Journal of Machine
Construction
and Maintenance
QUARTERLY
ISSN 1232-9312 4/2018(111)

p. 99–104

Jarosław MOLENDA*
Institute for Sustainable Technologies – National Research Institute, Radom, Poland
* Corresponding author: jaroslaw.molenda@itee.radom.pl

THE INFLUENCE OF THE PROTECTIVE PYROLYSIS ATMOSPHERE OF VEGETABLE WASTE ON BIOCARBON CONSTRUCTION

Key words: biocarbon, vegetable waste, biomass, pyrolysis, waste pyrolysis, biocarbon structure.

Abstract: The aim of the study was to investigate the influence of the type of the protective gas used during the pyrolysis of selected plant waste on the chemical structure and microstructure of produced biocarbons. The following types of vegetable waste were selected for tests: wheat straw, maize waste, flax straw, and cherries stones. Carbon dioxide or nitrogen was used as a protective gas during the pyrolysis. The pyrolysis was carried out of cascade conditions to increase of the temperature to a maximum of 500°C. The produced biocarbons were analysed by Raman spectroscopy, FTIR spectrophotometry, and the SEM/EDS technique. It was found that protective gas has a clear influence on the microstructure and chemical structure of the pyrolysis product only in the case of biocarbons obtained from maize waste. It was confirmed that the biocarbon obtained in an atmosphere of carbon dioxide is characterized by a higher proportion of oxygen compared to the product produced in a nitrogen atmosphere. This is due to the presence of oxygen-organic functional groups. In addition, it has been spectrally demonstrated that the biocarbon produced from maize waste in a nitrogen atmosphere is characterized by a high microstructural ordering. However, in the biocarbon obtained in the atmosphere of carbon dioxide are also amorphous areas.

Wpływ atmosfery ochronnej procesu pirolizy odpadów roślinnych na budowę otrzymywanych biowęgli

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

Streszczenie: Celem pracy było zbadanie wpływu rodzaju gazu ochronnego stosowanego podczas pirolizy wybranych odpadów roślinnych na budowę chemiczną i mikrostrukturalną wytwarzanych biowęgli. Do testów wybrano następujące rodzaje odpadów roślinnych: słoma pszeniczna, odpady kukurydziane, paździerze lniane oraz pestki wiśni. Podczas pirolizy prowadzonej w warunkach kaskadowego wzrostu temperatury do maksymalnej wartości 500°C stosowano ditlenek węgla lub azot jako gaz ochronny. Wytworzone biowęgle zbadano następnie za pomocą spektroskopii Ramana, spektrofotometrii FTIR oraz techniką SEM/EDS. Stwierdzono, że jedynie w przypadku biowęgli otrzymywanych z odpadów kukurydzianych zauważa się wyraźny wpływ gazu ochronnego na mikrostrukturę i budowę chemiczną produktu pirolizy. Potwierdzono, że biowęgiel otrzymany w atmosferze ditlenku węgla w porównaniu z produktem wytwarzanym w atmosferze azotu charakteryzuje się większym udziałem tlenu, co wynika z obecności tlenoorganicznych grup funkcyjnych. Poza tym wykazano spektralnie, iż biowęgiel wytwarzany z odpadów kukurydzianych w atmosferze azotu charakteryzuje się wysokim uporządkowaniem mikrostrukturalnym. Natomiast w biowęglu otrzymanym w atmosferze ditlenku węgla występują również obszary amorficzne.

Introduction

Pyrolysis is a process of thermal decomposition of biomass. Pyrolysis is carried out in an anaerobic atmosphere and leads to the breakdown of chemical compounds included in the building material of vegetable raw materials, i.e. mainly cellulose. The chemical reactions take place concurrently during the biomass pyrolysis process, which determines the molecular structure of the biocarbon being formed as well as other liquid and gaseous products. The final composition of the products generated is significantly influenced by both primary reactions and secondary reactions. The secondary reactions occur directly between the molecules of the product formed or between free radicals generated during the thermal treatment of plant waste. The kinetics of chemical changes depends in a significant way on the process temperature and the time of its realization. An important factor is also the protective atmosphere. The gas molecules may be involved in structural conversion or affect the chemical structure of pyrolysis products and kinetics and the efficiency of chemical reactions [1–4].

