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ORIGINAL PAPER

FT-IR ANALYSIS AND THE CONTENT OF PHENOLIC COMPOUNDS IN EXOGENOUS ORGANIC MATTER PRODUCED FROM PLANT BIOMASS*

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ABSTRACT

Pyrolysis causes changes in physical and chemical properties of plant biomass, which consequently determine its further use. For this reason, this study aimed at: (i) comparing the effect of the temperature of a pyrolytic process (350°C and 550°C) on the content of total phenolic compounds (TPC) and water soluble phenolic compounds (WSPC) in plant biomass and biochars; (ii) verifying changes in the content of functional groups identified by the FT-IR method; and (iii) assessing the elemental composition, porosity, and morphological properties of plant biomass before and after pyrolysis. The FT-IR analysis showed that biochars produced at 550°C underwent partial decomposition of hemicellulose, cellulose, and lignin, in addition to which the temperature affected the degradation of aromatic C fractions. Biochars produced at 350°C had a lower content of functional groups and lower hydrophilicity compared to biochars produced at 550°C. The pyrolytic process significantly changed the elemental composition, porosity, and morphological properties of biochars. Both temperatures, 350°C and 550°C, significantly

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decreased the content of total and water soluble phenolic compounds. Morphological analysis of biochars revealed that biochars retained the specific surface area and pore volume similar in value to these parameters measured in the feedstocks from which they had been produced. The pyrolysis of wheat and miscanthus straw also reduced the polarity (O+N)/C in biochars, which is a desirable finding, testifying to the development of functional groups.

Keywords: biochar, FT-IR, elemental composition, phenolic compounds, SEM analysis.

INTRODUCTION

Plant biomass is one of the most accessible and significant renewable energy sources in any country's economy (Li et al. 2013). In recent years, one of the most popular ways of managing this type of biomass has been its thermal transformation into biochar (TSAI et al. 2007, MARY et al. 2016, GONDEK et al. 2017, MIERZWA-HERSZTEK et al. 2017). The constantly growing interest in biochar results from its properties, including the ability to mitigate effects of global warming, improve soil quality, and neutralize contaminants (JINDO et al. 2014, AMELOOT et al. 2015, AMINI et al. 2016, MIERZWA-HERSZTEK et al. 2018). The variety of biochar applications depends on its physical and chemical properties, which result from the process parameters (i.e. temperature, time, pressure) or the type of feedstock, i.e. straw, sewage sludge, woody biomass (PETRE et al. 2011, MARY et al. 2016). Generally, biochars produced at low temperatures ($\leq 400^{\circ}\text{C}$) have a substantial content of volatile compounds and easily degradable substances, which may be a source of nutrients for soil microorganisms and plants (MUKHERJEE, ZIMMERMAN 2013, JINDO et al. 2014, MIERZWA-HERSZTEK et al. 2018). On the other hand, biochars obtained at higher temperatures ($\geq 500^{\circ}\text{C}$) are characterized by a large specific surface area and high porosity. In addition, biochars produced at higher temperatures contain more aromatic carbon structures affecting sorption capacity (desirable for remediation) and simultaneously making them resistant to microbial decomposition (KRULL et al. 2009).

The declining content of organic matter in soils has been recognized by the Commission of the European Communities (2006) as one of the main causes of soil degradation. This problem can be resolved by adding exogenous organic matter (EOM), such as biochar, to soil. With its high carbon content ($>50\%$), biochar is thought to be capable of significantly improving soil fertility. Moreover, the incorporation of exogenous organic matter into soils can have great impact on the cycling of soil organic carbon (PETRE et al. 2011). EOM covers a very wide range of biodegradable organic materials from agriculture, forestry, industry, or urban green areas. Therefore, the physical and chemical properties of these materials are highly varied and they have different effects on soil properties.

There is a wide number of tools to assess chemical and physical properties of EOM. Nowadays, the use of Fourier Transform Infrared (FT-IR) spec-

trosopy has been considered as one of the most effective techniques to study and understand the chemical and surface chemistry in various types of biomass (i.e. identification of functional groups). Another useful tool to assess morphological changes of biomass before and after pyrolysis is Scanning Electron Microscopy (SEM). The main functional groups of biochar are aromatic and heterocyclic carbons, which are claimed to be stable in soil due to their chemical recalcitrance. Characterization of functional groups in biochar is critical to our understanding of mechanisms of pyrolysis and how EOM affects chemical and physical properties of soil. Moreover, recognition of biochar functional groups is important to gain benefits from the use of biochar products.

The assessment of total phenolic compounds (TPC) and water soluble phenolic compounds (WSPC) in plant biomass and in biochars is an important stage in the characterization of these materials. This notwithstanding, there is hardly any information on this subject in the literature. The data published so far concern only the content of phenolic compounds in soils fertilized with different kinds of fertilizers (MIN et al. 2015, QUARTACCI et al. 2017) or the modification of a pyrolytic process in order to increase the TPC content in pyrolytic bio-oils (CZAJCZYŃSKA et al. 2017). Recent studies suggest that it is the form rather than the chemical structure of phenolics that can determine their fate in soils, which raises doubts about the conventional classification of phenolics into a slow, recalcitrant pool in the C dynamic climate model. For example, physically and chemically protected phenolic compounds can persist longer than WSPC forms, providing feedback to soil organic matter decomposing microorganisms via changing soil pH, enzyme activities and nutrient availability (MIN et al. 2015). Fertilization of soil with organic materials such as straw or biochar causes an increase in the content of phenolic compounds, which can control SOM decomposition processes (TOBERMAN et al. 2010, MIN et al. 2015), nutrient cycling (SADEJ et al. 2016, QUARTACCI et al. 2017), and biotic processes (soil microbial activity and diversity). The missing information about the TPC and WSPC content in biochars implicates a future direction in research into phenolic compounds in these materials, in addition to studying their role and effect on the organic matter decomposition in soil after an application of biochar.

