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Effect of Thermal Conditions of Pyrolysis Process on the Quality of Biochar Obtained from Vegetable Waste

Wpływ warunków termicznych procesu pirolizy na jakość biowęgli otrzymanych z odpadów roślinnych

An effective way of managing natural waste, including waste from the agri-food industry or products that are economically useful can be offered by production of biochar. Biochar is used not only as an energy product, but also as a sorption material for e.g. groundwater treatment, sewage treatment, as well as biogas valorization. Therefore, the aim of the study was to determine the effect of the conditions of cascade heating of selected types of vegetable waste in carbon dioxide on the microstructure and chemical composition of the obtained biochar. Wheat straw, corn waste in the form of dried leaves and stems, as well as flax shives and cherry stones were subjected to pyrolysis. Cascading temperature conditions were programmed for a total time of 100 minutes, including 15 minutes of final heating at 500°C in one variant and at 700°C in the other. After final heating, the products were left in the pyrolytic chamber to cool down spontaneously to room temperature. The biochar samples were next subjected to microscopic examinations coupled with X-ray microanalysis (SEM/EDS) and infrared spectral examination (FTIR). It was found that the pyrolysis yielded biochar in the amount from 26 to 32.3% of the initial charge mass, depending on the conditions of the process and the type of waste. Furthermore, the differences observed in the chemical structure of the surface of the biochar concerned mainly the occurrence of organic oxygen functional groups whose type depends on the pyrolysis temperature. An increase in the temperature of pyrolysis leads to a decrease in the oxygen content of the products obtained, which results in a relative increase in the proportion of char in the product. Biochar obtained at temperatures of up to 500°C contains aromatic rings and quinone groups, whereas those obtained at higher temperatures (up to 700°C) have ether groups embedded mainly in aliphatic cyclic groups.

Keywords: **biochar, biochar structure, carbonate, pyrolysis, waste pyrolysis, vegetable waste, biomass**

Introduction

The analysis of current research trends both in Poland and worldwide indicates that there is an intensive increase in scientific interest and development of industrial technologies of thermal processing of biomass into economically useful products. One of the key directions of research and development is to obtain biochar, which

is a product of thermal conversion of plant biomass, biodegradable waste, or sewage sludge [1, 2]. Particularly interesting is pyrolytic processing of waste from the agri-food sector, which allows for rational management of the generated vegetable waste by producing biochar with wide opportunities for applications used - among others, for adsorption-based removal of pollutants from soil, water and organic matrices, improvement of properties of soils used for agricultural purposes, modification of the composting process, carbon sequestration in soil, and as an auxiliary material for biogas production [2-7]. For example, stones of various fruits, including plums and cherries characterized by low content of inorganic matter, high density and developed surface, are a promising raw material for the production of active carbons intended for the removal of various types of chemical pollutants [8-11]. Another group of wastes that can be used in the production of carbon adsorbents is cereal straw or fibrous vegetable waste (e.g. flax straw) [12, 13].

Biochar obtained during pyrolysis of vegetable waste materials is characterized by a complex chemical structure of their surface, which depends on the conditions of the process, with particular focus on the rate and temperature of pyrolysis [14-16]. The product of vegetable waste pyrolysis is biochar, containing in its structure numerous organic oxygen functional groups, with their occurrence and chemical structure depending on thermal conditions of biochar production. The presence of functional groups on the carbon surface is illustrated in Figure 1 [17].

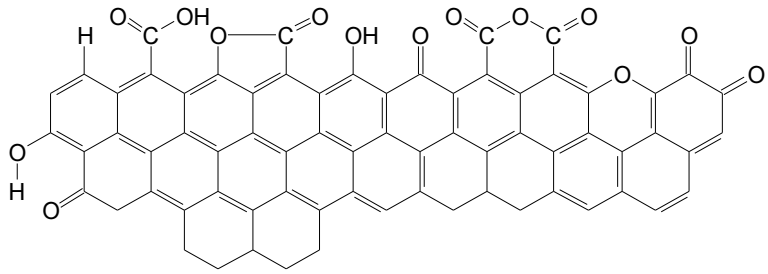


Fig. 1. Diagram of the chemical structure of the carbon surface [17]

A number of oxygen functional groups may be present on the surface of carbon structures, among which the most frequently found in the literature include carboxylic, lactone, phenolic, carbonylic, anhydride, ether, and quinone groups. Chemical structure of the surface of biochar obtained from pyrolysis significantly impacts on its adsorption, acid-base, oxidation-reduction, catalytic and electrochemical properties [18-20]. Heat treatment leads to the destruction of oxygen groups, whereas the obtained gas products, mainly carbon monoxide and carbon dioxide, are removed from the reaction zone. Depending on the type of the function group, structural conversion occurs at different temperatures. For example, decarboxylation may take place at 200°C, the removal of phenolic groups from the carbon surface takes place at a temperature of about 600°C, whereas conversion of carbonyl or quinone groups can only occur at approximately 700÷800°C [14, 17]. In previous technological solutions, pyrolysis has been conducted for relatively short times, using

a gradient temperature increase [21, 22]. Such processes can significantly degrade the porous microstructure and eliminate the presence of active functional groups on the biochar surface. Therefore, obtaining the biochar with the preserved microstructure with the presence of polar oxygen groups requires the pyrolysis process conducted in cascade conditions. They are characterized by an initially prolonged period of the temperature rise, which can prevent from pore closing in the microstructure of the plant material, and then isothermal heating in steady conditions.