For example, during free pyrolysis of walnut shells conducted in a carbon dioxide or nitrogen atmosphere to 600°C, it was found that the presence of CO_2 accelerates the thermal degradation process both at low and at high heating rates. However, the type of protective atmosphere does not affect the yield of biocarbon, which was at the level of 24% of the weight of the charge. However, the influence of the type of protective gas on the amount of tar and gas products as well as the chemical structure of tar yields was observed. In particular, a higher content of furans and aliphatic oxygen compounds was found in tar products obtained from walnut shells in a carbon dioxide atmosphere than in a nitrogen atmosphere [5].

The literature reports also indicate the possibility of using other protective gases in addition to carbon dioxide and nitro gen, which modify the pyrolysis process, thus affecting the chemical structure and the performance of individual products [6]. A frequently used gas introduced into the pyrolysis reactor is water vapour, which affects the oxidation of biomass while gasifying it. This process is called steam pyrolysis. In this case, the inhibition of the secondary cracking reaction in the gas phase and the increase in the efficiency of the products containing oxygen functional groups are observed [7]. The influence of the protective atmosphere, such as nitrogen, carbon dioxide, methane, and hydrogen on the pyrolytic oil yield, as well as the chemical structure of the products formed were studied. It was found that the presence of carbon dioxide and carbon monoxide is responsible for the formation of monosubstituted phenols and methoxy derivatives [8]. Other studies have shown that carbon dioxide affects both the chemical composition of the pyrolytic oil and the structure of biocarbon. Biocarbon obtained pyrolytic in the atmosphere of carbon dioxide in comparison to the product formed in the inert atmosphere was characterized by an increased surface area. The biocarbon also had different chemical structure, which determined the sorption capacity of heavy metals [9]. The aim of the work was to examine the chemical structure of biocarbons obtained pyrolytically from selected types of agro-food plant waste, differing in microstructure. It is fibrous cellulosic waste such as wheat straw, maize waste (leaves and stems), and flax straw, as well as non-fibrous waste, i.e. cherry stones.

1. Materials and methods

The research objects

Four types of plant waste were selected for research, i.e. wheat straw, maize waste, flax straw, and cherry stones. The natural waste was used during the laboratory work was dried and characterized by moisture content, determined by the weighting method, at a level not exceeding 10% (w/w), each time a sample of known weight was prepared for the pyrolysis process. This allowed the assessment of the percentage loss of mass during thermal treatment, and consequently, the calculation of biocarbon yield.

The conditions of the pyrolysis process

The pyrolysis was carried out under the following cascade heating conditions: an increase of the temperature from 20°C to 300°C in 20 minutes, heating at 300°C for 15 minutes, another increase in temperature to 400°C in 15 minutes, heating at 400°C for 15 minutes, an increase in temperature from 400°C to 500°C in 20 minutes, and a final heating at 500°C for 15 minutes. After completion of the final heating, the furnace was turned off and the sample was left for 12 hours to self-cool to room temperature. During the heating and the cooling in the chamber, a flow of nitrogen or carbon dioxide at a speed of 5.0 litres/min was provided. The pyrolysis process was carried out on a laboratory scale equipped with a Czylok muffle furnace, type FCF-V12RM.

The parameters of the instrumental analysis

A scanning electron microscope Hitachi SU-70 (SEM) equipped with an EDS X-ray microanalyser was used to study the microstructure of the obtained pyrolysates and to identify their elemental composition. The analyses were carried out under the following conditions: 2000 times magnification, 15 kV acceleration voltage, 30º reception angle, and 10^{-8} Pa pressure. The infrared spectra of the obtained biocarbons were made using a FTIR 6200 spectrometer (Jasco company), in the reflection mode, using a Pike-type adapter with a diamond crystal. During the spectral measurements, the following apparatus parameters were used: spectral range: 4000–650 cm^{-1}, spectral resolution: 4 cm^{-1}, TGS detector, and spectrum averaging from 30 scans.

