Solid tailings after supercritical CO_2 extraction of lignocellulosic biomass as a source of quality biochar for energetic use and as soil improvement

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Abstract

Lignocellulosic biomass is a rich source of bioactive compounds extracted industrially from different parts of the plant. The extraction process generates residues containing 75 to 95% of the raw material, depending on the species. There is biochar among the many potential products of post-extraction residue' processing.

The research objective was: i) to evaluate the parameters of biochars derived from post-extraction bark, wood and bark and wood of four lignocellulosic species; and ii) to discuss the parameters in the context of biochar functionality as an energy carrier and soil improver. The residues were subjected to pyrolysis at the three temperatures, 170, 270, and 370°C, which correspond to the initiation of carbonisation, and two biochars that differ in the decomposition rates of hemicelluloses, cellulose, and lignin. On average, biochars had a high energy value owing to the increased total and fixed carbon and calorific value content by 77.0-78.4% DM, 64.6-66.7% DM and 25.8-30.1 MJ kg^{-1}, respectively. The higher quantity of ash after processing bark residues than wood residues implicates a lower energy value but, at the same time, the ash obtained is a better source of mineral compounds in soil fertilisation. Concerning using biochar as a soil improver, the biochars demonstrated lower hydrogen/carbon and oxygen/carbon molar ratios, indicating raised stability and resistance to the geochemical decomposition in soil. It was proven that the bark-based biochars had much higher concentrations of micro- and macronutrients, and a higher pH, while processed wood fractions resulted in higher concentrations of total carbon and fixed carbon in the biochar. The research results suggest that lignocellulose biomass extraction residues can serve as a valuable input material for biochar production.

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Introduction

Lignocellulose biomass serves to produce a wide range of bio-based products, such as bioenergy, biofuels, biochemicals, and biomaterials. Furthermore, lignocellulose biomass is still awaiting greater recognition as a source of many valuable bioactive substances which cannot be synthesised chemically. Production of bio-active compounds from wood or bark in a biorefinery entails generating large amounts of extraction waste. In line with the concept of a close-looped economy (European Commission, 2015), lignocellulose biomass residual waste after the extraction process can become raw material for the manufacture of new products, thereby helping to improve the economic and energy generation efficiency of a lignocellulosic biorefinery, which in turn would be fundamental to the sustainable processing of biomass. Extraction waste can be upgraded *via* thermochemical conversion, such as combustion, pyrolysis, and gasification (van der Stelt *et al.,* 2011; Mohan *et al.,* 2014). Combustion of waste biomass ranks relatively low in the hierarchy of end-of-life processes, while the processes of pyrolysis and gasification, owing to their potential for producing various products, are considered to have a higher priority.

Pyrolysis generates three types of products – solid, liquid, and gaseous. Each one is the subject of many studies on parameters and conditions of a pyrolytic process considering i) use to produce energy, improve soil fertility or use as a raw material in industrial production; ii) determination of the relationship between physical and thermochemical parameters of biochar in the context of its functionality; iii) widening aspects of potential industrial use, including the use of biochar as an adsorbent (Knowles *et al.,* 2011; Lehmann *et al.,* 2011; Tang *et al.,* 2013; Zheng *et al.,* 2013; Mumme *et al.,* 2014; Nelissen *et al.,* 2014; Radawiec, 2014; Białowiec *et al.,* 2017). Depending on the temperature of a pyrolytic process, the heating-up rate, rate of temperature rise, and retention time, there are considerable differences in quantitative proportions and properties of products. The highest quantities of biochar are obtained from a slow pyrolytic process at relatively low temperatures (van der Stelt *et al.,* 2011; Mohan *et al.,* 2014).

As a consequence of the thermochemical conversion of lignocellulose substrate, the biomass undergoes a series of changes in physical, chemical, and energy-related properties. In general, the biochar obtained in the process is characterised by much lower moisture content, higher grindability, and homogeneity of the matter while possessing considerably higher calorific value than the substrate (Bergman and Kiel*,* 2005; van der Stelt *et al.,* 2011; Lee *et al.,* 2013; Liu *et al.,* 2013; Troy *et al.,* 2013; Mohan *et al.,* 2014; Białowiec *et al.,* 2017). The elevated dry matter concentration allows the biochar to be used as an energy carrier. Moreover, biochar has a higher content of total carbon, fixed carbon, nitrogen, and minerals, which in turn makes it useful for soil fertilization (Bergman and Kiel*,* 2005; Kan *et al.,* 2016; Tan *et al.,* 2017; Zhao *et al.,* 2018). The neutral to alkaline pH of biochar is conducive to increasing the soil pH, which can be an important yield-stimulating factor when many soils are acidified (De Bhowmick *et al.,* 2018; Weber and Quicker, 2018). Biochar contributes to the improved retention of nutrients and reduces and suppresses greenhouse gases CO_2, N_2O, CH_4 emission, thereby weakening the greenhouse effect (Nelissen *et al.,* 2014). Moreover, due to its elevated content of total carbon and fixed carbon, which have a direct impact on the resistance and stability of biochar in soil, the incorporation of biochar into soil has a positive effect on the carbon balance, thus contributing to the sequestration of carbon in soil (Lehman *et al.,* 2011; Bai *et al.,* 2014; Sigua *et al.,* 2014).