The following research hypotheses were verified in the study: (i) the pyrolytic process reduces the content of TPC and WSPC in plant biomass, (ii) thermal conversion of biomass increases the content of functional groups identified by the FT-IR method, and (iii) the temperature of plant biomass pyrolysis has a significant effect on the elemental composition, porosity, and morphological properties of biochars.

MATERIAL AND METHODS

Wheat and miscanthus biomass, pyrolytic process and characteristics of biochars

The research material consisted of wheat and miscanthus biomasses originating from the Malopolska Province (southern Poland). Samples of the two types of biomass were dried at 65°C, ground in a laboratory mill and 5 mm sieved. The thermal processing was carried out in laboratory conditions using a biomass gasification unit with a limited supply of air (1-2%), (IBI 2015). The temperatures in the combustion chamber were set at 350°C and 550°C. The exposure time was 15 min and the heating rate was 10°C min⁻¹.

Wheat and miscanthus biomass samples after and before the pyrolysis were ground and 0.5 mm sieved. The percentage of biochar yield was calculated as follows (MARY et al. 2016):

$$\text{Yield}_{\text{biochar}} = \frac{m_{\text{biochar}}}{m_{\text{raw}}} \cdot 100\%,$$

where: Yield_{biochar} = yield of biochar, %;

m_{biochar} = mass of biochar, kg;

m_{raw} = mass of raw biomass, kg.

pH, ash content, elemental composition and content of macroelements and trace elements

The following parameters were determined in the wheat biomass (WS), miscanthus biomass (MS), wheat biomass biochar (WSB), and miscanthus biomass biochar (MSB): dry matter content at 105°C for 12 h, ash after ashing a sample in a chamber furnace at 450°C for 12 h (AGRAFIOTI et al. 2013), pH of materials (material:water = 1:5) was electrochemically determined using a pH - meter (pH - meter CP – 505, Elmetron Sp.jul., Zabrze), electrical conductivity (material:water = 1:5) using a conductivity meter (Conductivity/Oxygen meter CCO – 501, Hotek Technologies, Tacoma, Washington, USA) (RAJKOVICH et al. 2011, GONDEK, MIERZWA-HERSZTEK 2017).

The elemental composition (C, H, N, S) of wheat and miscanthus biomasses and biochars was determined using a CHNS analyzer (Vario EL Cube, Elementar Analysensysteme). The total content of oxygen was derived according to the DIN 51733 (EBC 2017) method as follows:

$$\text{O (\%w/w)} = 100 - \text{ash (\%w/w)} - \text{C (\%w/w)} - \text{N (\%w/w)} - \text{H (\%w/w)} - \text{S (\%w/w)}$$

The total content of macroelements (P, K, Ca, Mg, Na) and trace elements (Cu, Cd, Cr, Fe, Pb, Mn, Ni, Zn) was determined after incineration of wheat and miscanthus biomasses and biochars in a chamber furnace (at 450°C for 12 h) and mineralization of the residue in a mixture of concentrated nitric and perchloric acids (3:2) (v/v). Mercury was determined on an AMA 254 apparatus to which it was released from an amalgamator and

measured by the atomic absorption method at a wavelength of 254 nm. Arsenic content was determined using the inductively coupled plasma mass spectrometry technique (ICP-MS, Agilent 7500ce ICP-MS apparatus) after previous extraction of the wheat and miscanthus biomass and biochars in a microwave system (MARS XPRESS, CEM Corp.) in a mixture of concentrated HCl and HNO₃ acids (3:1) (v/v) (OLESZCZUK et al. 2007).

Content of total and water soluble phenolic compounds

Total phenolic compounds (TPC) were isolated from the wheat and miscanthus biomasses and biochars using an extraction mixture of ethyl alcohol (96% v/v) + redistilled water and acetic acid in a ratio of 70:28:2 (v/v/v) in a ratio of 1:10 (w/v) (wheat and miscanthus biomasses and biochars: extraction mixture). The samples were placed in polyethylene bottles and shaken on a rotary shaker for 24 h (twice) at a speed of 40 rpm, and then filtered through a cellulose filter. The extracted phenolic compounds were determined using the spectrophotometric method, performing the absorbance measurements at a wavelength $\lambda=730$ nm in relation to catechine solution as a standard (HRUSZKA 1982*a*, 1982*b*). Water soluble phenolic compounds (WSPC) were also determined by the colorimetric method, in aqueous extracts (1:10 w/v – wheat and miscanthus biomass and biochars : redistilled water), using the Folin-Ciocalteu reagent (Sigma-Aldrich®), and performing the absorbance measurement at a wavelength of $\lambda=750$ nm in relation to vanillic acid solution as a standard (HRUSZKA 1982*a,b*, LOWE 1993).

Specific surface area (S_{BET})

The specific surface area (S_{BET}) as well as pore volume and diameter of wheat and miscanthus biomasses and biochars were determined using the multifunction accelerated surface area and porosimetry analyzer ASAP 2010 (Micrometics, USA). The samples were degassed and their specific surface area (S_{BET}) was determined by physical nitrogen adsorption using the Brunauer-Emmett-Teller equation (BARRET et al. 1951).

Surface morphological changes (SEM analysis)

Morphological changes in the surface of wheat and miscanthus biomass and biochars were tested under a scanning electron microscope (SEM). For SEM observations, samples were applied to a polycarbonate membrane filter with a 3 μm mesh, attached to aluminum stubs and sputtered with 20 nm of gold using a Turbo-Pumped Sputter Coater Quorum Q 1500T ES. Diatoms were observed using a Hitachi SU 8010 at 5 kV (STANEK-TARKOWSKA et al. 2016).