The aim of the study was to investigate the effect of cascade thermal conditions of pyrolysis on the microstructure and chemical structure of biochar obtained from selected types of vegetable waste, which may determine sorption properties of coal products.

1. Research methodology

1.1. Research material

Four types of vegetable waste, i.e. wheat straw, flax shives, corn waste (mixture of leaves and stems) and cherry stones were examined in the study. Natural waste which was used during laboratory experiments was characterized by hygroscopic moisture content, determined by means of the drying and weighing method to be at a level not exceeding 10%. For the pyrolysis process, a sample with specific mass was prepared each time, which allowed for the evaluation of the percentage loss of mass during thermal treatment.

1.2. Pyrolysis process conditions

The pyrolysis process was performed under cascade heating conditions, according to two temperature programs, with their pattern illustrated in Figure 2.

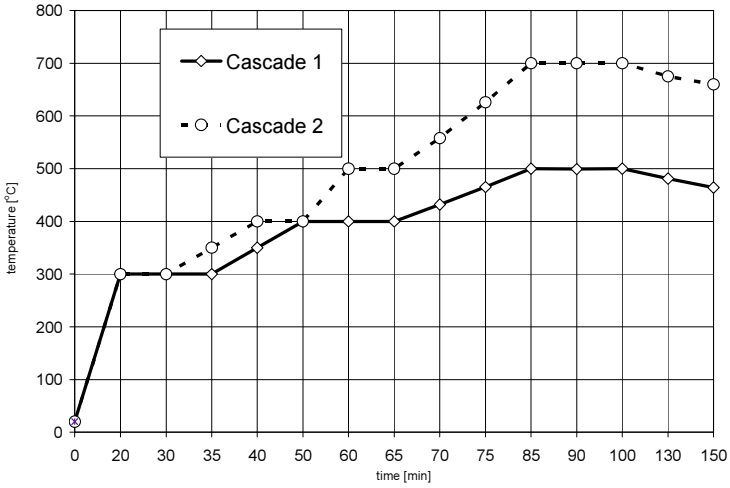


Fig. 2. Diagram of heating cascades used during pyrolysis of vegetable waste

Cascade 1 was programmed with the following heating stages: temperature rise from 20 to 300°C in 20 minutes, heating in 300°C for 15 minutes, the subsequent temperature rise to 400°C for 15 minutes, heating in 400°C for 15 minutes, temperature increase from 400 to 500°C in 20 minutes, and final heating at 500°C for 15 minutes. Cascade 2 was characterized by a longer stage of heating at 300 and 400°C and the subsequent heating to the final temperature of 700°C. After completion of the final heating, the furnace was shut down and the sample was left to cool down spontaneously to reach room temperature for 12 hours. During heating and cooling, the flow rate of carbon dioxide in the chamber was set at 5.0 L/min. The pyrolysis process was conducted on a laboratory stand equipped with the Czylok furnace (FCF-V12RM).

1.3. Instrumental analysis parameters

Loss of mass of vegetable waste due to pyrolysis was expressed in weight percentages determined as the difference between the mass of the material charge prior to pyrolysis and the biochar mass obtained through thermal treatment of waste relative to the waste mass prior to pyrolysis. Mass of individual samples was determined to the nearest 0.1 mg using the analytical balance AG 204 manufactured by Mettler Toledo.

A scanning electron microscope with field emission (model SU-70, Hitachi) equipped with an X-ray EDS microanalyser from Thermo Scientific was used to examine the microstructure of the obtained biochar samples and to identify their elemental composition. The EDS technique was used to determine the mass percentages of carbon and oxygen in biochcar and vegetable waste. The analyses were performed for the following conditions: magnification of 500x or 1000x, acceleration voltage 15 kV, take-off angle 30°, and negative pressure 10^{-8} Pa.

Infrared spectra of biochar samples were obtained using the FTIR 6200 spectrometer (by Jasco), in reflective mode. In the case recording of biochar spectra, the *Pike* type attachment with diamond crystal was used, while the pyrolytic oil spectrum was obtained by means of the ATR attachment equipped with zinc selenide crystal. During spectral measurements, the following apparatus parameters were used: spectral range: 4000÷650 cm^{-1}, spectral resolution: 4 cm^{-1}, TGS detector, spectrum averaging from 30 scans. The spectra containing overlapping spectral bands were subjected to mathematical processing consisting in normalization of the base line over the selected spectral range and deconvolution of the selected spectral range with the use of *Spectra Manager version 2* computer software from Jasco.