Aim

The objective of this paper is: i) to assess the physiochemical properties of biochars obtained from residues after supercritical extraction of different parts of lignocellulosic plants; ii) to discuss the properties in the context of biochar functionality as an energy carrier and soil improver; iii) to assess the potential for the use of biochar produced in the temperature range 170-370°C.

Materials and Methods

Materials

The material for this research consisted of residual biomass remaining after the extraction of four woody plant species: osier willow (*Salix viminalis*) (SV), purple osier willow (*Salix purpurea*) (SP), false acacia (*Robinia pseudoacacia*), and black polar (*Populus nigra x P. Maximowiczii*) (P), and tested in the three forms: bark (B), wood (W), and bark and wood (BW). Post-extraction biomass was composed of the remains of supercritical carbon dioxide extraction performed to acquire bio-active substances from the whole plant (bark and wood) and previously prepared fractions of bark or wood (*e.g*., Ostolski *et al.,* 2021). The extraction process was applied to biomass representing the three mentioned fractions ground to a size of 1 mm in an analytical mill IKA KMF 10 basic.

Reactor

Experimental pyrolytic treatments were conducted in a reactor used for the thermal conversion of waste biomass from biogas plants and lignocellulose biorefinery. The temperature in this reactor can be raised to and maintained at 600°C. The reactor (Figure 1) is a thermally insulated pressure tank made of stainless steel, wrapped with a heating band. The chamber, equipped with thermocouples and a manometer, has a working capacity of 4 dm^3. It also has needle valves to regulate the supply of oxygen or to fill the chamber with neutral gas, *e.g*., nitrogen. The reactor is coupled with a system for collecting and analysing quantities of the three fractions produced: solid, liquid, and gaseous. This paper focuses on the analysis of the solid fraction, *i.e*., biochar.

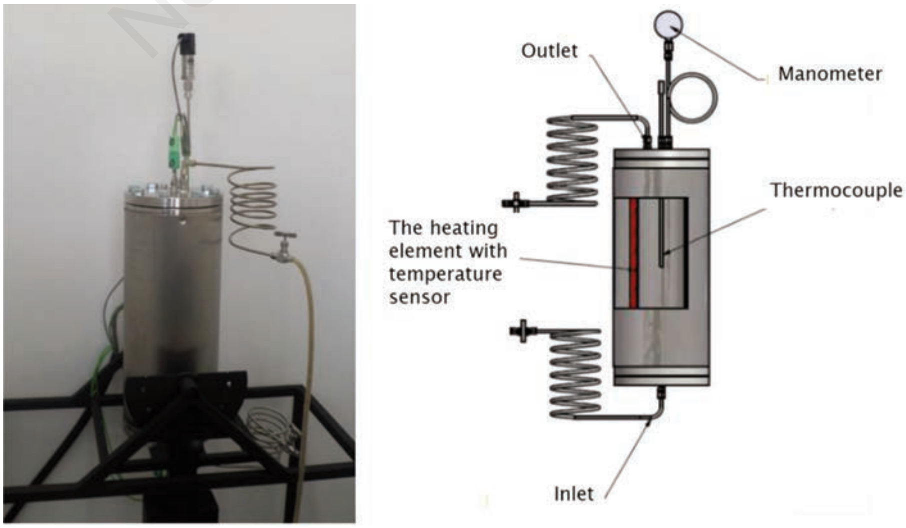

Figure 1. The reactor used for the thermal conversion of waste biomass.