Fourier-transform infrared (FT-IR) spectroscopy

Fourier-transform infrared (FT-IR) spectroscopy of wheat and miscanthus biomass as well as biochars was performed on a Thermo Scientific

Nicolet 6700 spectrometer, using the Praying Mantis accessory for the DRIFT technique in the wave number range of 4000 - 400 cm^{-1} and the resolution of 1 cm^{-1} . Chemical functional groups were assigned to wave numbers from FT-IR spectra as follows (WU et al. 2012, GUO, CHEN 2014):

- 3600-3200 cm^{-1} to O–H stretching of hydroxyl groups from alcohols, phenols, and organic acids;
- 2950-2850 cm^{-1} to C–H stretching of aliphatic CH_x and alkyl structures;
- 1740-1700 cm^{-1} to C=O stretching of carboxyl and ketones;
- 1630-1600 cm^{-1} to C=C stretching of aromatic components and to a smaller extent to C=O stretching in quinones and ketonic acids;
- 1590-1580 cm^{-1} to COO^- asymmetric stretching;
- 1440 cm^{-1} to C=C stretching of aromatic C;
- 1375 cm^{-1} to aliphatic deformation of CH_2 or CH_3 groups or O–H bending of phenolic –OH
- 1280-1270 cm^{-1} to O–H stretching of phenolic compounds;
- 1110-1030 cm^{-1} to C–O–C.

Statistical analysis

All the analyses were carried out in triplicate and the results were expressed in average values \pm standard deviation.

RESULTS AND DISCUSSION

The yield of biochars

The literature shows that the yield of biochar is closely related to the settings of a pyrolytic process, such as temperature, pressure, heating rate and heating time, as well as the the type of biomass used in the process (MARY et al. 2016, GONDEK et al. 2017, MIERZWA-HERSZTEK et al. 2017). Parameters of the pyrolytic process also have a direct impact on the chemical and physical properties of the pyrolysed biomass (JINDO et al. 2014, GONDEK, MIERZWA-HERSZTEK 2017). The right temperature for obtaining the highest yield of biochar from plant biomass residues is 350°C (MARY et al. 2016). In our study, the yields of biochar obtained from wheat and miscanthus biomasses were 48 and 54%, respectively (Figure 1). Lower yields of biochar produced from wheat biomass (32.4%) and miscanthus biomass (35.5%) were presented by MARY et al. (2016). The yield of biochars after pyrolysis at 550°C more than halved, down to 21% (WSB 550) and 18% (MSB 550), respectively. This may probably be due to different content of lignin, hemicellulose, cellulose, and oxygen in pyrolysed biomass (WU et al. 2012). As stated by SUGUMARAN et al. (2012), a higher lignin content results in higher biochar yield, and a higher hemicellulose and cellulose content in the biomass leads to the formation of volatile compounds.

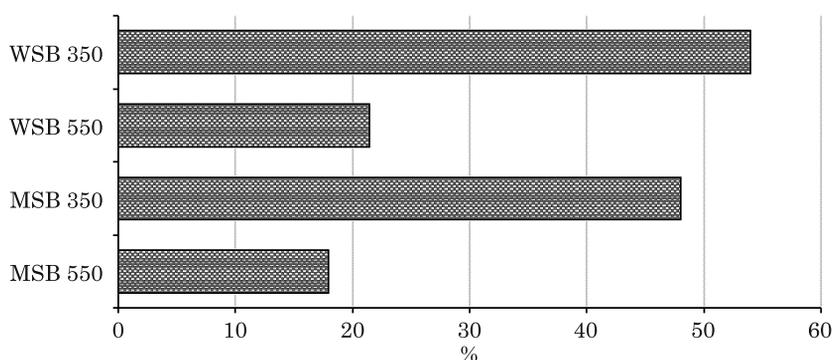


Fig. 1. Effect of pyrolysis on the yields of wheat and miscanthus biomass, where: WSB 350 – wheat biomass biochar produced at 350°C, WSB 550 – wheat biomass biochar produced at 550°C, MSB 350 – miscanthus straw biochar produced at 350°C, MSB 550 – miscanthus straw biochar produced at 550°C

Chemical composition of plant biomass and biochars

Biomass used in our study, i.e. wheat straw (WS) and miscanthus straw (MS), had lower pH and electrical conductivity (EC) values, and less ash and dry matter than WSB and MSB biochars produced from these two types of biomass at both temperatures (Table 1). The ash content in the tested biochars was similar and ranged from 104 g to 134 g kg⁻¹. The ash content in biochars can influence the immobilization of mineral and organic contaminants in soil, and it usually tends to increase gradually with rising pyrolysis temperatures. However, according to VITHANAGE et al. (2017), an increased ash content resulting from increased temperature is not a rule, because the former is strictly related to the content of alkaline elements and organic matter in feedstocks.

The results of the elemental analysis for C, H, N, O and S showed that pyrolysis of wheat and miscanthus biomasses increased the C and N content and decreased the S, H, and O content (Table 1). Wheat biochars produced at both temperatures had more C than miscanthus biochars (MSB 350, MSB 550). Our results are similar to those obtained by SUGUMARAN et al. (2012) and GONDEK et al. (2017) for biochars produced from different agricultural biomasses. On the other hand, LI et al. (2013) reported that biomass pyrolysed at 300 to 800°C only contributed to an increase in the carbon content, while the levels of other components, like H, N, O, and S were reduced. As noted by LANGE et al. (2018), the nitrogen content in biochar usually does not exceed 6% and decreases as the pyrolysis temperature increases; however, the N content in biochars derived from plant feedstocks does not usually exceed 1%. This theory is confirmed by our research results (Table 1). LANGE et al. (2018) also argued that N retention in biochars produced at temp. around 300°C can be increased by increasing the size of feedstock particles. Also VITHANAGE et al. (2017) reported that almost half of the N and S content can be lost during pyrolysis when the temp. increases from 300 to 600°C.