The Raman spectra were taken at room temperature using an NRS 5100 spectrometer from Jasco (Japan), using excitation with a laser at a 532 nm wavelength and an exposure time of 100 seconds. The spectra were recorded in the range of Raman shifts from 260 cm^{-1} to 3900 cm^{-1} with a resolution of 3.2 cm^{-1}, using microscope lens with a magnification of 20 times.

2. Results and discussion

Comparisons of mass yields of biocarbons obtained during pyrolysis in various protective atmospheres of selected plant waste are shown in Fig. 1.

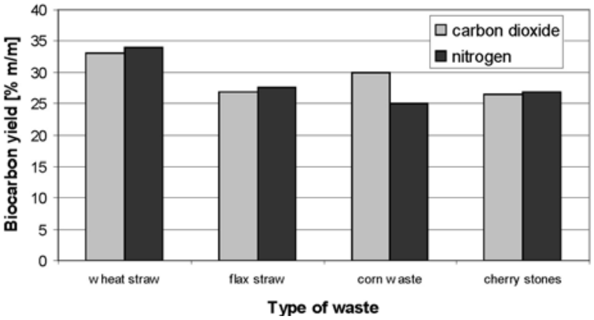

Fig. 1. **The comparison of the efficiency of biocarbon production during pyrolysis of plant waste conducted in various protective atmospheres**

The results of gravimetric measurements indicate that the type of protective atmosphere in the majority of samples tested (i.e. wheat straw, maize waste, flax straw, and cherry stones) did not affect the amount of biocarbon formed. An important difference is observed in the case of biocarbons obtained from maize waste. A comparison of the yields of the percentage of biocarbons indicates that, in the nitrogen atmosphere, almost 17% less biocarbon from maize waste is obtained than in the case of biocarbon obtained in the atmosphere of carbon dioxide. The observed differences may result from the different structure of maize waste, in comparison to the other raw materials examined, which determines the directions of chemical conversion during pyrolysis and, as a consequence, the chemical structure of biocarbon.

A comparison of the obtained infrared spectra of biocarbons obtained during the pyrolysis of plant waste carried out in the atmosphere of nitrogen and carbon dioxide is shown in Figs. 2–5.

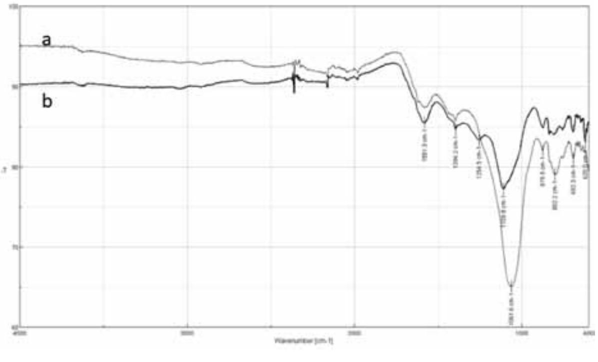

Fig. 2. **A comparison of the FTIR spectra of biocarbon from wheat straw obtained at a temperature of 500ºC in an atmosphere (a) of nitrogen, (b) of carbon dioxide**