The experiment

Samples of biomass, each weighing approximately 50 g, were submitted to pyrolysis at three different process temperatures by heating the reactor to 170, 270 and 370°C, respectively. The selection of the three temperatures was preceded by preliminary research on the pyrolysis of the post-extraction residues. The obtained results revealed that thermochemical degradation of pyrolytic material and formation of carbonisate begins at 170°C followed by intensive carbonisation of hemicelluloses and partial decomposition of lignin and cellulose at 270°C and finally, the great amount of cellulose and lignin at 370°C. Therefore, in our study, only the solid products obtained at 270 and 370°C can be assumed to fulfill the standardised criteria of biochar. The samples were maintained in the reactor for 60 minutes. In order to ensure anoxic conditions inside the reactor, an adequate volume of neutral gas, nitrogen of a purity of 99.999%, was passed through the reactor's tank. The rate of temperature increment was 0.2-0.4°C/s. When the process was finished, the solid products were subjected to analyses of chemical and energy-related properties.

Characteristics of the input material and biochar

The methodology employed in this experiment adhered to the guidelines provided in the EBC (2019). The moisture content in the substrates and products was determined by drying at 105°C. pH was measured in a solution with deionised water, where the produced biochar/deionised water ratio was 1/10 (w/v). Thermogravimetric assays were carried out on an ELTRA TGA-THERMOSTEP thermogravimetric analyser. The purpose was to determine the content of fixed carbon, ash, and volatile particles. The heat of combustion was determined with the dynamic method in an IKA C 2000 calorimeter. Afterwards, a sample's calorific value was determinedby the sample's working moisture content (Kopetz *et al.,* 2007). Total carbon, hydrogen, and sulphur concentrations were measured on an ELTRA CHS 500 analyser. The oxygen content was calculated from the formula: $O=1-(Ash+H+N+C+S)$. The nitrogen content was determined according to Kjeldahl's method, using a K-435 mineraliser and B-324 BUCHI distillation unit. Determinations of the content of micro- and macronutrients (P, Mg, Ca, K, Na, Fe) as well as metals (Pb, Cd, Cu, Zn, Cr, Mn, Al, B) were made on an iCAP 7000 Series ICP-OES spectrometer (Thermo). The efficiency of producing biochar (mass yield, %), energy (energy yield, %), and fixed carbon (C_{fixed} yield, %) was calculated from the formulas provided by Weber and Quicker (2018), while the total carbon yield efficiency (C_{total} yield, %) was derived from the formula given by Mašek *et al.* (2013).

Statistical analysis

Assessment of the experimental factors, namely the plant species, types of biomass, and temperature of pyrolysis, was based on an analysis of variance for a 4×3×3 factorial design. Mutual correlations between the variables were evaluated according to Pearson's correlation coefficients (Table 1). Statistical significance was estimated at $P<0.05$.

Results and Discussion

Mass and energy yield

The biochar yield at the lowest temperature of the pyrolytic process ranged within 89.4-98.7%, then decreased to 56.31-70.04% at 270°C, not differing statistically significantly between the bark and wood fractions, whereas at the temperature of 370°C the mass of biochar obtained from bark corresponded to 43.3-46.7%, and 34.2-35.8% in the case of biochar from wood (Table 2). These results coincide with the reports from other studies, which indicate that biochar yield depending on the applied technology and processing temperature, oscillates within 30-90 wt. % of biochar, and is negatively correlated with the temperature of pyrolysis (Tsai *et al.,* 2012; Al-Wabel *et al.,* 2013; Liu *et al.,* 2013; Mašek *et al.,* 2013; Troy *et al.,* 2013; Mumme *et al.,* 2014; Zhao *et al.,* 2018). Zhao *et al.* (2018) demonstrated experimentally that the most extensive mass losses occurred in the temperature range of 200-300°C, where the efficiency of the process was 80 to 36%, respectively, while any further rise in the process temperature up to 700°C caused less rapid changes in mass yield. Mašek *et al.* (2013) showed changes in the mass yield of biochar produced from willow chips at a temperature of 250°C: 83.2%, at 300°C: 53.2%, and at 350°C: 39.8%. Mass loss is primarily due to the removal of moisture and labile organic volatile substances as well as non-condensable gases, such as CO_2, CO, H_2, CH_4 (Zhao *et al.,* 2018). Differences in the production efficiency are due to the chemical composition of lignocellulose biomass, namely the degree of polymerisation of hemicelluloses, cellulose, and lignin, which in turn determines their recalcitrance to thermal decomposition (De Bhowmick *et al.,* 2018). The degree of polymerisation of hemicellulose is the lowest, and this fraction is the first to undergo decomposition at a temperature between 250°C and 350°C. Degradation of cellulose and afterwards of lignin occurs at higher temperatures, such as 325-400°C. Lignin is a biopolymer characterised by the greatest complexity of composition; it is resistant to degradation and undergoes decomposition at temperatures of 300 up to 550°C (Kan *et al.,* 2016; De Bhowmick *et al.,* 2018). Thus, the biggest mass losses during thermal treatment are observed within the temperature range of 250 to 350°C when hemicellulose is nearly completely decomposed, while only some cellulose and lignin is broken down at this stage (Weber and Quicker, 2018). The average composition of bark submitted to pyrolysis in our experiment was as follows: 10.9% of hemicellulose on dry matter, 28.1%

Table 1. Pearson's correlation coefficient matrix.