Table 1

Chemical and physical properties of wheat and miscanthus biomass and biochars

Determination	Unit	WS	MS	WSB 350	MSB 350	WSB 550	MSB 550
pH in H ₂ O	-	5.84±0.15	6.18±0.43	6.52±0.60	6.28±0.42	10.4±0.01	10.3±0.02
EC	(mS cm ⁻¹)	4.48±0.21	3.23±0.45	3.78±21	3.45±18	1.35±0.04	0.68±0.04
Dry matter	(g kg ⁻¹)	952±0.2	947±0.3	966±2	977±1	993±0.1	995±0.3
Ash	(g kg ⁻¹ DM)	55.8±3.1	60.8±3.6	118±1	134±4	119±3	104±5
Carbon	(%)	46.1±1.0	47.2±0.9	62.9±1.8	67.7±3.3	76.4±2.69	82.0±1.13
Nitrogen	(%)	0.37±0.04	0.25±0.05	1.00±0.05	0.50±0.06	0.86±0.10	0.65±0.04
Sulfur	(%)	0.06±0.01	0.03±0.00	0.05±0.01	0.02±0.00	0.10±0.01	0.11±0.01
Hydrogen	(%)	6.39±0.20	6.63±0.08	4.58±0.09	4.67±0.19	2.95±0.49	2.85±0.06
Oxygen	(%)	41.0±1.1	40.3±1.0	18.0±1.9	15.4±3.5	9.27±0.6	4.58±0.26
H/C	-	0.14	0.14	0.07	0.07	0.04	0.03
(O + N) / C	-	0.90	0.86	0.30	0.23	0.14	0.06
Specific surface area (S _{BET})	(m ² g ⁻¹)	0.55±0.02	0.39±0.04	0.67±0.09	0.44±0.01	276±0.10	333±0.10
Total pore volume	(cm ³ g ⁻¹)	0.0009	0.0007	0.0016	0.0023	0.171	0.178
Pore diameter	(nm)	6±2	7±1	12±3	23±3	3.37±0.05	2.14±0.05
Maximum pore volume	(nm)	67	77	123	108	66	112

± standard deviation, *n*=3

The H/C ratio is often used as an index for assessing the degree of aromaticity and stability of biochar, which is important for its long-term carbon sequestration in the environment (KRULL et al. 2009). In our research, the H/C ratio of biochars WSB 350 and MSB 350 was 0.07, and of biochars WSB 550 and MSB 550 0.04 and 0.03, respectively (Table 1). The calculated H/C values indicated that the structure of biochars WSB 350 and MSB 350 would be closer to biomass composition than to graphite and would have a mean residence time < 100 years. Conversely, biochars with the O : C ratio in the range of 0.2-0.6 would be expected to have the mean residence time of 100-1000 years (KRULL et al. 2009, MARY et al. 2016). The pyrolysis of wheat and miscanthus biomass also reduced the polarity (O+N)/C in all biochars, especially in biochars produced at 550°C. It is a very beneficial effect, which gives rise to the development of functional groups (AHMAD et al. 2012). Generally, the values of H/C and (O+N)/C decreased as the temperature increased. The reduction in both indexes in all biochars compared to the raw materials is due to the dehydration and decarboxylation processes. In addition, it is associated with the formation of structures containing con-

centrated aromatic carbon structures, such as aromatic rings determined by the FT-IR method (1600 cm^{-1}), that take place during the pyrolysis of biomass (Figures 2, 3). Data in Table 1 suggest that an increase in the temperature results in a larger loss of H and O compared to C. Moreover, the dehydrogenation of CH_3 as a result of pyrolysis indicates a change in the biochar recalcitrance. According to RUTHERFORD et al. (2012) and JINDO et al. (2014), biomass typically comprises labile and recalcitrant O fractions. Labile O frac-