2. Results and discussion

Comparison of the results of gravimetric measurements of vegetable waste charge and the obtained biochar allowed for the evaluation of the loss of mass of thermally treated waste, and thus to determine process efficiency. Comparison of

the results that characterize pyrolysis processes at specific temperature conditions is presented in Table 1.

Table 1. **Effect of thermal conditions of pyrolysis process on loss of mass of the natural waste in the CO_2 atmosphere**

Waste	Mass loss during pyrolysis, %	
	Cascade 1 (up to 500°C)	Cascade 2 (up to 700°C)
Wheat straw	67.0	67.7
Flax shives	73.2	74.0
Corn waste	70.0	72.5
Cherry stones	73.5	73.9

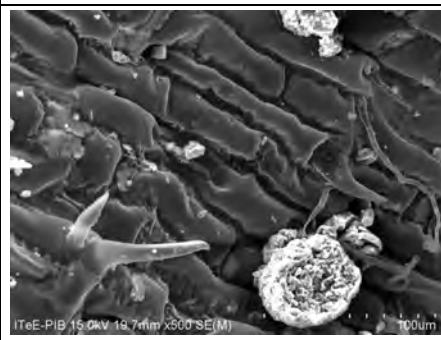
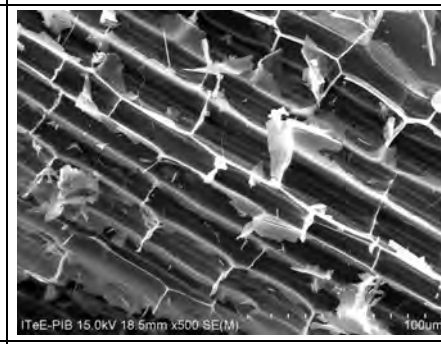
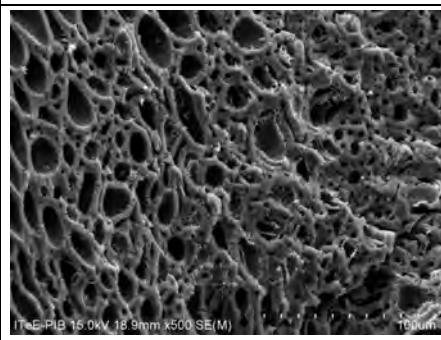
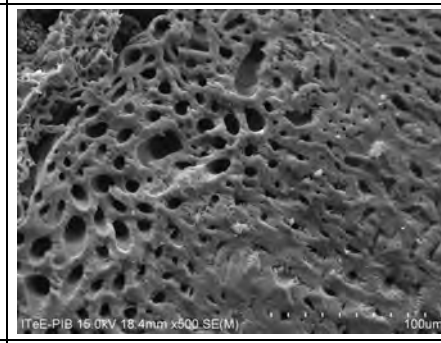
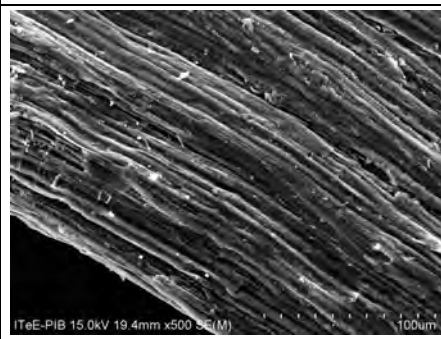
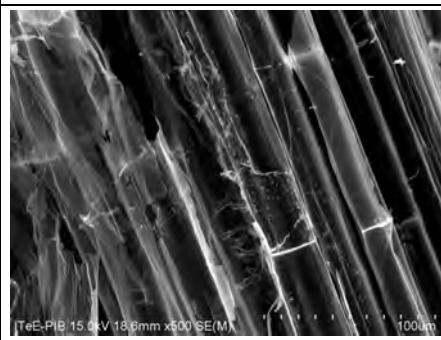
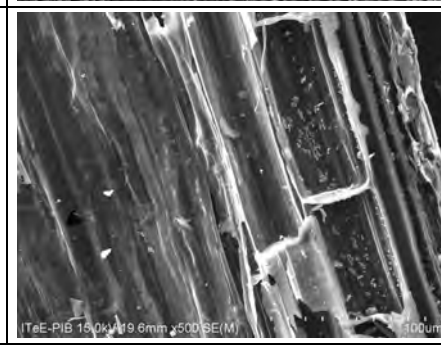
The analysis of the results reveals that the highest mass loss for the vegetable waste subjected to pyrolysis under thermal conditions of Cascade 1 (i.e. up to 500°C) was observed for cherry stones, reaching 73.5% of the initial mass of the charge. A similar mass loss, i.e. 73.2%, was also found in the case of flax shive pyrolysis. Modification of the thermal conditions of the process and its performance according to Cascade 2 (with the final temperature of 700°C) causes only a slight increase in the mass loss compared to heat treatment at lower temperatures. Compared to the values obtained for the pyrolysis at lower temperatures (Cascade 1), biochar mass at higher temperatures (Cascade 2) showed a 0.4% higher mass loss for cherry stones, whereas a mass loss for flax shives was higher by 0.8%. Mass loss was determined in relation to the mass of the charge subjected to pyrolysis.