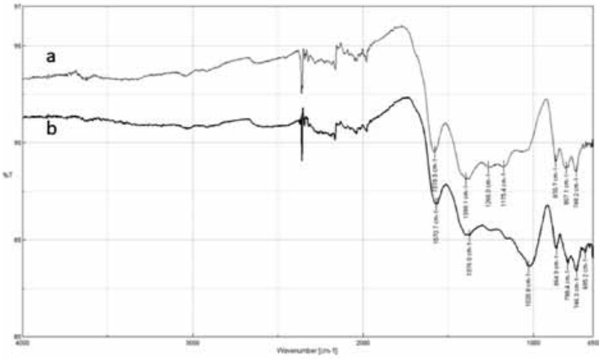

Fig. 3. **A comparison of the FTIR spectra of biocarbon from a flax straw obtained at a temperature of 500ºC in the atmosphere of (a) carbon dioxide (b) nitrogen**

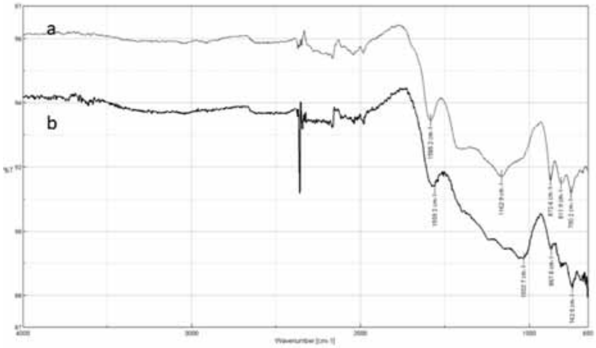

Fig. 4. **A comparison of the FTIR spectra of biocarbon from cherry stones obtained at 500ºC in the atmosphere of (a) carbon dioxide (b) nitrogen**

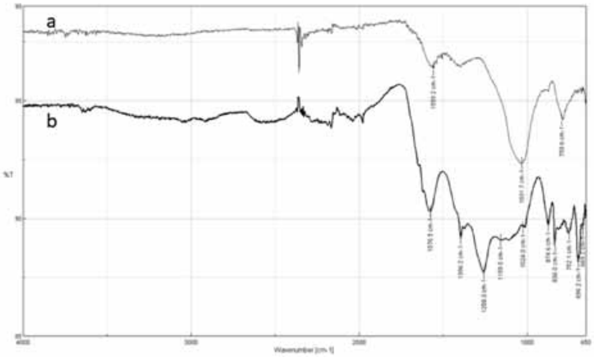

Fig. 5. **A comparison of the FTIR spectra of biocarbons from maize waste obtained at 500ºC in the atmosphere (a) of nitrogen (b) of carbon dioxide**

The analysis of the obtained spectra indicates that biocarbons obtained pyrolytically from wheat straw, flax straw, and cherry stones are characterized by a similar chemical structure, regardless of the type of protective atmosphere used during pyrolysis, which results from the analogous course of recorded spectra. Interpretation of biocarbon spectra allows us to state that functional groups containing oxygen and nitrogen are present in the products obtained. In the biocarbon spectra, a pronounced vibration signal of conjugated bonds C=C and C=O is observed, which indicates that aromatic ketone ring structures may be formed. A relatively broad band vibration of carbonyl groups suggests overlapping other signals that may be derived from the vibration of the carbon-nitrogen [10]. Significantly different infrared spectra that were dependent on the applied protective atmosphere during pyrolysis were observed for biocarbon obtained from waste maize. The IR spectrum of the product of maize waste pyrolysis, carried out in a nitrogen atmosphere, has three intense spectral bands, located at 1559 cm^{-1}, 1031 cm^{-1}, and 793 cm^{-1}, the presence of which confirms the heterocyclic structure of biochar with embedded oxygen atoms. On the other hand, biocarbons obtained in the atmosphere of carbon dioxide are characterized by a more complex chemical structure than biocarbons produced pyrolytically in an atmosphere of nitrogen. The spectrum of products obtained in the carbon dioxide atmosphere contains a number of spectral bands (e.g., at wavenumbers 1576 cm^{-1}, 1258 cm^{-1}, and 874 cm^{-1}), whose position indicates vibrations of substituted aromatic rings as well as ether structures (band at the wavenumber 1024 cm^{-1}). In connection with the above, the biocarbon pyrolytically obtained from maize waste in the presence of carbon dioxide contains more oxygen and hydrogen atoms in their structure than the biocarbon obtained in the presence of nitrogen.