Variable	C_t	Nitrogen	C_f	Volatiles	Ash	LHV
C_t	1.00	-	-	-	-	-
Nitrogen	0.14	1.00	-	-	-	-
C_f	0.98*	0.17	1.00	-	-	-
Volatiles	–0.96*	–0.28	–0.99*	1.00	-	-
Ash	0.36	0.87	0.41	–0.52	1.00	-
LHV	0.96*	0.26	0.97*	–0.97*	0.49	1.00

C_t, total carbon; C_f, fixed carbon; LHV, calorific value; *significant at $P\leq0.05$.

of cellulose, and 18.0% of lignin, the dry matter of wood was composed of 17.4% of hemicellulose, 57.4% of cellulose and 16.0% of lignin. Hence, the smaller yield of biochar obtained from wood than from bark at 370°C may be associated with the highest hemicellulose and cellulose content in wood, meaning that bark was more readily decomposed by thermal treatment within the set range of temperatures.

The energy efficiency of a pyrolytic process (energy yield) expresses the quantity of energy contained in the substrate which remains in biochar. Research results implicate that the energy yield decreases as the temperature of the process increases, and it may vary within 77-90% of the input (Liu *et al.,* 2013; Troy *et al.,* 2013; Mumme *et al.,* 2014). Moreover, higher energy yield is obtained from substrates based on woody plants than from biomass like straw (Weber and Quicker, 2018). As reported by Weber and Quicker (2018), energy yield may vary over a wide range, depending on the type of substrate and processing parameters, and it can range from 60 to 98% even within such a narrow temperature range as 200-300°C. In our experiments (Table 2), the energy yield of biochar produced at 170°C was within 90-98%, compared to 73-83% at 270°C and 52-73% at 370°C. The energy yield from bark was consistently higher than that from wood, regardless of the temperature of a pyrolytic treatment. Noteworthy is the fact that differences in energy yield between those two materials increased as the temperature of the pyrolytic processing was raised.

Calorific value increased as the temperature of pyrolysis was raised, not being different between biochars produced from bark and wood. More specifically, only a slight increase was achieved in the calorific value of biochar generated at 170°C, while at 270°C it reached 22.0-24.1 MJ/kg, and at 370°C it increased to 25.8-30.1 MJ/kg. A rise in calorific value relates to a loss in moisture and changes in hydrogen and carbon atomic ratio and oxygen and carbon atomic ratio (Liu *et al.,* 2013; Troy *et al.,* 2013; Mumme *et al.,* 2014). Depending on the type of biomass, it can vary from 20 to 36 MJ/kg (Zhao *et al.,* 2018). Figure 2 shows changes per unit in the mass and energy yields and calorific value corresponding to a rise in temperature by 1°C.

When the substrate consisted of willow residue, the highest unit losses of mass and energy were noted within the temperature rise from 170 to 270°C, whereas for poplar and false acacia, such results appeared at higher temperatures, namely from 270 to 370°C. These findings are reflected in the calorific value of biochar, with minimal changes in the range of temperatures up to 170°C, and the highest increment in the biochar from willows at a temperature increasing to 270°C, and in the biochar from extraction mass obtained from poplar and false acacia at a further rise in temperature up to 370°C.

