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Impact of the biomass pyrolysis parameters on the quality of biocarbon obtained from rape straw, rye straw and willow chips

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Abstract. In the article the results of studies conducted regarding the thermal processing of rape straw, rye straw and willow chips applying various parameters of the pyrolysis process are presented. Samples of biomass were subject to thermal processing at various temperatures and process durations, assessing the impact of the applied conditions on physicochemical parameters of the obtained pyrolysis products. The contents of phosphorus, potassium, magnesium, carbon and nitrogen were analysed. The studies have indicated that the pyrolysis process can be used to refine biomass, among others obtained from straw and chips, in the context of using it for fertilization. Modification of the pyrolysis process parameters (temperature, time) significantly impacted the concentration of the analysed macroelements. It has been stated that the highest content of phosphorus, potassium and magnesium in biocarbon (rape straw, rye straw and willow chips) can be obtained performing pyrolysis at the temperature of 5000C for 10 minutes. A significant impact of the pyrolysis parameters – temperature and time on the total content of macroelements in the obtained biocarbon was observed. The highest contents of phosphorus, potassium and magnesium were observed in the case of biocarbon obtained at the temperature of 5000C during 10 minutes, while the temperature of 4000C and duration of 10 minutes allowed to obtain the maximum content of carbon and nitrogen.

Key words: biomass, straw, willow chips, pyrolysis, biocarbon, macroelements.

INTRODUCTION

Due to the physical and chemical properties of biocarbon, it can be used in sequestration of carbon in the soil, production of fertilizers, as well as soil recultivation [13]. Biocarbon has a positive impact on fertility and productivity of the soil and it can protect plants from infections causing diseases [17]. Introduced into the soil, it can contribute to an increase of water capacity of the terrain and decrease soil acidity [8]. One characteristic of biocarbon is its capacity for retention and exchange of nutrients which translates into an increased availability of nutrients for plants and improvement of soil properties [6, 13]. Biocarbon properties also allow its use in remediation of polluted soils, therefore limiting bioavailability of pollution for living organisms [3].

The purpose of the presented study was to examine the impact of parameters of the pyrolysis process on the properties of the obtained biocarbon regarding the content of phosphorus, potassium, magnesium, carbon and nitrogen.

THE ANALYSIS OF RECENT RESEARCHES AND PUBLICATIOS

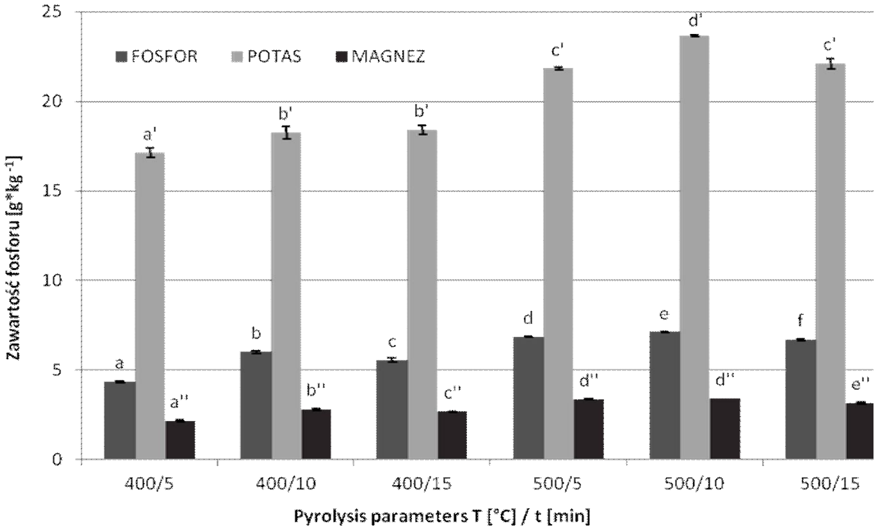
The study material included rape straw, rye straw and willow chips, which were subject to thermal processing. In order to prepare samples for analysis, homogenization of the study material was conducted, which was later divided into equal parts according to the following standards: PN-EN 14780:2011(U) and PN-EN 14778:2011(U). The pyrolysis process was conducted using the LECO TGA 701 thermogravimetric analyser. Thermal conversion of biomass was conducted at the temperatures of 400 and 500oC for 5, 10 and 15 minutes in the nitrogen (99.99% pure) atmosphere. The gas flow was 10l/min, and the level of temperature increase was 30oC/min. The pyrolysis products obtained from rape straw, rye straw and willow chips were subject to studies in the TrueSpec device in order to determine the content of carbon and nitrogen (CHN module) according to standard PN-EN 15104:2011(U). The analysis conducted using the TrueSpec device for simultaneous marking of carbon and nitrogen was based on the principles of the Dumas method, also determined as the method of high-temperature combustion in oxygen. Application of this method allowed to mark elements within a time period not exceeding 4 minutes. The analysed material was also subject to microwave digestion with the concentrated nitrogen acid under increased pressure in Teflon containers in the Milestone ETHOS ONE microwave digestion system. The digestion of the studied material was conducted in three parallel repetitions. Marking the total content of phosphorus, potassium and magnesium in the analysed samples was conducted by means of the optical emission spectrometry of the inductively coupled plasma (ICP-OES) using the Thermo Scientific iCAP Dual 6500 device. To calculate the content of the analysed macro-elements, calibration curves were used, which were prepared using the patterns of the studied compounds.

