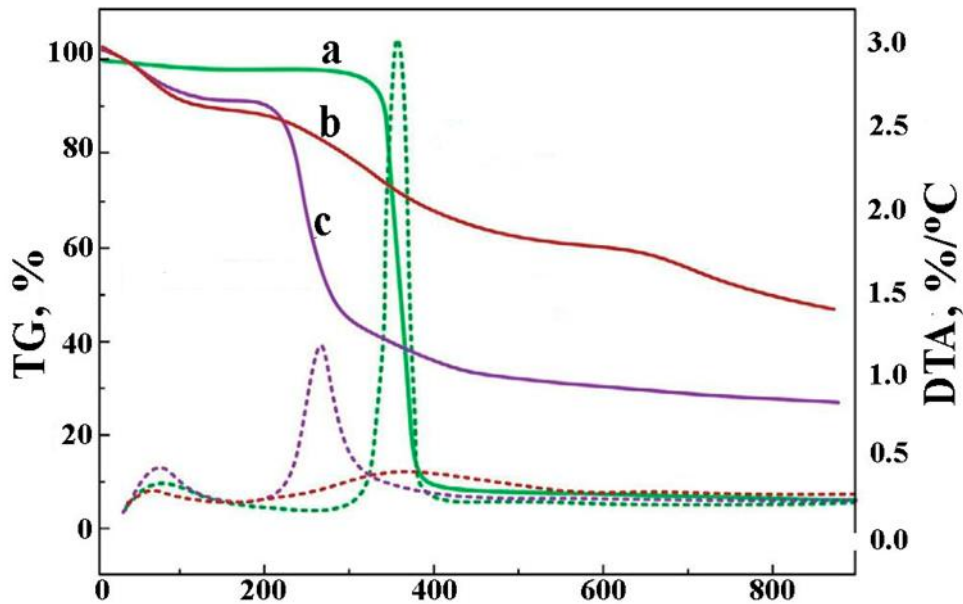

Fig. 1. Thermogram a) pulp, b) lignin in) hemicellulose. (- TG, ••• DTA) [1].

The study of chemical reactions and physical changes, that occur by heat in non-carbonated (ankle apricot, plum, cherry, coconut shell) and carbonated (coal from the pits of apricots, plums, coconut, cherry, fiber flax) materials, are conducted in derivatograph MOM Q-1500 D at a heating rate of 10 and 20 °C per min in air and the temperature range 20 ÷ 900°C. The empty crucible of Al_2O_3 was used as a comparative standard. The sample was heated with a reference sample and recorded current temperature of the sample and the temperature difference between the sample and the standard. The change in mass of the samples presented by heating TG curve, the rate of change of weight - DTG, the change in enthalpy curve - DTA.

3. RESULTS AND DISCUSSION

The analysis of the DTA and TG curves shows that carbonated materials (Figure 2) loss weight due the heating of the specified temperature range of 85-90% of the total mass of the sample (Table. 1). At relatively low temperatures (120-130°C) the reducing of mass of the samples to 10% can be explained by the release of the sorbed forms of water, which are contained in the material. This is evidenced by at least endothermic DTA curve at this temperature (Tab. 2; Fig. 2, curve DTA), that is an additional absorption of heat by evaporation of water. The next small horizontal plateau at temperatures of 170-210 ° C indicates the resistance of the materials in this temperature range and the absence of any significant chemical reactions that consists with Figure 1. The maximum reduction of weight (approximately 75-80%) (Tab. 1) feedstock occurs in the temperature range 250-900 ° C (Fig. 2, TG