These observations were verified using SEM/EDS tests. The exemplary results obtained during the biocarbon investigations as a result of the pyrolysis of maize waste are presented in Fig. 6.

In the pyrolysis products, the building elements (carbon, oxygen, and nitrogen) and small amounts of other elements (potassium, chlorine, phosphorus, calcium, and magnesium) were identified during the investigations of the elemental composition. The coefficients of atomic proportions of oxygen to carbon and nitrogen to carbon were also determined. They allow the assessment of the influence of the protective atmosphere of the pyrolysis process on the presence of aerobic and nitrogenous structural moieties in the biocarbon products. The obtained results are presented in Table 1.

Table. 1. The comparison of the atomic ratios of oxygen and nitrogen in reference to coal in maize waste before and after pyrolysis carried out in the atmosphere nitrogen or carbon dioxide

Type of coefficient	The value of the atomic share coefficient		
	in waste before pyrolysis	in biocarbons	
		pyrolysis in N_2	pyrolysis in CO_2
$^{N}/_{C}$	0.11	0.08	0.09
$^{O}/_{C}$	1.08	0.29	0.65

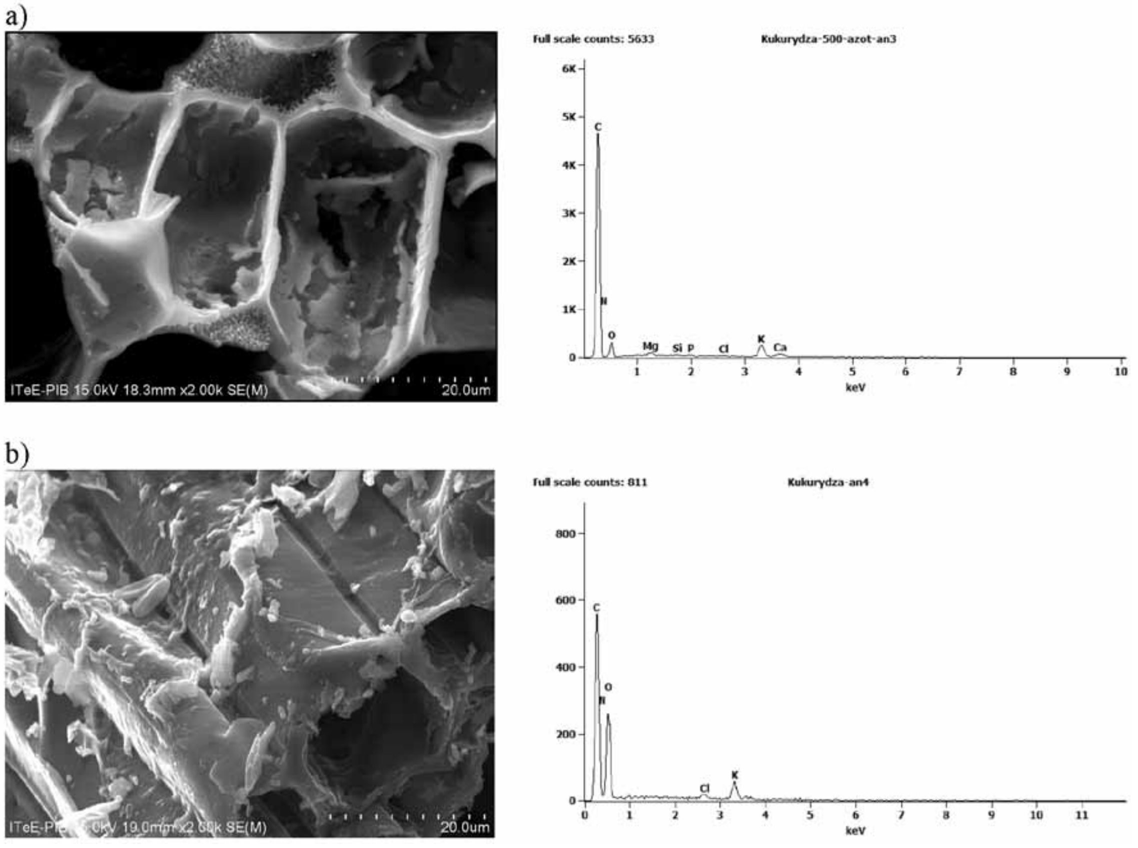

Fig. 6. The SEM images (magnification 2000 times) and EDS spectra of biocarbon obtained pyrolytic from maize waste in the atmosphere a) nitrogen, b) carbon dioxide