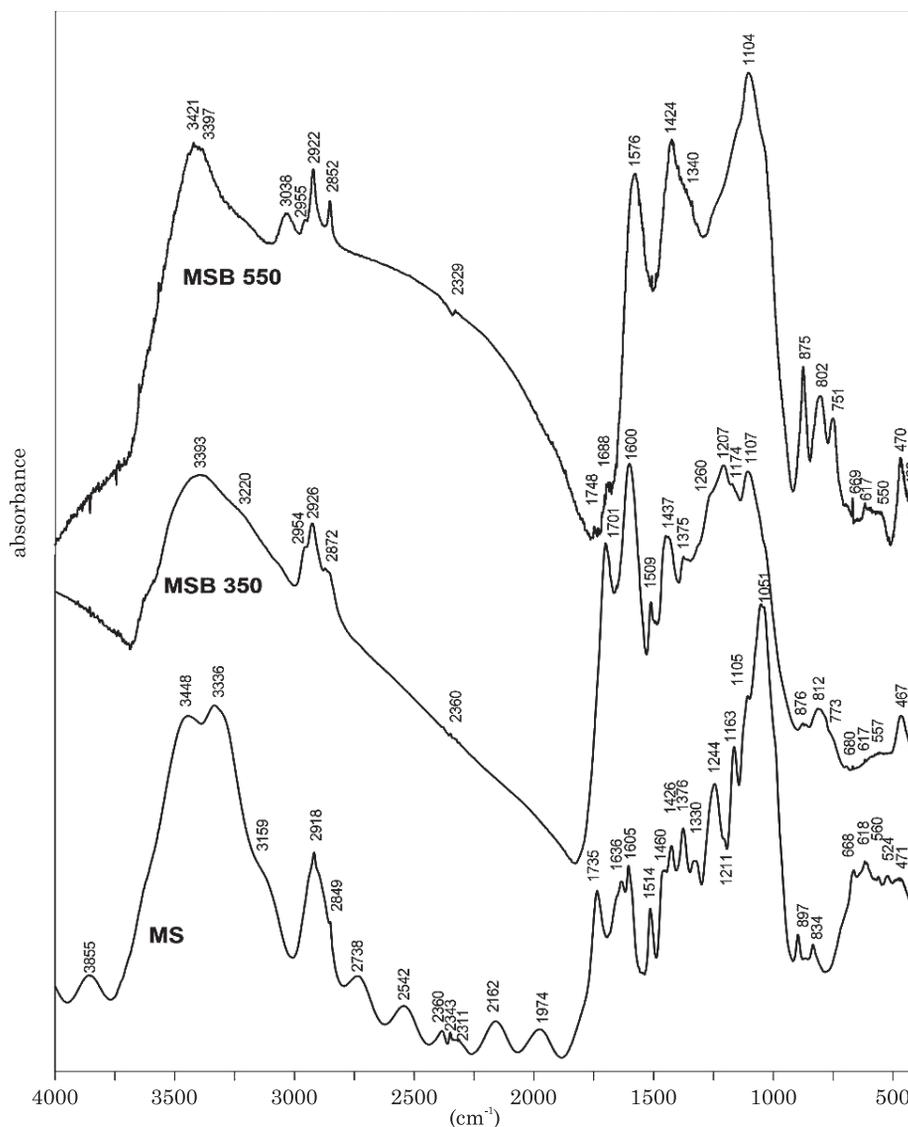


Fig. 2. The spectra of miscanthus biomass (MS) and miscanthus biochar produced in 350°C (MSB 350) and in 550°C (MSB 550)

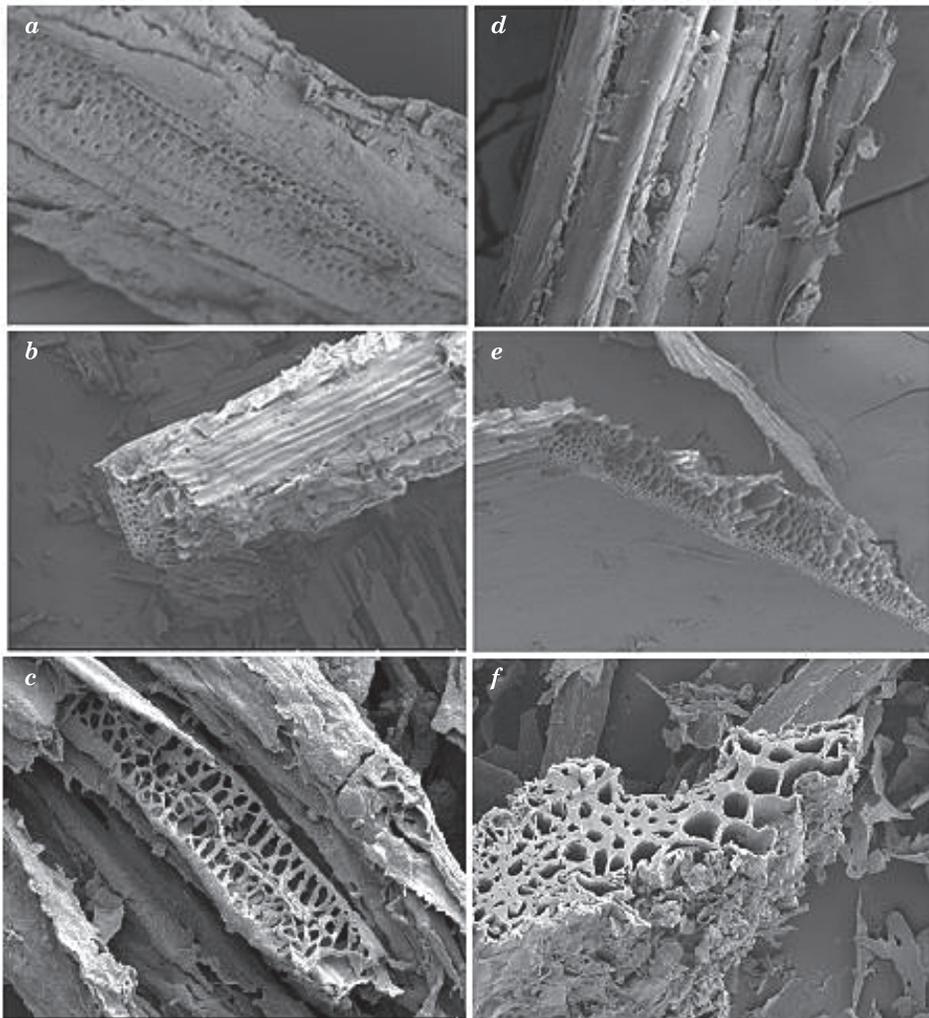


Fig. 3. Representative scanning electron micrographs of WS (a), WSB 350 (b), WSB 550 (c), MS (d), MSB 350 (e) and MSB 550 (f)

tions are rapidly lost after the initial heating, while recalcitrant O fractions are retained in the biochar. Significant reductions in the H/C and (O+N)/C ratios in biochars are also due to the high hemicellulose and cellulose content in plant biomass (including straw), which are much easier than lignin to decompose during pyrolysis (WU et al. 2012). The results obtained by AHMAD et al. (2012) and VITHANAGE et al. (2017) also indicate that the O/C molar ratio is an indicator of surface hydrophilicity and can be used for estimating polar functional groups on the biochar surface. These authors showed that at higher temp., the O/C ratio is smaller and the biochar surface presents greater aromatic character and lower hydrophilicity due to the high degree

of carbonization and the loss of polar functional groups. According to Li et al. (2013), the most favourable values of the O/C and (O+N)/C atomic ratios can be obtained at a temp. exceeding 500°C. However, as mentioned before, numerous studies showed that the most favorable temperature for the production of agricultural-use biochar is the range of 300-350°C (Wu et al. 2012, AMELOOT et al. 2015). Biochars obtained in this study also have a larger specific surface area (S_{BET}), (especially biochars produced at 550°C), pore volume and diameter compared to the raw materials (Table 1). It should be noted that both the specific surface area and pore volume of wheat biomass and biochar produced from this material were higher than those of miscanthus biomass and miscanthus biochar. A reverse relationship was observed for the pore diameter.