The differences in masses recorded for biochar obtained from different types of vegetable waste for different thermal conditions may result from both microstructure remodelling and chemical conversion leading to the removal of gaseous or liquid pyrolysis products. Further analysis by means of microscopy coupled with X-ray analysis allowed for identification of changes occurring during pyrolysis under adopted thermal conditions. A comparison of biochar microstructure obtained for different vegetable waste samples is presented in Table 2.

Analysis of microscopic images of biochar samples reveals that an increase in pyrolysis temperature leads to closing the porous structures in biochars obtained from cherry stones, whereas in the case of corn waste, mass loss for the material is observed, with preserved parallel wall structure. However, no significant changes in microstructure of biochar obtained from pyrolysis of fibrous waste such as flax shives and wheat straw were observed. In order to verify the observations of microstructure of biochar samples obtained from fibrous waste, SEM tests were conducted using 1000x magnification, with examples of images presented in Figure 3.

The analysis of microscopic images (Fig. 3) confirmed the previous observations that the increase in the cascade temperature of the pyrolysis process of wheat straw and flax shive waste does not lead to the destruction of the fibrous microstructure of the biochar obtained.

Table 2. **SEM images of biochar microstructure obtained during pyrolysis under various temperature conditions (magnification 500x)**

Waste	Microstructure of the product after pyrolysis up to 500°C (Cascade 1)	Microstructure of the product after pyrolysis up to 700°C (Cascade 2)
Corn waste		
Cherry stones		
Flax shives		
Wheat straw		

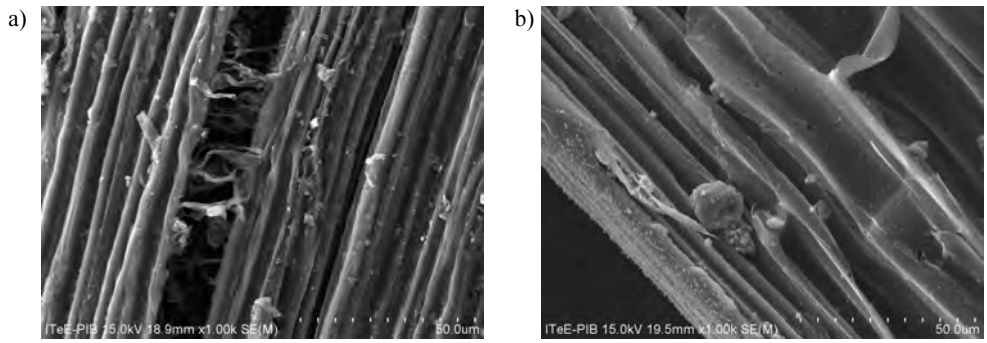


Fig. 3. SEM images of the microstructure of vegetable waste following the pyrolysis at temperatures of up to 700°C (magnification 1000x): a) flax shives, b) wheat straw

Simultaneously with microscopic examinations, EDS microanalyses were performed, allowing for identification of the elemental composition of the biochar obtained. Examples of X-ray spectra, which represent the dependence of the number of counts vs. energy of characteristic radiation for a given element of biochar obtained from corn waste are presented in Figure 4.

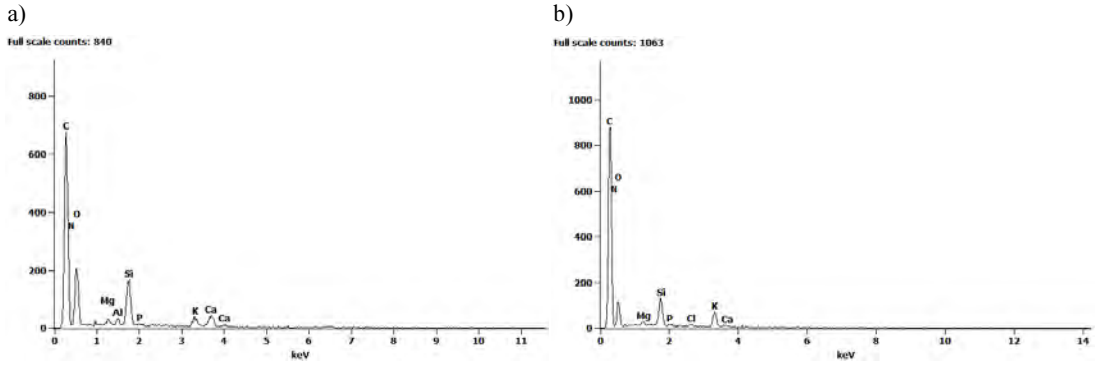


Fig. 4. Comparison of EDS spectra of biochar derived from corn waste for cascade heating to temperatures of: a) 500°C (Cascade 1), b) 700°C (Cascade 2)