curve). The heat is in the temperature range 220-500 ° C (Tab. 2; Fig. 2, curve DTA). As a result of decomposition of organic material and burning a large amount are released of organic volatiles (CO, CO_2) and volatile organic compounds. Simultaneously with this process another process is, that is accompanied by increased carbon content that processes at temperatures above 600 ° C in the material 85% from the total mass of the sample.
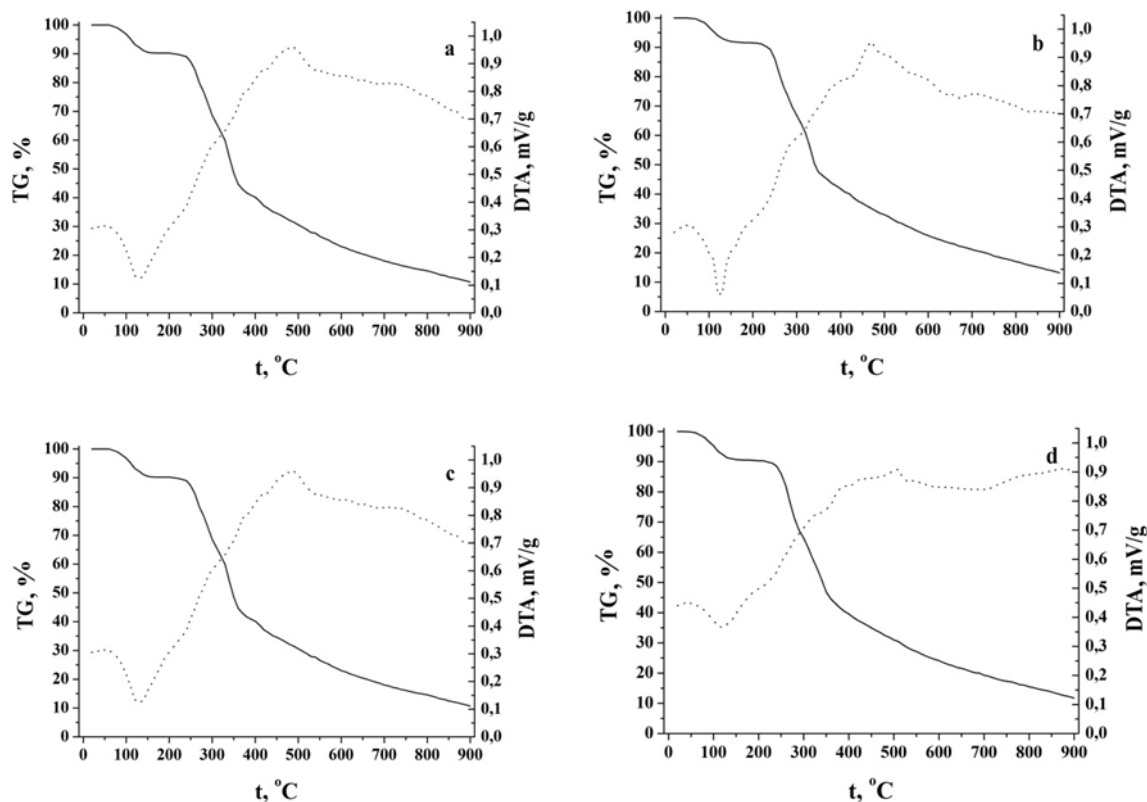

Fig.2. Thermography curves: a) apricot b) plums and) cherry and d) coconut shell. (--- TG, ••••• DTA).

The temperature range, ^0C	The loss of samples mass, %			
	Plum pits	Cherry pits	Apricot pits	Coconut shell
20-900	86	90	89	89
20-130	7,5	8,5	8,1	8,5
240-900	77	77,2	79,5	77,1

Tab. 1. The lose of weight for carbonated samples due to heat.

Sample	Non-carbonated samples			
	Plum pits	Cherry pits	Apricot pits	Coconut shell
Endothermic minimum, ^0C	120	125	130	120
Endothermic maximum, ^0C	470	475	480	485

Tab. 2. Temperature values of the endo-(exo)thermal effects for carbonated samples.

The final schedule of glucose residues occurs at temperatures above 500°C. In the temperature range 650-900°C, the process of polycondensation is with loss of oxygen, hydrogen, nitrogen and sulfur

is further carbonization material and carbon matrix transformation, namely the transformation of semicoal into structure of coal.