The obtained results were subject to statistical analysis in the Statistica 10 program. Average values were compared using the Duncan test at the significance level of p=0.05 for n=3.

THE MAIN RESULTS OF THE RESEARCH

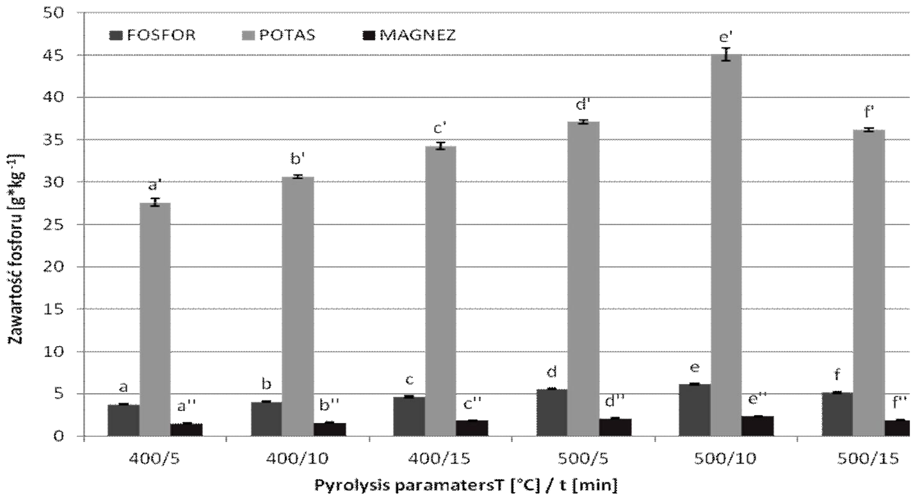
In Fig. 1 the content of phosphorus, potassium and magnesium in biocarbon obtained from rape straw applying various temperature and pyrolysis time parameters was presented. The content of phosphorus, potassium and magnesium in the pyrolysis products suited the relevant ranges: 4.4 – 7.1 $g*kg^{-1}$; 17.1 – 23.6 $g*kg^{-1}$; 2.1 to 3.4 $g*kg^{-1}$. An increase of temperature and extension of duration significantly impacted an increase of the content of the analysed elements. The highest values of phosphorus, potassium and magnesium were observed in biocarbon (rape straw) which occurred at the temperature of 500^0C applied for 10 minutes.

In Fig. 2 the impact of the applied rye straw pyrolysis parameters on the content of phosphorus, potassium and magnesium in the obtained products was presented. The content of phosphorus, potassium and magnesium was observed, accordingly, at the levels of 6.1 $g*kg^{-1}$, 45.1 $g*kg^{-1}$, 2.3 $g*kg^{-1}$. Together with an increase of temperature and duration of the process the content of the studied macro-elements increased significantly reaching the highest values at the temperature of 5000C and in the period of 10 minutes. Further extension of duration of pyrolysis resulted in a significant decrease of the elements' levels.



Legend: Fosfor: Phosphorus, Potas: Potassium, Magnez: Magnesium, Zawartość fosforu: The content of phosphorus

Fig. 1.The content of phosphorus, potassium and magnesium in biocarbon obtained from rape straw depending on the pyrolysis parameters (temperature, time). Various letters indicate statistically significant differences between average values within group x, x', x'' (for $p \leq 0,05$)