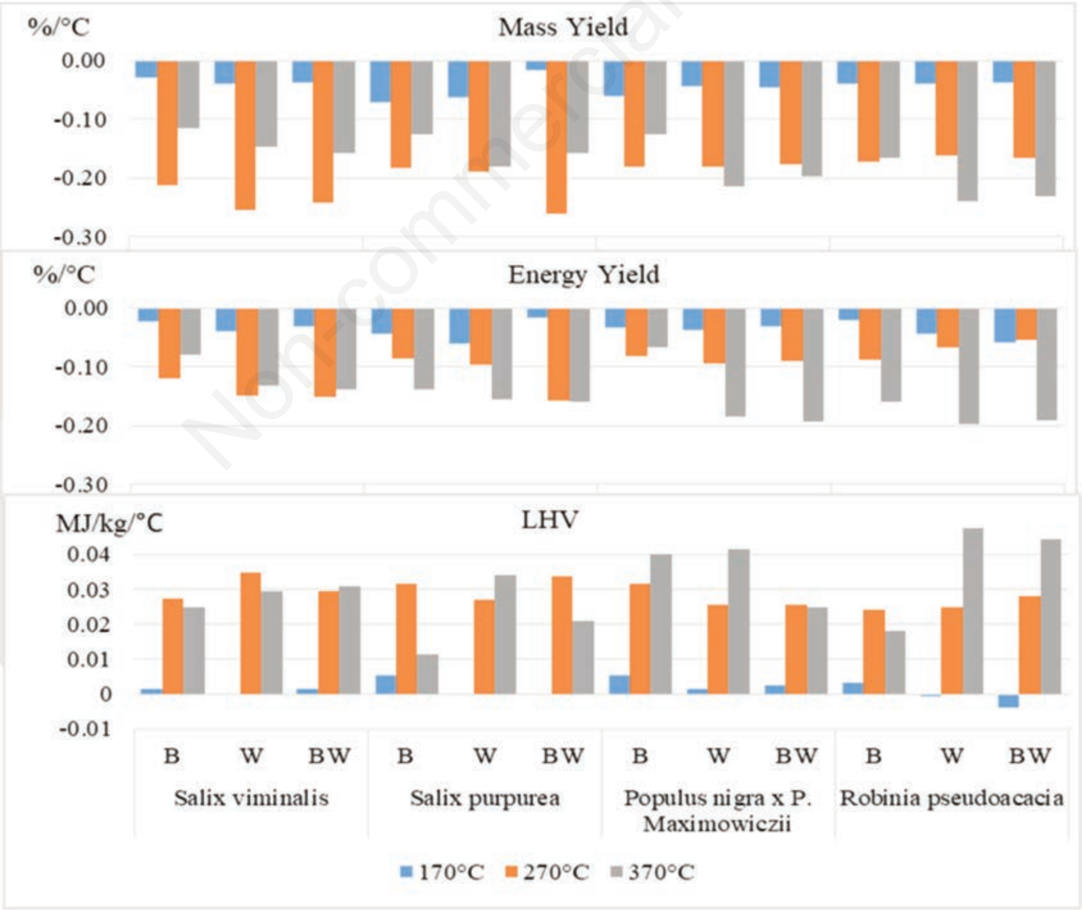

Figure 2. Unit changes in decreasing mass and energy yield and increasing calorific value of biochars in relation to species, type of biomass, and temperature of pyrolysis.

Total carbon and fixed carbon content and yield

As the temperature of a pyrolytic process increased, the degree of carbonisation increased, and the content of both total and fixed carbon rose (Table 3).

Extraction waste mass submitted to pyrolysis was characterised by the total carbon content of around 51.4-57.8% d.m, not being significantly different from the extraction mass from wood or bark. Biochars obtained at 270°C contained from 60.1 to 65.5% C_t in d.m., while the corresponding values for the bark extraction mass undergoing pyrolysis at 370°C were 66.7-71.6% C_t in d.m, with the significantly higher total carbon concentration determined in biochars produced from wood extraction biomass: 77.0-78.4% C_t in d.m.

The fixed carbon content was significantly higher in bark extraction biomass, equalling 20.5-25.8% C_f in d.m. It did not change significantly at the lowest tested temperature (170°). However, higher pyrolysis temperatures caused an increase in fixed carbon, with much higher values obtained in the pyrolytic treatment of wood extraction mass. At 270°C, fixed carbon content was 29.8-38.6% C_f in d.m. for bark extraction mass and 32.0-

Table 2. Changes in the mass yield, energy yield and calorific value depending on the plant species, type of biomass, and temperature of pyrolysis.