The carbon, which was gotten in carbonization process, is characterized by specific surface area of the maximum value of ≈400 m^2 /g [2]. The additional process of the carbonated carbon is required to increase the area and pore volume such as, for example, temperature or chemical activation. Air, water vapor, carbon dioxide, nitrogen oxide and sulfur dioxide can be used at the activation temperature as the oxidizing gases. The thermogravimetric study of materials with linear heating and isothermal aging at a certain temperature were made to study the effect of thermal activation in air and argon atmospheres conducted.

Data analysis TG and DTA, which are obtained for carbonated samples (coal apricot, plum, coconut, cherries), shows that the loss of mass due the heating in air atmosphere around the test temperature range is approximately 40-45% of the original mass (Fig. 3 curve TG), and the carbon was derived from waste flax weight loss due to heating is 57% (Fig. 4, curve TG), which is considerably less than in the case of carbonated material.
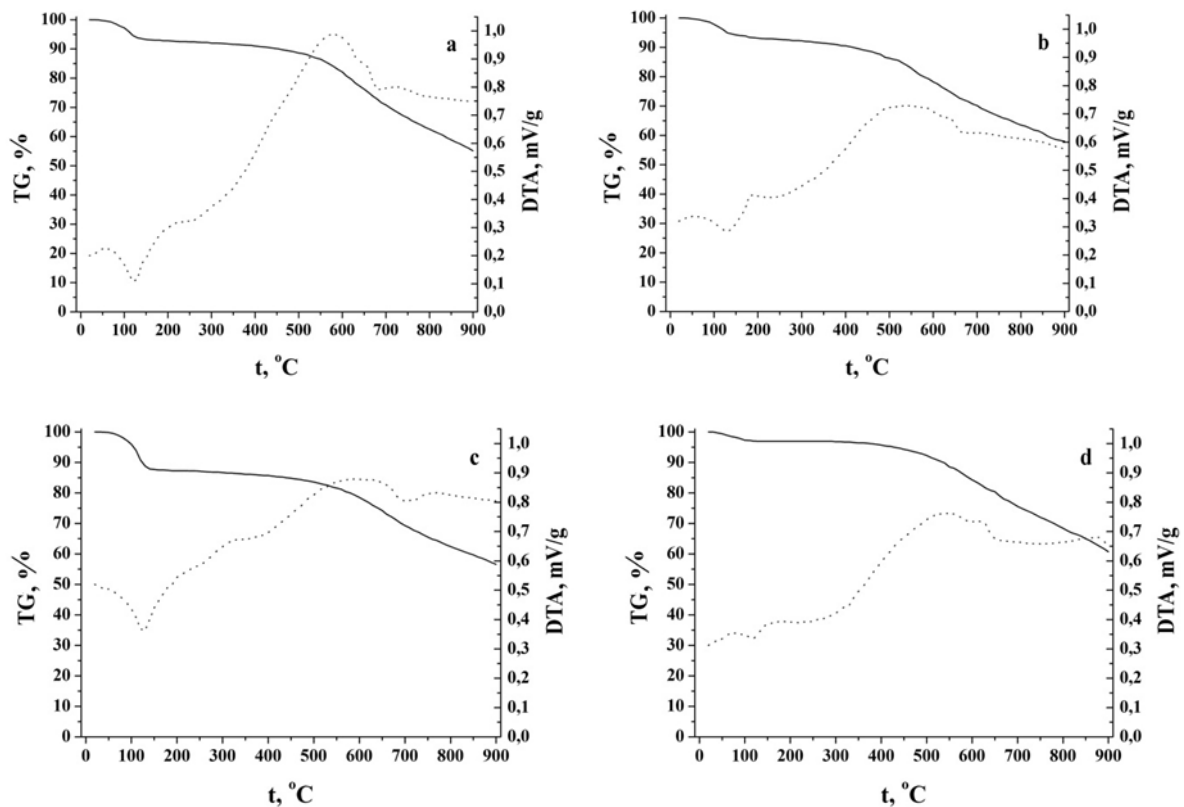

Fig. 3. The thermographs of the carbon that was obtained from: a) coconut shell; b) pitted plums, c) pitted cherries; d) apricot pits. (--- TG, •••• DTA)