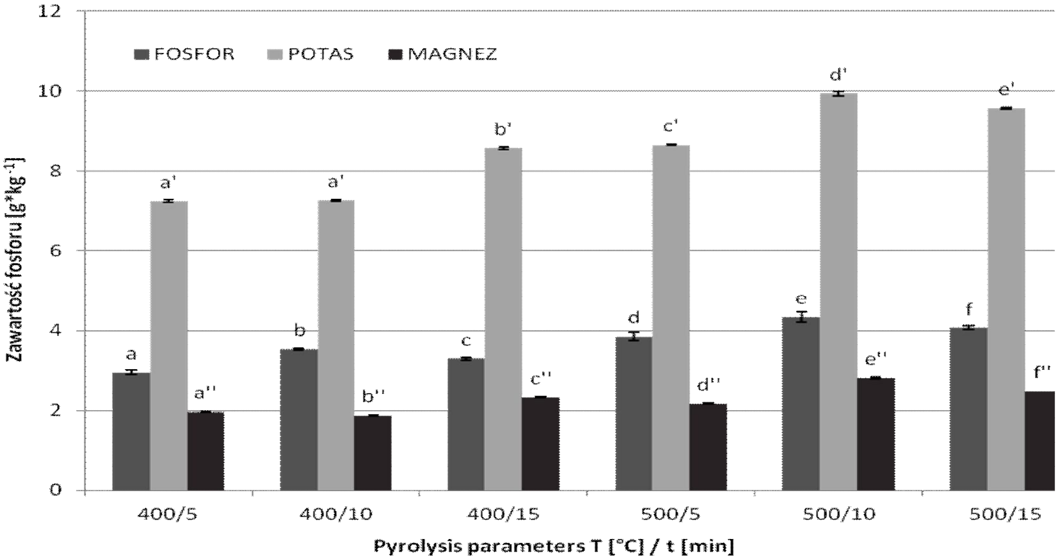
Legend: Fosfor: Phosphorus, Potas: Potassium, Magnez: Magnesium, Zawartość fosforu: The content of phosphorus

Fig. 2.The content of phosphorus, potassium and magnesium in biocarbon obtained from rye straw depending on the pyrolysis parameters (temperature, time). Various letters indicate statistically significant differences between average values within group x, x', x'' (for $p \leq 0,05$)

In Fig. 3. The results regarding the content of phosphorus, potassium and magnesium in the studied biocarbon obtained from willow chips depending on temperature and duration of the pyrolysis process were presented.

The maximum values for P, K and Mg, accordingly, at the level of 4.3 g*kg^{-1}; 9.9 g*kg^{-1}; 2.8 g*kg^{-1} were determined for the pyrolysis process at the temperature of 500^{0}C and in the period of 10 minutes. The highest content among the analysed elements was observed in the case of potassium – 9.9 g*kg^{-1}, similar as in the case of the pyrolysis products obtained from rape straw – 23.6 g*kg^{-1} and rye straw – 45.1 g*kg^{-1}. While the lowest content was observed in the case of magnesium: rape straw – 2.1 to 3.4 g*kg^{-1}, rye straw – 1.9 to 2.3 g*kg^{-1}, willow chips – 1.9 to 2.8 g*kg^{-1}.

In Tab. 1. the impact of the applied pyrolysis parameters on the content of carbon and nitrogen in the obtained biocarbon was presented. The highest contents of carbon and nitrogen were obtained in the pyrolysis process conducted at the temperature of 400^{0}C and in the period of 10 minutes. Biocarbon obtained from willow chips was characterized by the highest level of carbon, the value of which reached between 67.6 to 73.6%, while in the case of rye straw and rape straw these values were at the levels of 69.5 and 59%. The maximum concentration of nitrogen in the pyrolysis products was obtained from rye straw, rape straw and willow chips and it was 1.1, 1.9 and 1.6%, respectively. Analysing the substrates used in the pyrolysis process we can determine that biocarbon obtained from rape straw was characterized by the highest concentration of nitrogen. According to [2], the content of carbon in the products obtained in thermal processing at the temperatures 220-300^{0}C was 52-64%, while the content of nitrogen was between 0.2-2%.



Legend: Fosfor: Phosphorus, Potas: Potassium, Magnez: Magnesium, Zawartość fosforu: The content of phosphorus

Fig. 3. The total content of phosphorus, potassium and magnesium in biocarbon obtained from willow chips applying various pyrolysis parameters (temperature, time).Various letters indicate statistically significant differences between average values within group x, x', x'' (for $p \leq 0,05$)

Table 1.The content of carbon and nitrogen in biocarbon obtained applying various pyrolysis parameters (temperature, time)

	T [°C] / t [min]					
	400/5	400/10	400/15	500/5	500/10	500/15
	C [%]					
Rye straw	65.61 ± 0.09	69.52 ± 0.65	64.35 ± 0.36	67.13 ± 0.04	65.23 ± 0.06	65.98 ± 0.66
Rape straw	58.43 ± 034	59.01 ± 0.21	57.63 ± 0.60	57.14 ± 0.64	56.84 ± 0.42	57.89 ± 0.49
Willow chips	67.65 ± 0.54	73.60 ± 0.02	67.70 ± 0.16	71.50 ± 0.09	73.15 ± 0.33	70.79 ± 0.22
	N [%]					
Rye straw	0.71 ± 0.01	1.12 ± 0.01	0.87 ± 0.11	0.80 ± 0.04	1.03 ± 0.01	0.84 ± 0.07
Rape straw	1.28 ± 0.05	1.92 ± 0.06	1.42 ± 0.01	1.45 ± 0.12	1.54 ± 0.03	1.42 ± 0.01
Willow chips	1.18 ± 0.02	1.60 ± 0.06	1.07 ± 0.01	1.35 ± 0.01	1.45 ± 0.07	1.47 ± 0.12