Neither during the analysis of spectra for biochar obtained from corn waste nor that obtained after the pyrolysis of other samples of vegetable waste showed significant changes in the qualitative composition of biochar. A chlorine signal with low intensity observed in EDS spectra was recorded during the examinations of only some of the biochar samples. This was due to randomly selected samples of the charge material for the pyrolysis process as the vegetable waste used was likely to contain residue of e.g. chlorinated fertilisers. Furthermore, quantitative analyses of EDS examinations confirmed the increase in carbon content at the expense of the decreasing percentage of oxygen content in the biochar samples as evidenced by the data presented in Table 3.

Table 3. **Comparison of relative percentages of carbon and oxygen in biochar samples obtained from pyrolysis of vegetable waste under different temperature conditions in the carbon dioxide atmosphere**

Waste	Chemical composition of biochar samples obtained under thermal conditions of Cascade 1 (up to 500°C)		Chemical composition of biochar samples obtained under thermal conditions of Cascade 2 (up to 700°C)	
	Element	wt.%	Element	wt.%
Corn waste	carbon	43.79	carbon	55.54
	oxygen	38.08	oxygen	25.70
Cherry stones	carbon	58.54	carbon	69.18
	oxygen	24.84	oxygen	6.12
Flax shives	carbon	59.03	carbon	58.96
	oxygen	23.17	oxygen	13.64
Wheat straw	carbon	53.33	carbon	55.59
	oxygen	34.45	oxygen	23.83

The analysis of the data presented in Table 3 shows that the greatest difference between the oxygen concentration in biochar obtained from heat treatment according to Cascade 1 and its content in biochar obtained during pyrolysis according to Cascade 2 occurred for heat treatment of cherry stones. Oxygen content in the biochar studied decreased by 18.72 wt.%. A relatively high loss of oxygen concentration was also observed in the case of pyrolysis of corn waste, where the oxygen content was by 12.38% lower in the biochar obtained under Cascade 2 conditions (up to the temperature of 700°C), compared to the biochar obtained under Cascade 1 conditions (up to 500°C). The smallest difference between the oxygen content in the biochar samples occurred for flax shives (9.53 wt.%). The reduction of oxygen content in the products obtained leads in most cases to increasing carbon content in the product examined. The highest increase in relative carbon content in pyrolysis products was observed for the products of thermal treatment of corn waste (11.75 wt.%) and cherry stones (10.64 wt.%). Analysis of the results for biochar obtained from wheat straw reveals that the differences in the percentage contents are at the level of 2.26% by weight, and, in the case of products obtained from flax shives, the carbon content was at a comparable level. By referencing the results obtained for carbon and oxygen content to the levels measured for the initial materials (Table 4), it can be found that in all investigated cases an increase in carbon content in pyrolytic products is observed compared to the content in natural waste before pyrolysis. However, oxygen content was reduced.

Based on the EDS examinations, a decrease in oxygen content in biochar caused by higher temperature of pyrolysis process was observed, which suggests opportunities for conversion of oxygen function group and removal of oxygen in e.g. gaseous products generated during pyrolysis. Changes in the chemical structure of biochar were evaluated based on FTIR spectra for individual products. A typical spectra pattern is shown in Figure 5-8.

Table 4. **Carbon and oxygen concentrations in vegetable waste before pyrolysis [23]**

Waste	Chemical composition before pyrolysis	
	Element	wt.%
Corn waste	carbon	36.01
	oxygen	51.76
Cherry stones	carbon	44.91
	oxygen	43.60
Flax shives	carbon	45.94
	oxygen	43.09
Wheat straw	carbon	35.13
	oxygen	54.16

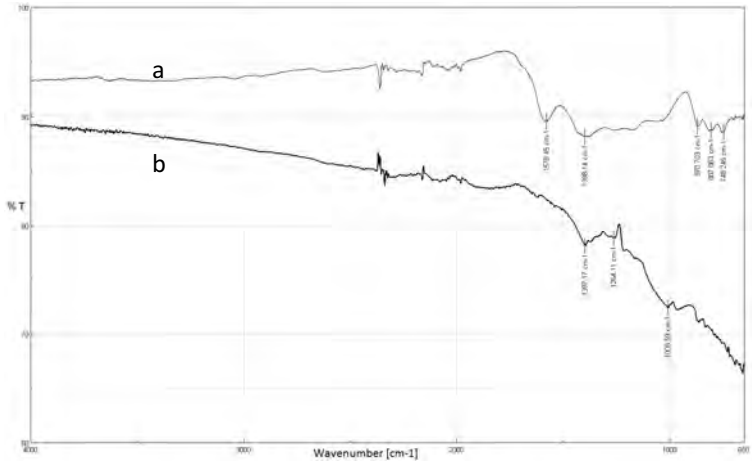


Fig. 5. Comparison of FTIR spectra of biochar obtained from flax shives in the carbon dioxide atmosphere for the following thermal conditions: a - Cascade 1 (up to 500°C), b - Cascade 2 (up to 700°C)