Obviously, in the case of carbonated material weight loss is possible mainly by burning carbon material as a result of the exothermic reaction $2C + O_2 \rightarrow 2CO$, as the part of bound water and other organic components of the source material were removed during carbonization.
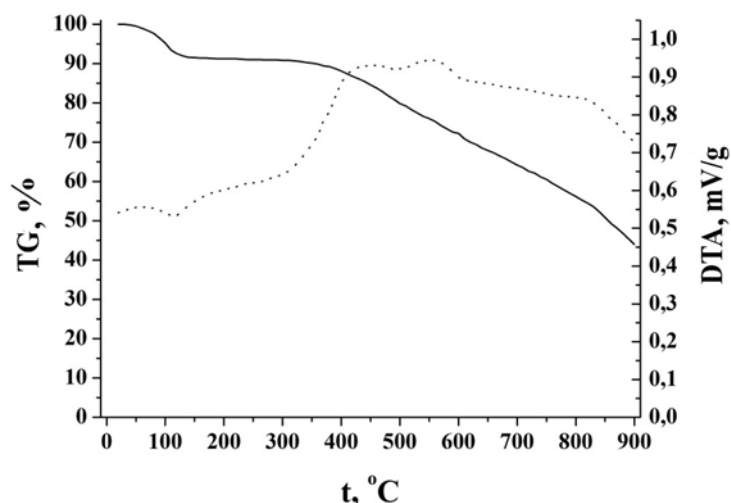
Fig. 4. The thermogram of the carbon that was obtained from flax fibers. (--- TG, ••••• DTA)

The obtained dependence for carbonated samples (coal apricot, plum, coconut, cherries) give reason to believe that at relatively low temperatures (120-130°C), the weight loss is only 5.7% (Tab. 3) by removing sorbed water forms. As feedstock at 120-130°C DTA curve reaches its minimum (Tab. 4; Fig. 3, curve DTA), which indicates endothermical process in this temperature range.

The temperature range, °C	The lose of samples weight, %			
	Carbon from plum	Carbon from cherry	Carbon from apricot	Carbon from coconut
20-900	43	43,7	42	45
20-130	5	5,5	5,8	6,5
450-900	32	33,7	34	34

Tab. 3. The lose of weight for carbonated samples due their heating.

Sample	Carbon from plum	Carbon from cherry	Carbon from apricot	Carbon from coconut
Endothermic minimum, °C	130	125	125	125
Endothermic maximum, °C	190, 560	560	550	220, 580

Tab.4. The temperature values of endo-(exo) thermal effects for carbonated samples.

Unlike raw materials of plant origin, the sharp weight reduction of carbonated material occurs at temperatures of 450-500°C (Fig. 3, curve TG) and is about 32-34% of the total weight (Table. 3), which is two times less than in the case of carbonated samples. In the temperature range 170-770 °C (Fig. 3, curve DTA) is the heat, which is obviously associated with the oxidation and subsequent outgassing of organic residues. Exothermic peaks are observed at 220°C and 580°C for coal from coconut and at 190°C and 560°C for coal from plums (Tab. 4) indicate the intensification of these processes.