Species	Type of biomass	Temperature °C	Mass yield %	Energy yield %	LHV MJ/kg
Salix viminalis	B	RM	-	-	18.4
	B	170°C	95.7	96.7	18.6
	B	270°C	64.0	78.9	22.7
	B	370°C	46.7	67.1	26.4
	W	RM	-	-	18.6
	W	170°C	94.2	94.2	18.6
	W	270°C	56.3	71.9	23.8
	W	370°C	34.4	52.1	28.2
	BW	RM	-	-	18.7
	BW	170°C	94.4	95.5	18.9
	BW	270°C	58.5	73.0	23.3
	BW	370°C	35.0	52.3	27.9
Salix purpurea	B	RM	-	-	18.6
	B	170°C	89.4	93.4	19.4
	B	270°C	62.2	80.7	24.1
	B	370°C	43.3	60.1	25.8
	W	RM	-	-	18.8
	W	170°C	90.8	90.9	18.8
	W	270°C	62.8	76.4	22.8
	W	370°C	35.8	53.3	27.9
	BW	RM	-	-	18.8
	BW	170°C	97.5	97.7	18.8
	BW	270°C	58.6	74.2	23.8
	BW	370°C	35.2	50.3	26.9
Populus nigra x P. Maximowiczii	B	RM	-	-	18.6
	B	170°C	91.0	94.9	19.4
	B	270°C	64.1	82.8	24.1
	B	370°C	45.2	72.9	30.1
	W	RM	-	-	18.9
	W	170°C	93.5	94.5	19.1
	W	270°C	66.5	80.4	22.9
	W	370°C	34.5	53.0	29.1
	BW	RM	-	-	18.9
	BW	170°C	93.3	95.3	19.3
	BW	270°C	67.1	82.0	23.1
	BW	370°C	37.6	53.3	26.8
Robinia pseudoacacia	B	RM	-	-	19.1
	B	170°C	94.2	96.8	19.6
	B	270°C	68.6	83.7	23.2
	B	370°C	44.0	59.8	25.9
	W	RM	-	-	18.4
	W	170°C	94.1	93.6	18.3
	W	270°C	70.0	83.5	22.0
	W	370°C	34.2	54.1	29.1
	BW	RM	-	-	18.5
	BW	170°C	94.4	91.3	17.9
	BW	270°C	69.7	83.1	22.1
	BW	370°C	35.2	54.6	28.7

LHV, calorific value; B, bark; W, wood; BW, bark and wood; RM, …

42.9% C_f in d.m. for wood extraction biomass. At 370°C, the respective values were 46.1-56.5% C_f in d.m. (bark) and 64.7-66.7% C_f in d.m. (wood).

The total carbon content in biochar may vary from 53 to 96% (Zhao *et al.,* 2018), or from 67.8 to 86.8% (Tan *et al.,* 2017). The wide range and high variability of the total carbon content of biochar are mainly a consequence of the original carbon content in the substrate and the temperature of pyrolysis. The results of this study are consistent with data provided in other reports, which show an increase in the total carbon content observed in parallel with a rise in the temperature of pyrolytic processing (Medic *et al.,* 2012; Al-Wabel *et al.,* 2013; Lee *et al.,* 2013; Mašek *et al.,* 2013). Aside from considerable changes in the total carbon content, there are also significant changes in the labile and fixed carbon ratio, as depolymerisation of lignocellulose leads to the transformation of labile carbon into permanent carbon, known as fixed carbon (Zhao *et al.,* 2018). An increase in the total carbon content positively influences the usefulness of biochars for energy generation. In turn, the content

Table 3. Changes in the content of volatile matter, ash, total carbon (Ct), and fixed carbon (Cf), depending on the plant species, type of biomass, and temperature of pyrolysis (B, bark; W, wood; BW, bark, and wood) (mean value±standard deviation, n=3).