The analysis of the value of atomic coefficient of key elements in biocarbons in relation to the feedstock indicates that there were no significant differences between the content of nitrogen structures in the waste before pyrolysis and biocarbons obtained in two different protective atmospheres. However, there were significant differences in the content of oxygen structures. On the basis of the values of the indices determined, it can be concluded that the type of protective gas affects the content of oxygen structures in the biocarbon. The use of carbon dioxide in the pyrolysis process results in a higher content of these oxygen structures in the biocarbons being formed than in the case of using nitrogen as a protective gas. The quantitative measurements confirm the conclusions resulting from infrared spectral tests.

A further analysis of the structure of the obtained biocarbons, including the assessment of the orderliness of the microstructure, was possible by using Raman spectroscopy studies. The exemplary spectra that allow comparing the characteristics of biocarbons obtained in various protective atmospheres are shown in Figs. 7 and 8.

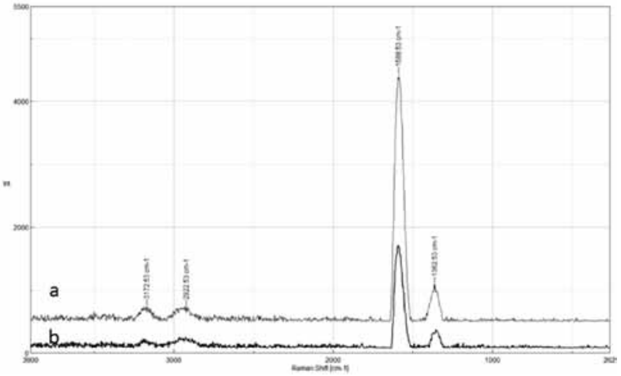

Fig. 7. The comparison of the Raman spectra of biocarbons obtained during the pyrolysis of cherry stones in the atmosphere of carbon dioxide (a) and nitrogen (b)

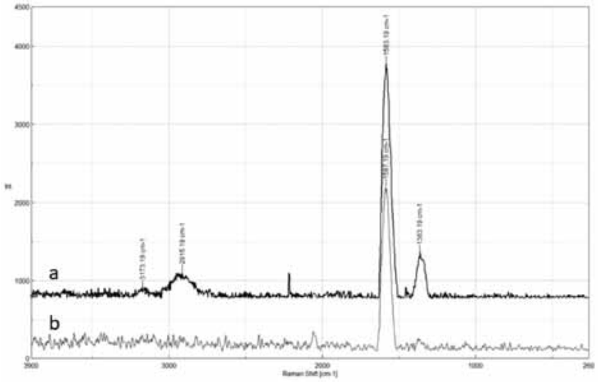

Fig. 8. The comparison of the Raman spectra of biocarbons obtained during the pyrolysis of maize waste in the atmosphere of carbon dioxide (a) and nitrogen (b)