The study of differences in the TG and DTA curves for coal, that was obtained at a pressure of 5-10 bar [2] and atmospheric pressure, shows that charcoal was derived from apricot pits, weight loss in the first case is 41%, while the second - 52%. The comparing of DTA curves (Fig. 3, g and Fig. 5, curve DTA) shows that charcoal was derived from the seeds of apricot at atmospheric pressure, there are two distinct maximum of exothermic effect at temperatures of 520°C and 640°C, which is likely due to the restructuring and stabilization system formed pores (Fig. 5, curve DTA). Also at 600-700°C, the process of annealing can be due to the passage of the exothermic reaction between carbon and oxygen.
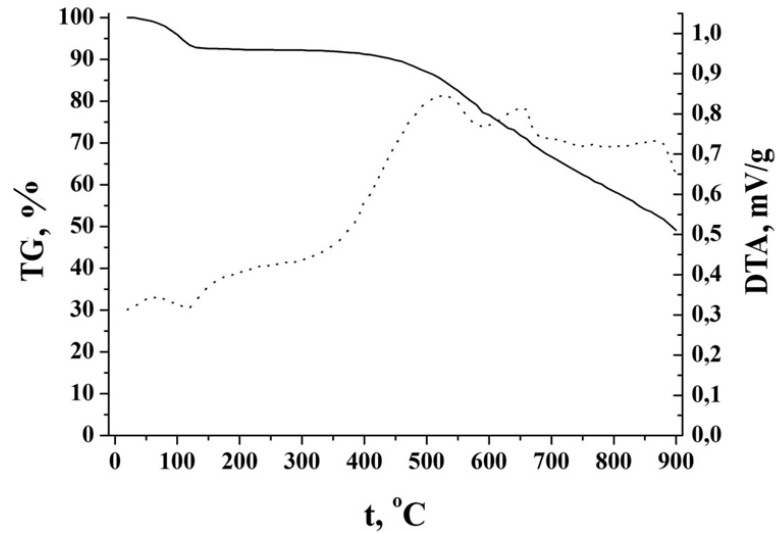
Fig. 5. The thermogram of carbon that derived from apricot pits at the atmosphere pressure (--- TG, DTA ••••••).
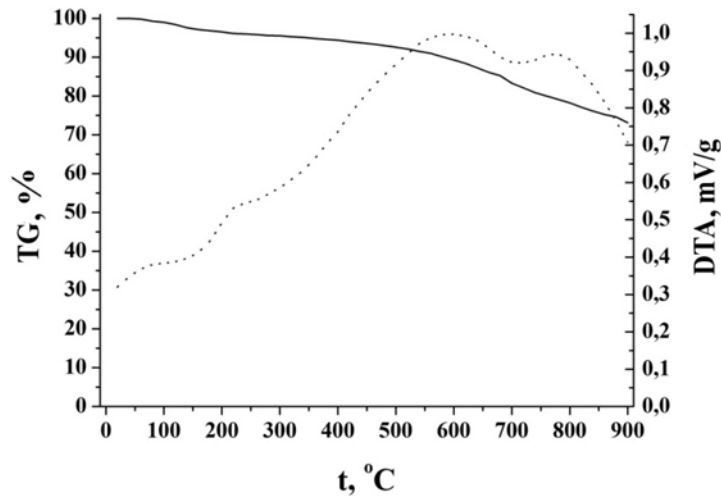

Fig. 6. The thermogram of carbon that obtained from coconut shell (heating rate 20 °C /min) (--- TG, DTA ••••••).

It is known that the temperature endothermic process of beginning and end depends on the rate of heating of the sample, and with increasing heating rate the temperature range of the main stage of dehydration is shifted towards higher temperatures. In particular, the carbon of coconut at heating rate of 20°C/min the endothermic least, that is consistent the temperature of 125°C at a heating rate of 10°C/min, it is less pronounced and shifted towards more temperatures (~ 175°C) (Fig. 6, curve 2).

The study of carbonated carbon mass change at the isothermal aging in an argon atmosphere was performed on synchronous termoanalizator STA 449 F3 Jupiter (Fig. 7). Samples were kept at temperatures of 300, 400, 500, 600 and 700°C for 4 h. [3].
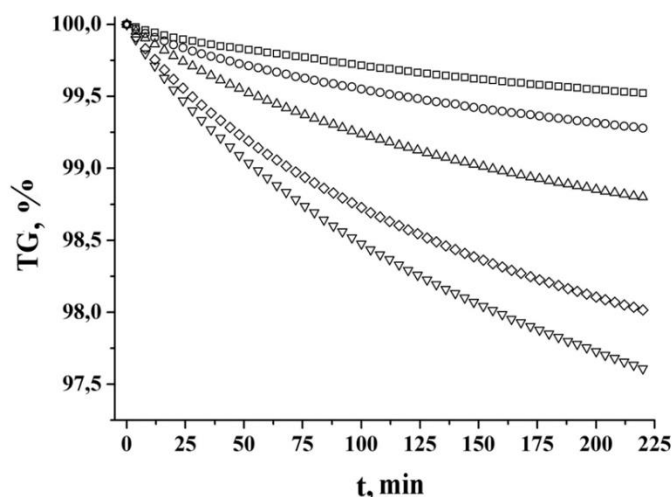
Fig. 7. TG curves of the carbonated carbon at isothermal aging at temperatures: □ - 300°C, ○ - 400°C - 500°C, ◊ - 600°C - 700°C.