Species	Fraction of biomass	Pyrolysis temperature	Volatile matter (% wt)	Ash (% wt)	C_t content (% wt)	C_f content (% wt)
Salix viminalis	B	RW	71.0±0.0	3.2±0.0	52.4±0.4	25.7±0.0
	B	170°C	69.3±0.2	3.4±0.0	53.7±0.2	24.6±0.2
	B	270°C	56.8±0.1	4.6±0.0	62.0±0.1	38.6±0.1
	B	370°C	34.7±0.3	6.8±0.1	71.4±0.3	56.0±0.1
	W	RW	79.3±0.0	0.8±0.0	54.9±0.2	19.9±0.0
	W	170°C	78.8±0.1	0.9±0.0	53.2±0.3	19.0±0.1
	W	270°C	55.6±0.1	1.5±0.0	63.7±2.1	42.9±0.1
	W	370°C	29.3±0.0	2.4±0.0	78.4±0.2	65.0±0.0
	BW	RW	77.1±0.1	1.4±0.0	53.7±0.5	21.6±0.1
	BW	170°C	76.4±0.3	1.5±0.0	50.9±0.2	20.6±0.3
	BW	270°C	55.4±0.1	2.4±0.0	64.7±0.2	42.1±0.1
	BW	370°C	27.8±0.2	4.2±0.1	78.4±0.2	65.6±0.3
Salix purpurea	B	RW	73.5±0.0	4.1±0.0	51.4±0.1	22.4±0.0
	B	170°C	71.5±0.1	4.4±0.0	54.3±0.1	24.1±0.1
	B	270°C	55.3±0.2	6.5±0.0	64.3±0.1	38.1±0.2
	B	370°C	37.8±0.2	9.0±0.1	69.9±0.0	51.3±0.2
	W	RW	79.6±0.0	0.6±0.0	55.8±0.2	19.8±0.0
	W	170°C	78.4±0.3	0.8±0.0	51.3±0.7	20.8±0.3
	W	270°C	62.0±0.1	1.1±0.0	63.7±0.2	36.8±0.1
	W	370°C	30.4±0.3	2.0±0.0	77.0±0.2	64.6±0.4
	BW	RW	77.7±0.1	1.5±0.0	54.8±0.4	20.8±0.1
	BW	170°C	77.3±0.1	1.4±0.0	51.3±0.3	21.3±0.1
	BW	270°C	55.0±0.2	2.3±0.0	65.5±0.0	42.7±0.2
	BW	370°C	29.9±0.1	3.8±0.0	75.0±0.4	63.8±0.1
Populus nigra x P.Maximowiczii	B	RW	73.7±0.1	3.6±0.0	57.4±0.2	22.7±0.1
	B	170°C	72.6±0.1	3.8±0.3	55.0±0.2	23.2±0.1
	B	270°C	59.1±0.8	4.2±0.6	64.3±0.2	35.7±0.2
	B	370°C	32.8±0.0	8.8±0.1	71.6±0.4	56.5±0.1
	W	RW	79.2±0.2	0.5±0.0	57.8±0.0	20.3±0.2
	W	170°C	79.0±0.2	0.5±0.0	56.4±0.1	20.2±0.2
	W	270°C	62.5±0.1	2.1±0.1	63.7±0.2	34.3±0.0
	W	370°C	28.7±0.1	2.7±0.0	77.5±0.2	66.7±0.1
	BW	RW	77.1±0.1	1.6±0.1	55.2±0.2	21.3±0.0
	BW	170°C	76.5±0.6	1.9±0.1	54.7±0.3	21.3±0.5
	BW	270°C	62.1±0.2	2.8±0.1	62.6±0.0	34.1±0.1
	BW	370°C	29.7±0.2	6.2±0.1	74.1±0.2	62.0±0.2
Robinia pseudoacacia	B	RW	74.5±0.0	5.0±0.0	52.4±0.1	20.5±0.0
	B	170°C	73.7±0.1	5.2±0.0	53.3±0.1	20.3±0.1
	B	270°C	62.2±0.0	7.3±0.1	60.7±0.2	29.8±0.1
	B	370°C	40.0±0.0	12.7±0.2	66.7±0.1	46.1±0.1
	W	RW	79.6±0.0	0.6±0.0	55.3±0.4	19.8±0.0
	W	170°C	79.1±0.0	0.7±0.1	54.2±0.0	19.5±0.1
	W	270°C	65.5±0.5	1.3±0.0	60.5±0.8	32.0±0.4
	W	370°C	30.7±0.1	2.3±0.1	77.5±0.2	64.9±0.0
	BW	RW	78.3±0.0	1.2±0.0	55.5±0.4	20.6±0.0
	BW	170°C	77.2±0.2	1.5±0.0	54.1±0.2	19.9±0.1
	BW	270°C	65.2±0.0	2.2±0.0	61.5±0.1	31.7±0.0
	BW	370°C	29.6±0.2	4.2±0.0	76.6±0.2	64.0±0.2

C_t, total carbon; C_f, fixed carbon; B, bark; W, wood; BW, bark and wood; RW, …

of fixed carbon is directly associated with the role biochar can play in carbon sequestration in soil; therefore, this parameter is seen as an indirect indicator of the stability of biochar in soil. Greater stability of biochar, and hence its higher resistance to decomposition, can contribute to carbon sequestration in soil (Medic *et al.,* 2012; Al-Wabel *et al.,* 2013; Zhao *et al.,* 2013). The positive effect of temperature on the content of fixed carbon, revealed in this study, has also been demonstrated by Zhao *et al.* (2018), who showed that the fixed carbon content increased from 13.3 to 75.6% as the temperature of pyrolysis rose from 200 to 700°C.

Ash and volatile particles

It has been demonstrated that a rise in the temperature of a pyrolytic treatment is accompanied by an increase in the concentration of ash with a simultaneous decrease in the content of volatile substances. The average input ash content in dry matter of biochar was significantly different between bark and wood equalling 3.22-5.02% for bark and 0.47-0.80% for wood. The ash content did not undergo significant changes at 170°C. However, at 270°C, ash constituted 4.21-7.27% of the total composition for biochar obtained from bark and 1.14-2.07% in biochar derived

Table 4. Changes in the content of macro- and micronutrients and heavy metals in biochars, depending on the species, type of biomass, and pyrolytic temperature.