The spectra of the studied biocarbons contain bands directly related to the vibrations of carbon and hydrocarbon structures. Two bands allowing for inference about the degree of ordering of carbon structures, i.e. the G-band (graphite) occurring in the range of 1580–1600 cm^{-1} and the D-band (disorders), occurring in the range of 1260–1390 cm^{-1}, are important [11]. The registered biocarbon spectra have an intense band with maxima located at the Raman movement of 1580 cm^{-1}. It comes from vibrations of tensile sp^2 carbon bonds, which occur in ring structures. In the majority of biocarbon spectra, there is also the D-band at the Raman movement of about 1360cm^{-1}, which is characterized by the level of amorphous carbon structures. This band is not identified in the biocarbon spectrum obtained from the pyrolysis of maize waste in the nitrogen atmosphere (Fig. 8b). Thus, it can be unequivocally stated that this type of biocarbon is characterized by a high ordering degree.

Conclusion

Among the tested products produced during the pyrolysis of wheat straw, cherry stones, flax straw, and maize waste, only the biocarbon from maize waste indicate the clear influence of the type of protective gas on the construction of biocarbon. In particular, a higher ratio of oxygen in the product obtained in a carbon dioxide atmosphere than in nitrogen was found. This is due to the presence of the oxygen of organic functional groups in the biocarbon structure, the presence of which has been confirmed by means of infrared spectrophotometry. On the other hand, the analysis of Raman spectra shows that the products obtained from maize waste in the nitrogen atmosphere were characterized by a larger ordering of the structure, than in the case of biocarbon produced in the presence of carbon dioxide.

References

1. Jeguirim M., Limbusy L.: Biomass chars: elaboration, characterization and applications. *Energies*, 2017, 10, pp. 2040–2046.
2. Azargohar R., Nanda S., Kozinski J., Dalai A., Sutarto R.: Effects of temperature on the physicochemical characteristics of fast pyrolysis bio-chars derived from Canadian waste biomass. *Fuel*, 2014, 125, pp. 90–100.
3. Qing M., Su S., Gao J., Sun Z., Xu K., Xu J., Hu S., Wang Y., Xiang J.: Effects of CO_2/H_2O on the characteristics of chars prepared in $CO_2/H_2O/N_2$ atmospheres. *Fuel Processing Technology*, 2018, 173, pp. 262–269.
4. Senneca O., Cerciello F., Cortese L., Heuer S., Schiemann M., Scherer V.: Effects of CO_2 enriched atmosphere on chars from walnut shells pyrolysis in a drop tube reactor. *Fuel*, 2018, 229, pp. 235–240.

5. Senneca O., Cerciello F., Heuer S., Ammendola P.: Slow pyrolysis of walnut shell in nitrogen and carbon dioxide. *Fuel*, 2018, 225, pp. 419–425.
6. Kan T., Strezov V., Evans T.J.: Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis. *Renewable and Sustainable Energy Reviews*, 2016, 57, pp. 1126–1140.
7. Putun E., Ates F., Putun A.E.: Catalytic pyrolysis of biomass in inert and steam atmospheres. *Fuel*, 2008, 87, pp. 815–824.
8. Zhang H.Y., Xiao R., Wang D.H., He G.Y., Shao S.S., Zhang J.B., Zhong Z.: Biomass fast pyrolysis in a fluidized bed reactor under N_2, CO_2, CO, CH_4 and H_2 atmospheres. *Bioresource Technology*, 2011, 102(5), pp. 4258–4264.
9. Fan B., Jia L., Li B., Yao Y., Huo R., Zhao R., Qiao X., Jin Y.: Study on the effect of the pyrolysis atmosphere on the elemental mercury adsorption characteristics and mechanism of biomass char. *Energy Fuels*, 2018, 32(6), pp. 6869–6878.
10. Molenda J., Swat M., Wolszczak M.: Budowa chemiczna i mikrostrukturalna biowęgli otrzymanych pirolitycznie z odpadów roślinnych. *Przemysł Chemiczny*, 2018, 97(8), pp. 1380–1386 (in Polish).
11. Ferrari A.C., Robertson J.: Interpretation of Raman spectra of disordered and amorphus carbon. *Physical Review B*, 2000, 61(20), pp. 14096–14107.