The content of macronutrients and trace elements in biochars varied, depending on the type of feedstock and pyrolysis temperature (Table 2). Wheat biomass contained more macronutrients than miscanthus straw did, and the same dependency was visible for biochars derived from these feedstocks. The total trace element content varied due to the kind of pyrolysed feedstock and pyrolysis temperature (Table 2). Except for the content of Cd in WSB 350 (1.20 mg Cd kg⁻¹ DM), the content of the other trace elements

Table 2

Content of macroelements and trace elements in wheat and miscanthus biomass and biochars

Element	WS	MS	WSB 350	MSB 350	WSB 550	MSB 550	EBC* basic quality grade	EBC* premium quality grade	IBI**
P (g kg ⁻¹ DM)	1.04	0.94	1.17	0.73	2.16	2.08	D***	D	D
K (g kg ⁻¹ DM)	4.95	1.34	11.9	2.81	12.7	8.61	D	D	D
Ca (g kg ⁻¹ DM)	1.36	0.91	7.19	2.00	9.12	6.91	D	D	D
Mg (g kg ⁻¹ DM)	0.43	0.28	1.13	0.57	1.73	1.44	D	D	D
Na (mg kg ⁻¹ DM)	60.1	39.0	48.4	38.4	101	45.9	D	D	D
Cu (mg kg ⁻¹ DM)	1.32	1.78	3.19	4.14	8.16	6.20	<100	<100	143–6000
Zn (mg kg ⁻¹ DM)	32.9	14.4	48.8	32.0	120	73.8	<400	<400	416–7400
Fe (mg kg ⁻¹ DM)	127	200	326	505	1271	1139	–	–	–
Mn (mg kg ⁻¹ DM)	41.2	34.6	72.9	74.2	212	180	–	–	–
Pb (mg kg ⁻¹ DM)	0.73	1.15	1.62	2.44	4.62	4.37	<150	<120	121–300
Cr (mg kg ⁻¹ DM)	2.22	1.89	4.01	4.29	9.72	9.67	<90	<80	93–1200
Cd (mg kg ⁻¹ DM)	0.56	0.14	1.20	0.31	0.31	0.19	<1.5	<1.0	1.4–39
Ni (mg kg ⁻¹ DM)	1.12	0.82	1.97	1.78	4.55	4.98	<50	<30	47–420
As (mg kg ⁻¹ DM)	0.04	0.95	0.25	0.13	6.14	0.39	<13	<13	13–100
Hg (mg kg ⁻¹ DM)	0.02	0.01	0.08	0.05	0.02	0.04	<1	<1	1-17

n=3, * the maximum content of heavy metals referred to EBC (2017) and ** IBI (2015) standards
 *** D – declaration (% of total mass, dry basis)

in all the tested biochars was significantly lower than the values recommended for premium class biochars (EBC 2017). However, taking into account the criteria for biochars developed by the IBI (2015), the content of none of the analyzed trace elements exceeded the limit value. It should be noted, however, that the higher pyrolysis temperature resulted in higher concentrations of the tested elements, which corresponded with the mass loss (HOSSAIN et al. 2011). Also, arsenic (As) was discovered in the tested biochars and its content, as in the case of other elements, increased as the temperature increased (Table 2). As stated by Vithanage et al. (2017), like mercury, arsenic is one of the rare elements present in biochars, and its presence is mainly due to its content in a feedstock.

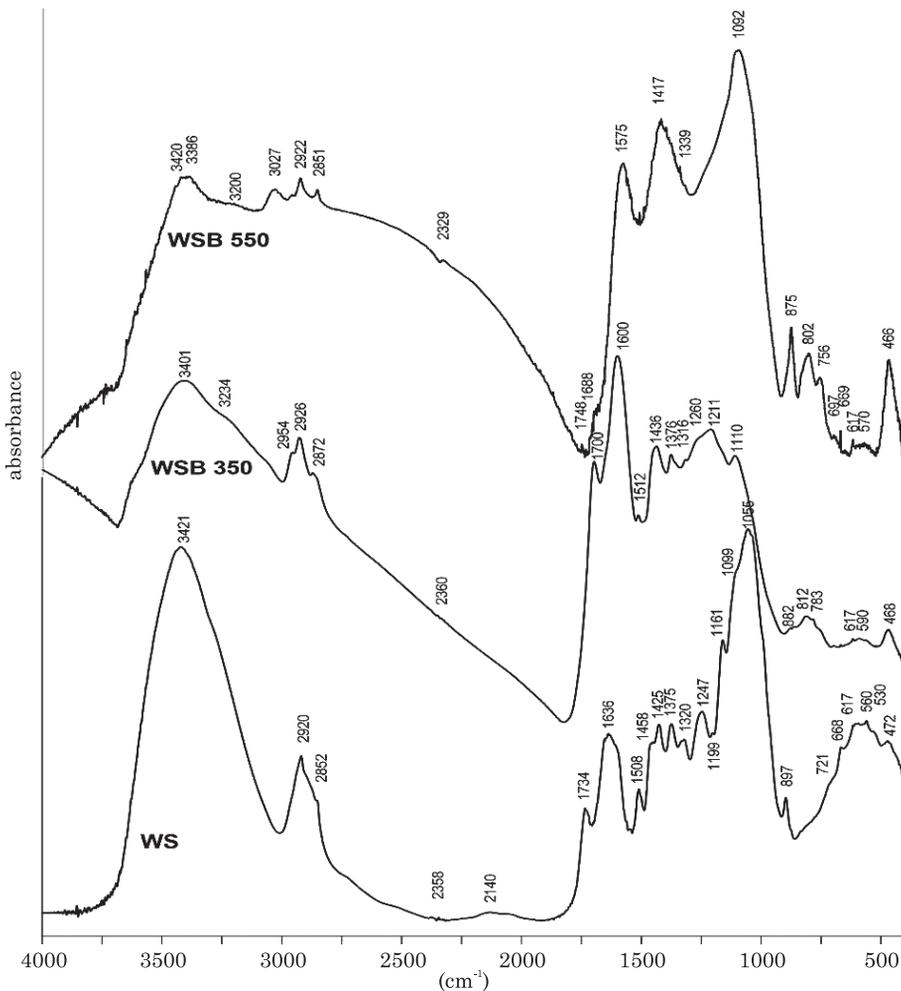


Fig. 4. The spectra of wheat biomass (WS) and wheat biochar produced in 350°C (WSB 350) and in 550°C (WSB 550)