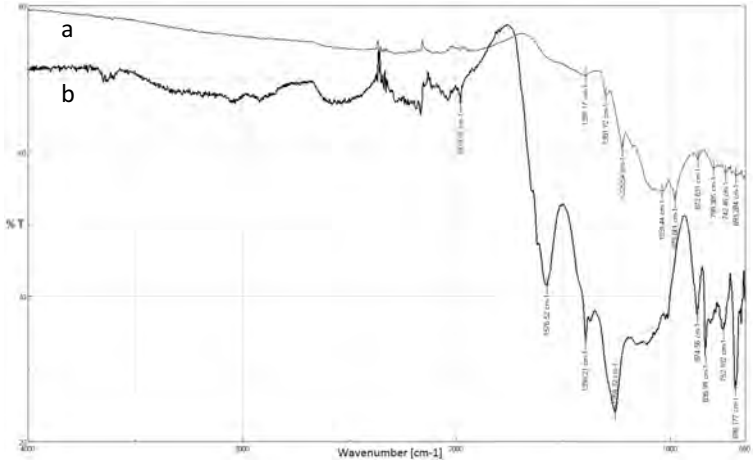


Fig. 6. Comparison of FTIR spectra of biochar obtained from corn waste in the carbon dioxide atmosphere for the following thermal conditions: a - Cascade 2 (up to 700°C), b - Cascade 1 (up to 500°C)

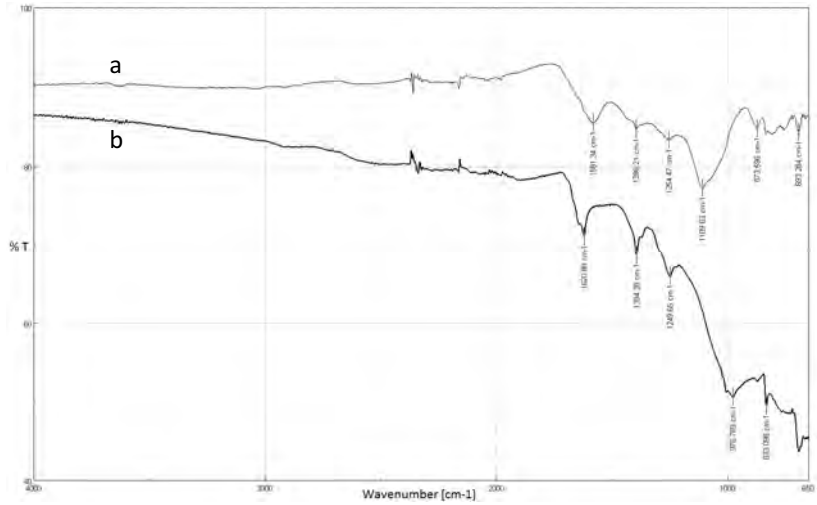


Fig. 7. Comparison of FTIR spectra of biochar obtained from wheat straw in the carbon dioxide atmosphere for the following thermal conditions: a - Cascade 1 (up to 500°C), b - Cascade 2 (up to 700°C)

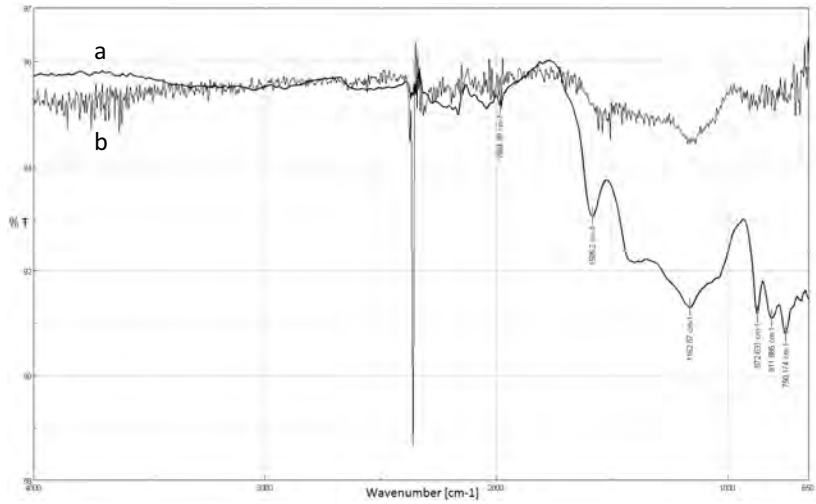


Fig. 8. Comparison of FTIR spectra for biochar obtained from cherry stones in the carbon dioxide atmosphere for the following thermal conditions: a - Cascade 1 (up to 500°C), b - Cascade 2 (up to 700°C)