For all samples on the DTA curves are no exo- and endothermic effects, this change of mass is not related to the release of reaction products with oxygen, and therefore the change in mass (tab. 5) is most likely caused by the release of hydrogen atoms [4].

T, ºC	300	400	500	600	700
TG, %	0,5	0,7	1,3	1,9	2,4

Tab. 5. The changes of carbon mass at isothermal aging.

The important characteristics of the changes, which occurs in the structure of raw materials at the molecular level, there is evidence of the elemental composition of particular significance atomic ratio C/H and C/O. In addition, the surface of activated carbon is characterized by the type and number of oxygen functional groups. We know that intensive reduction of hydrogen [4], is based on changes in the atomic ratio C/H and observed at higher temperatures of 600°C, and C/O - up to 600°C. Removal of oxygen at higher temperatures is slowed, but complete removal of oxygen can not be achieved even at a temperature of 1500°C (1500°C when the content is 0.09% by weight of coal [4]). Dehydrogenatin from the nanoporous carbon at isothermal conditions is due to the fact that when exposed to high temperatures hydrocarbons are decayed the deep break ties C-C or C-H. It formed products, the composition of which depends on the thermal action (temperature, pressure, duration of heating) and the nature of the hydrocarbon. is The free radicals are the primary products of chemical reactions in the thermal decomposition of hydrocarbons, which then come into interaction with each other and with other molecules. The mechanism of this process is rather complicated. Chemical reactions in the thermal decomposition of hydrocarbons lead to cracks on the surface of the carbon particles. Exposure at 400°C does not lead to the destruction of the surface of the carbon material. The devastated areas can be seen clearly at 500°C, an increase in temperature to 100°C led to extensive changes in surface structure [3]. This indicates the existence of an optimal temperature activation process dehydrogenation reactions of these materials. Note that, because the changes in the structure of isothermal holding are followed by removal of hydrogen, it can not be taken his role in the degradation of the material due to the destruction of porous structure, which is crucial in electrochemical power sources. Another reason for the destruction of the surface at 500°C can be extensive selection of ash that is presented in the structure of the material. However, this assumption is not confirmed by the thermographic analysis because most likely responsible for destruction is the process of dehydrogenation.

4. CONCLUSIONS

Depending on the process for activated carbon and the kind of the original plant material, the weight loss and allocation processes or heat absorption are not significantly different. The maximum weight loss for carbonated samples are ≈80% of the total weight in the temperature range 250-900°C.

Maximum of DTA curves in the temperature range 180-770°C shows the heat, which is obviously associated with the oxidation and subsequent outgassing of organic residues and the minimum at 120-130°C can be explained by the removal of the sorbed forms of water that contained in the material.

Formation of pores in the studied material are possible through the pore-creator, that is introduced from outside (water vapor), bound water that is presented in the bulk material and by heating in an air atmosphere.

It is established that due to five-hour isothermal aging at temperatures of 300, 400, 500, 600 and 700°C nanoporous carbon is carbonated weight reduction due to its dehydrogenation. The main causes of this process are breaking the bonds C-C or C-N by free radical mechanism, which are accompanied by cracking the carbon matrix. It was found that the optimal temperature activation process of dehydrogenation reactions of these materials is in the range 500-600°C.

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Робота присвячена вивченню термохімічних перетворень в процесі отримання і модифікації нанопористого вуглецю. Нанопористий вуглецевий матеріал, який отримали в процесі карбонізації, характеризується питомою площею поверхні. Термогравіметричні дослідження матеріалів з лінійним

нагріванням і ізотермічною витримкою при певній температурі були зроблені *для вивчення впливу термічної активації*, яка була проведена в повітряній і аргоновій атмосферах.

Ключові слова: нанопористий вуглецевий матеріал, нагрівання, термогравіметричні дослідження, втрата ваги.