FT-IR analysis

The FT-IR analysis showed similarity of the distribution of individual bands in the spectra of both biomasses and the similar effect of the pyrolysis process on the distribution of bands in the spectra of wheat biomass and miscanthus biochars (Figures 2, 4). It was demonstrated that there was a wide band at 3500-3300 cm^{-1} with a peak at approx. 3420 cm^{-1} in the spectra of all the researched materials, typical of stretching vibrations of -OH groups derived from water adsorbed by the material (Figures 2 and 4). However, the band was much more visible in feedstocks (before thermal conversion) and faded in biochars as a result of dehydration of cellulose and lignin, especially at the higher pyrolysis temperature (WU et al. 2012, ZHAO et al. 2014). The study by ZHAO et al. (2014) proved that the band may fade only at a temp. above 350°C, but this is not a rule. The spectra of wheat and miscanthus show bands between 3000-2800 cm^{-1} (a peak at about 2920 cm^{-1}) corresponding with the stretching and bending vibrations of aliphatic C-H groups (CH, CH₂ and CH₃). The results of spectral analyses of both biomasses confirmed the presence of a band with a peak at approx. 1735 cm^{-1} derived from the stretching vibration of -C=O groups and a band with a peak at 1636 cm^{-1} from bending vibrations of -OH groups derived from water adsorbed by the material or related to the vibrations of the C=O group. In addition, the presence of a skeletal vibration spectrum, typical of aromatic lignin fragments (C=C and -OCH₃) can be observed at the wave numbers of 1508 and 1452 cm^{-1} (LI et al. 2013, WU et al. 2012). The bands with a peak at 1320 cm^{-1} (-CH₂) and at approx. 1160 cm^{-1} corresponded to the asymmetric stretching vibrations of C-O-C groups derived from hemicellulose and cellulose. In the wheat straw spectrum, there was also a band with a peak at 1055 cm^{-1} corresponding to stretching vibrations of C-O groups at C3, C6 and C-C, as well as a band at approx. 900 cm^{-1} , which is characteristic of β -glycosidic bonds and derives from deformation and stretching vibrations of COC, CCO, and CCH groups.

During the pyrolysis, the pyrolysed components lead to the increasing upward drift in the baseline at a high wave number, which is attributed to low-energy electron excitations of condensed aromatic structures (WU et al. 2012, JINDO et al. 2014, VITHANAGE et al. 2017). In the process of plant biomass pyrolysis, KEILUWEIT et al. (2010) identified four phases that affect molecular changes in the biochars' structure and may explain differences in their stability in the environment and sorption capacity. As stated by these authors, (i) in transition biochars, the crystalline character of the precursor materials is preserved; (ii) in amorphous biochars, the heat-altered molecules and incipient aromatic polycondensates are randomly mixed, (iii) composite biochars consist of poorly ordered graphene stacks embedded in amorphous phases, and (iv) turbostratic biochars are dominated by disordered graphitic crystallites. However, despite these changes in the pyrolytic process, the obtained biochars retain the same structure and pore distribution as in feedstocks – Figure 3 (JINDO et al. 2014). In our study, in the FT-IR analysis

of wheat straw and miscanthus straw biochars' spectra produced at 350°C, the bands with peaks at 2926 cm⁻¹, 2872 cm⁻¹, approx. 1436 cm⁻¹ (aromatic C=C skeletal vibrations) and approx. 1375 cm⁻¹ (C-H deformation modes in alkenes) were visible, which corresponded to the vibrations of -CH₂ groups (Figures 2, 4). The presence of these bands in FT-IR spectra of the tested biochars was due to the presence of degradation and condensation products of the cellulose and lignin components (WU et al. 2012). On the other hand, in FT-IR spectra of biochars produced at 550°C, slight shifts of the bands were shown with peaks at 2926 cm⁻¹, 2872 cm⁻¹, approx. 1436 cm⁻¹ as well as band decrease at approx. 1375 cm⁻¹. As stated by VITHANAGE et al. (2017) low-temperature biochars (280-350°C) with low aromaticity contain more C=O and C-H functional groups that promote adsorption for contaminants, which can be observed also in our results. The band with a peak at 1600 cm⁻¹ probably corresponded to stretching vibrations of aromatic C=C and C=O groups. ZHAO et al. (2014) stated that this band is typical of biochars made of wood and plant biomass, and disappears only at a temperature above 650°C. The intensity of the band stretching decreases with increasing temperature (with a peak at approx. 1575 cm⁻¹ for WSB 550 and MSB 550) and, generally, shows no significant differences between biochars obtained from various plant residues. In WSB 350, there were also visible bands with a peak at 1512 cm⁻¹, corresponding to stretching vibrations of lignin-derived C=C groups. On the other hand, the absence of characteristic bands at approx. 1160 cm⁻¹ (C-O-C) and 1057 cm⁻¹ (C-O-H) in biochars WSB 350, WSB 550 and MSB 550 may indicate partial degradation of hemicellulose, cellulose and lignin. As stated by ZHAO et al. (2014), biochars produced at about 200°C retain the properties comparable to those of feedstocks used in the process. Only by raising the pyrolysis temperature to about 350°C quantitative changes of aliphatic and aromatic carbons in the product can be achieved (Figures 2, 4). The FT-IR analysis of rice straw biochar conducted by WU et al. (2012) showed that biochars produced at temp. below 400°C had the highest aromaticity. These authors also found that biochars obtained at temp. exceeding 400°C had markedly reduced functionality and hydrophilicity and a reverse tendency to oxidize. Also KEILUWEIT et al. (2010) showed that all functions of C are significantly reduced at high temp. (500-700°C), and at 700°C, the FT-IR spectrum of biochar resembles that of graphite. WU et al. (2012) proved that the decomposition of functional groups by thermal degradation takes place at temp. above 600°C. For this reason, biochars produced at high temperatures with a structure of fire-resistant graphene, exhibit higher stability. Both the cited and our results clearly confirm the relevance of producing biochar at lower temperatures if it is to be applied in agriculture to improve soil fertility. On the other hand, when using biochar for remediation purposes, for example, more suitable properties can be achieved by applying a temp. above 450°C because high-temperature pyrolysis promotes the formation of functional groups and C structures resistant to microbial decomposition.