The analysis of recorded infrared spectra indicates that the temperature conditions of pyrolysis determine the chemical structure of the products obtained. Under thermal conditions of Cascade 1 (maximum pyrolysis temperature of 500°C), carbon products are formed, containing organic oxygen structural groups coupled with double carbon-carbon bonds in aromatic rings. This is evidenced by spectral bands located in the spectra of biochar samples obtained from wheat straw for the wave number of 1581 cm^{-1}, in the spectra of biochar samples obtained from corn waste for the wave number of 1576 cm^{-1}, in biochar samples obtained from flax shives

for wave number of 1578 cm^{-1}, and in biochar from cherry stone for wave number of 1585 cm^{-1}. It should be noted that these values of wave numbers are extremes of wide peaks, overlapped by other bands, including those corresponding to organic oxygen functional oxygen groups. Visualisation of the bands associated with oxygen groups is possible through mathematical processing of the spectra, consisting in normalization of the base line in the selected spectral range, and then deconvolution of the range. An example outcome of mathematical operations conducted for the IR spectrum of the biochar obtained from pyrolysis (Cascade 1) of corn waste is presented in Figure 9.

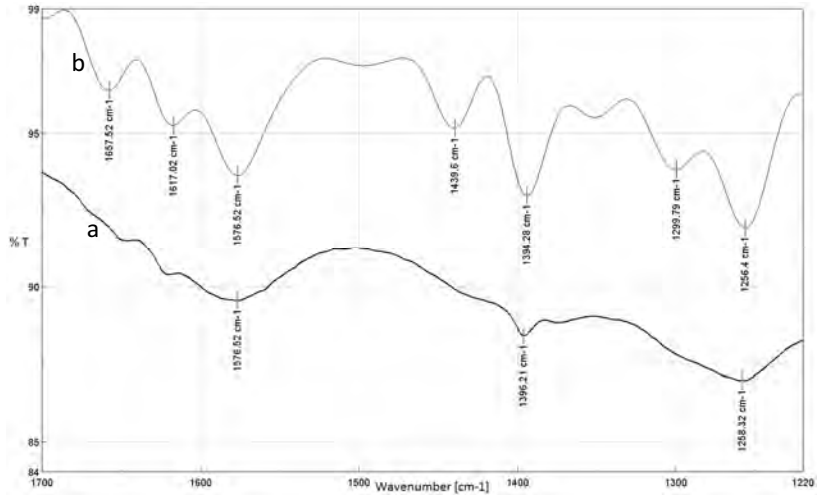


Fig. 9. Selected range of IR spectrum for biochar obtained from corn waste under thermal conditions of Cascade 1: a - before deconvolution, b - after deconvolution of spectral bands

The mathematical operations allowed for separation of the overlapping spectral bands, thus facilitating the interpretation of the data. In the case of the spectrum shown in Figure 9, the C=O bond vibration band in quinone occurs at 1657 cm^{-1}. Furthermore, at the wave number of 1617 cm^{-1}, the band corresponds to the vibrations of the aromatic ring. The presence of these molecular structures is confirmed by the previously discussed band at a wave number of 1576 cm^{-1}, associated with vibrations of the C=C group in the aromatic ring, coupled with the C=O carbonyl group. Next, the position of the bands was compared for the analogous spectral range after deconvolution of the spectrum for biochar from corn waste obtained under Cascade 2 conditions.

The increase in pyrolysis temperatures according to the Cascade 2 heating program (maximum temperature of 700°C) leads to fading the above mentioned bands in the FTIR spectra of biochar and, therefore, high-temperature pyrolysis limits the possibility of formation of active organic oxygen structures on the surface of biochar. This effect was also observed during analysis of the spectra of biochar samples obtained from other vegetable waste. However, particularly interesting are the results of spectral examinations of the biochar obtained after pyrolysis of cherry

stones, which clearly showed that for heating according to Cascade 2, biochar samples did not contain oxygen functional groups independently occurring on biochar surfaces, such as carbonyl or quinone groups, which can be identified by infrared spectrophotometry (Fig. 10).