The authors stated that modifications of parameters (temperature and time) in the torrefaction process of chips of apple tree branches can cause changes in the contents of carbon and nitrogen by 16 and 0.5%, respectively. [10] argue that the pyrolysis products obtained from straw and chips at the temperature of 350°C are characterized by the content of carbon at the level of 64, and 74%, respectively and nitrogen at the level of 1.3 and 0.3%. [19] note that an increase of temperature in the torrefaction process of oat straw results in higher carbonization of the material, the maximum level of which – 57.1% was determined for the product obtained at the temperature of 300^0C. Similar results were obtained by [5], who conducted pyrolysis of oak and pine wood at the temperatures 300, 400, 500 and 600^0C and observed significant changes of the content of carbon in the obtained pyrolysis products, the maximum value of which was 75%..

In Tab. 2. the highest marked concentrations of elements in biocarbon obtained using various pyrolysis parameters were presented in comparison to other natural fertilizers. It was stated that the temperature of 500^0C and duration of 10 minutes are the optimal pyrolysis conditions which allow to obtain the maximum contents of phosphorus, potassium and magnesium in biocarbon obtained from rape straw, rye straw and willow chips. In the case of carbon and nitrogen, the maximum contents of these elements in all the analysed materials were marked in the biocarbon obtained at the temperature of 400^0C during 10 minutes. The biocarbon obtained from rape straw was characterized by the highest concentration of phosphorus, magnesium and nitrogen, respectively, at the level of 7.1, 3.4 g*kg^{-1} and 1.9 %. In the pyrolysis products obtained from rye straw the maximum content of potassium was observed at the level of 45.1 g*kg^{-1}, while the highest content of carbon – 73.6% was identified in biocarbon obtained from willow chips. Biocarbon in comparison to biomass ash was characterized by a lower content of phosphorus, potassium and magnesium, but a higher concentration of carbon and nitrogen. In comparison to another natural fertilizer, such as cattle manure, the obtained biocarbon was characterized by a much higher content of the analysed elements.

Tab. 3. presents the values of the calculated correlation coefficients between the selected elements of analysed materials. A high positive correlation was determined between the contents of phosphorus and magnesium, as well as magnesium and carbon. The values of the correlation coefficients were 0.74 and 0.63, respectively.

Table 2.The highest contents of the analysed elements in biocarbon obtained from rape straw, rye straw and willow chips in comparison with other natural fertilizers.

	Rape straw	Rye straw	Willow chips	Biomass ash[1]	Cattle manure [1]
	[g*kg^{-1}]				
Phosphorus	7.1 ± 0.04*	6.1 ± 0.11*	4.3 ± 0.13*	14.7 ± 0.45	2.3 ± 0.12
Potassium	23.6 ± 0.07*	45.1 ± 0.72*	9.9 ± 0.05 *	70.5 ± 0.42	4.9 ± 0.21
Magnesium	3.4 ± 0.01*	2.3 ± 0.04*	2.8 ± 0.02*	27.2 ± 0.61	1.1 ± 0.05
	%				
Carbon	59.01 ± 0.21**	69.5 ± 0.65**	73.6 ± 0.02**	1.22 ± 0.03	19.2 ± 0.32
Nitrogen	1.9 ± 0.06**	1.1 ± 0.01**	1.6 ± 0.06**	0.2 ± 0.02	3.35 ± 0.07

* - biocarbon obtained at the temperature of 500^0C during 10 minutes.
** - biocarbon obtained at the temperature of 400^0C during 10 minutes.
[1]–authors' own studies

Table 3. Correlation coefficients between selected elements in the analysed materials.

	Phosphorus	Potassium	Magnesium	Carbon	Nitrogen
Phosphorus	1	0.48	0.74	0.48	0.22
Potassium		1	-0.18	-0.12	0.05
Magnesium			1	0.63	0.32
Carbon				1	-0.22
Nitrogen					1

CONCLUSIONS

1. The conducted studies indicated that the pyrolysis process of biomass significantly impacted the quality of the obtained biocarbon.
2. The obtained biocarbon was characterized by a high total content of phosphorus, potassium and magnesium, respectively, at the level of 7.1, 45.1, 3.4 g*kg^{-1} and it can be used as a valuable natural fertilizer.
3. A significant impact of the pyrolysis parameters – temperature and time on the total content of macroelements in the obtained biocarbon was observed.
4. The highest contents of phosphorus, potassium and magnesium were observed in the case of

biocarbon obtained at the temperature of 500^{0}C during 10 minutes, while the temperature of 400^{0}C and duration of 10 minutes allowed to obtain the maximum content of carbon and nitrogen.

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