Content of phenolic compounds

Literature data show that soil fertilization with organic fertilizers has a significant impact on the content of total phenolic compounds (TPC), which are considered the basic building blocks for the synthesis of humic compounds (MIN et al. 2015, QUARTACCI et al. 2017). A high content of phenolic compounds can be highly toxic to plant roots and soil microorganisms, contributing to the reduction of soil biological activity (SADEJ et al. 2016), which shows that the said compounds have a significant impact on the cycling of nutrients for plants. Thus, it is very important to determine their content in organic materials. The data presented in Figure 5 indicate that the highest TPC content was in the feedstocks used for pyrolysis (WS, MS). The pyrolysis of WS and MS at 350°C reduced the TPC content by 5% and 18%, respec-

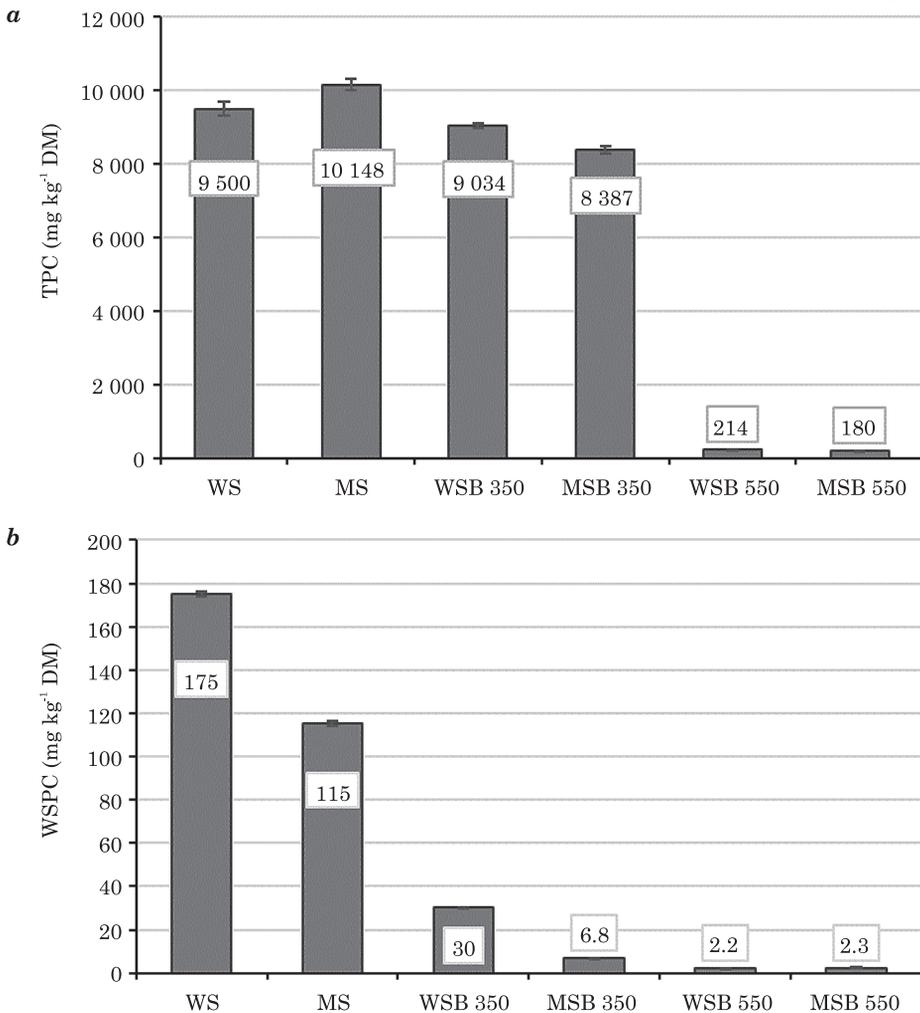


Fig. 5. Content of total (a) and water soluble phenolic compounds (b)

tively. A significant reduction of TPC in biochars was obtained after applying the temp. of 550°C. CZAJCZYŃSKA et al. (2017) indicated that as the temperature increased (above 400°C), the content of most phenolic compounds in the pyrolysed biomass was gradually reduced, while certain compounds (phenol, 2 and 3-methyl-phenol, and 1,2-benzenediol) rapidly increased with increasing the temperature. These authors also showed that during high-temperature pyrolysis, the main product of the process was bio-oil rich in phenolic compounds and thus constituting a high quality fuel. The content of water soluble phenolic compounds in the plant biomass and biochars produced at both temperatures was from 54- to 1231-fold lower than the content of TPC. Our results showed that pyrolysis at temp. of 350 and 550°C significantly reduced the WSPC content in biochars. This means that the process of thermal conversion of plant biomass, regardless of the temperature, has a very positive effect on limiting the fraction of phenolic compounds bioavailable to microorganisms.

CONCLUSIONS

1. Pyrolysis caused significant changes in physical and chemical properties of plant biomass, in particular, it improved their adsorption properties (S_{BET} , porosity).
2. The pyrolysis of wheat and miscanthus biomasses at 350°C reduced the TPC content by 5% and 18%, respectively. On the other hand, the temp. of 550°C reduced the content of TPC in biochars over 200 times on average.
3. The FT-IR analysis showed that biochars produced at 350°C had a lower content of functional groups and lower hydrophilicity compared to biochars produced at 550°C.
4. Morphological analysis of biochars revealed that biochars retain the specific surface area and pore volume similar to those of feedstocks from which they were produced.

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