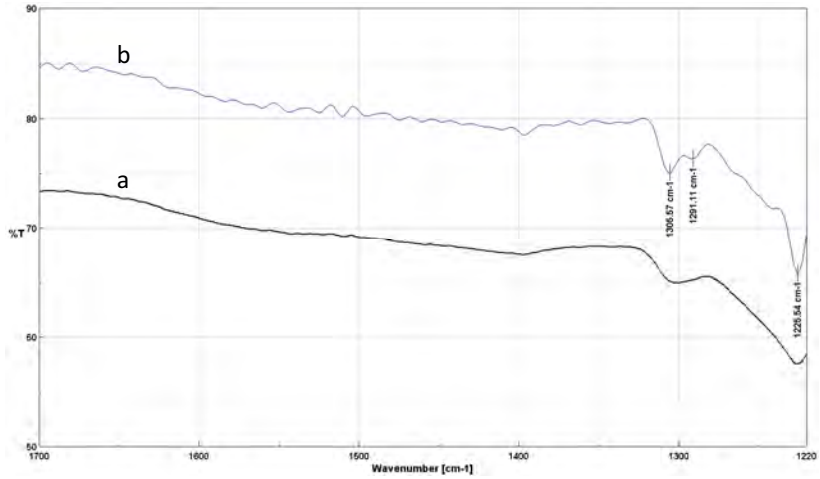


Fig. 10. Selected range of IR spectrum for biochar obtained from corn waste under thermal conditions of Cascade 2: a - before deconvolution, b - after deconvolution of spectral bands

Furthermore, it is likely that oxygen is embedded into cyclic carbon structures in the form of ether bridges, which can be evidenced by spectral bands present in the spectra of products obtained at higher temperatures, whose maxima occur in the range of 1020÷1075 cm^{-1} (aromatic ethers) or 1060÷1150 cm^{-1} (aliphatic ethers). However, the high noise recorded for the spectrum does not allow for effective deconvolution of spectral bands. Conclusions from spectral examinations indicating the removal of oxygen structures from biochar during pyrolysis of vegetable waste under thermal conditions of Cascade 2 (maximum temperature of 700°C) compared to pyrolysis under Cascade 1 conditions (maximum temperature of 500°C) are consistent with the results of the EDS examinations of elemental content in biochar, which show a reduction in the oxygen content in pyrolysis products.

Conclusions

Thermal conditions of pyrolysis essentially modify the chemical structure of the biochar while maintaining the fibrous and porous microstructures that depend on the microstructure of the initial raw material. However, it should be noted that high temperatures (i.e. 700°C) cause melting of cherry stone building material, which may lead to closing of porous structures. The pyrolysis yields biochar in the amount from 26 to 32.3% of the initial charge mass, depending on the conditions of the process and the type of waste. Temperature conditions also impact on the

chemical structure, especially the presence of carbonyl functional groups. Higher pyrolysis temperature leads to the elimination of this type of structural groups from biochar, which is also consistent with the results of the EDS examinations that demonstrated a decrease in oxygen content in biochar.

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Streszczenie

Efektywnym sposobem zagospodarowania odpadów naturalnych, w tym pochodzących z przemysłu rolno-spożywczego, na produkty użyteczne gospodarczo może być wytwarzanie biowęgli. Znajdują one zastosowanie nie tylko jako produkt energetyczny, ale także jako materiał sorpcyjny, wykorzystywany m.in. do uzdatniania wód gruntowych, oczyszczania ścieków, a także waloryzacji biogazu. W związku z powyższym celem przeprowadzonych prac było określenie wpływu warunków kaskadowego ogrzewania wybranych odpadów roślinnych w atmosferze ditlenku węgla na mikrostrukturę i budowę chemiczną powstających biowęgli. Pirolizie poddano słomę pszeniczną, odpady kukurydziane w postaci wysuszonych liści i łodyg, a także paździerze lniane i pestki wiśni. Kaskadowe warunki temperaturowe zaprogramowano na łączny czas 100 minut, w tym 15-minutowe wygrzewanie końcowe w jednym wariancie w temperaturze 500°C, a w drugim wariancie w temperaturze 700°C. Po końcowym wygrzewaniu pozostawiano produkty w komorze pirolitycznej do samoistnego wystudzenia do temperatury pokojowej. Otrzymane biowęgle poddano następnie badaniom mikroskopowym sprzężonym z mikroanalizą rentgenowską (SEM/EDS) oraz badaniom spektralnym w podczerwieni (FTIR). Stwierdzono, że w wyniku pirolizy otrzymuje się biowęgiel w ilości od 26 do 32,3% początkowej masy wsadu, zależnej od warunków prowadzenia procesu oraz rodzaju odpadów. Natomiast obserwowane różnice w budowie chemicznej powierzchni otrzymywanych biowęgli dotyczą w głównej mierze występowania tlenoorganicznych grup funkcyjnych, których typ jest zależny od temperatury procesu pirolizy. Wzrost temperatury pirolizy prowadzi do obniżenia zawartości tlenu w otrzymywanych produktach, co powoduje relatywne zwiększenie udziału węgla w produkcie. Biowęgle otrzymywane w temperaturach do 500°C posiadają w swej strukturze pierścienie aromatyczne oraz ugrupowania chinonowe, natomiast otrzymywane w wyższych temperaturach (do 700°C) posiadają ugrupowania eterowe wbudowane głównie w alifatyczne ugrupowania cykliczne.

Słowa kluczowe: biowęgiel, struktura biowęgla, karbonizat, piroliza, piroliza odpadów, odpady roślinne, biomasa