Species	Fraction of biomass	Pyrolysis temperature	P	Na	Mg	K	Fe	Mn	Zn	Al	B
Salix viminalis	B	RM	1665.5	1226.4	1150.4	6182.6	87.3	148.7	143.9	180.8	160.6
	B	170°C	1576.9	977.1	1124.7	5870.5	85.8	144.4	78.4	176.5	60.9
	B	270°C	2084.8	1389.5	1392.2	7575.5	127.4	177.3	106	180	123.4
	B	370°C	3122.6	1714.3	2181.9	11248.3	178.5	279.9	219.6	291	197
	W	RM	772.4	1057.8	344	2192.9	25.4	50.5	0	146.2	51.4
	W	170°C	775.1	1191.7	366.5	2277.7	32.2	52.2	0	162.6	66
	W	270°C	1358.1	1363.1	587	3532.3	40.4	82.1	0	166.5	175.3
	W	370°C	2379.2	1695.8	1081.6	6205.3	63.9	147.3	45.5	263.6	210.8
	BW	RM	1107.2	1140.1	545.7	3254.3	45.5	83.7	55.5	143.9	153.4
	BW	170°C	1070.2	1072.6	513.3	3137.8	36.3	78.1	1.8	140	50.8
	BW	270°C	1736.3	1126	790.2	4771.6	46.2	119	26.3	163.4	66.5
	BW	370°C	3005.8	1670.8	1449.1	8195.5	87	214.1	131.5	238.7	190.1
Salix purpurea	B	RM	1657	1129.9	1448.1	5961.1	182	80	112.1	286.6	131.1
	B	170°C	1617.1	1007.5	872	3722.2	70.5	42.3	23.4	231.9	62
	B	270°C	2339.3	1382.8	2022.2	8351	233.4	106.6	61.5	359.4	153.4
	B	370°C	3285.6	1485.7	3058.9	11968.1	396.5	164.1	187.9	518.4	176.6
	W	RM	726.8	730.4	274.1	1327.3	38.7	13.1	0	70.5	41
	W	170°C	810.2	741.6	320.7	1522.1	40.1	15.7	0	132.2	80.2
	W	270°C	1095.5	1176.5	441.7	2062.9	52.8	18.1	0	168.9	129.5
	W	370°C	2224.5	1586.8	775.3	3656.9	70	27.3	16.7	254.1	202.2
	BW	RM	983.7	1020.2	529	2430.1	46.6	28.1	18.5	155.1	166.8
	BW	170°C	886.6	821.3	433.4	2018.9	43.7	22.5	0	140.3	45.4
	BW	270°C	1676	1152.1	905.1	3799.9	71.9	43.4	25.8	193.3	129.6
	BW	370°C	2691.3	1751.1	1492.4	6140.2	122.6	71.9	65.9	300.3	195.9
Populus nigra x P. Maximowiczii	B	RM	2144.7	1186.6	864.1	9639.9	99.9	28	89.1	200.3	192.3
	B	170°C	1970.3	796.7	861.8	9637.6	96.7	27	19.4	164.1	57.8
	B	270°C	2716.1	1051.9	1154.1	12036.4	128.5	35.2	78.2	201.6	134.9
	B	370°C	4521.5	1335.7	1820.2	19496.3	304.4	57.5	153.6	329.1	213.9
	W	RM	802.5	883.7	219.1	1635.7	27.3	10.8	0	140.3	48.8
	W	170°C	813.9	1272.2	264.9	1899.6	34.2	11.8	1.3	146.4	125.8
	W	270°C	1506.8	1103.6	562.6	4312.3	96	20.4	19	169.7	195.8
	W	370°C	2501.8	1350.1	814.2	5534.9	103.1	25.6	29.6	270.4	207.3
	BW	RM	1192.5	1155.6	466.2	4708.2	50.9	16.8	0	171.5	31.7
	BW	170°C	1291.1	1210.7	491.9	4970.1	51.8	17.7	29.1	184.9	65.5
	BW	270°C	1787.5	1272.8	709.8	6676.1	71.6	23.8	82.9	177.6	135.9
	BW	370°C	3691.5	1339.4	1405.2	13129.9	187.8	43.6	170	256.7	187.3
Robinia pseudoacacia	B	RM	2128.2	1370.9	798.7	10781.2	82.8	24.6	0	183.6	174.4
	B	170°C	1701.9	1228.9	638.4	9556.4	65.2	20.7	0	183.9	80.1
	B	270°C	2969.3	1229.1	1153.4	15727.3	118.5	32.5	0	232.8	194.8
	B	370°C	4742.8	1568.1	1767.8	22855.9	184.5	46.8	0	264.9	227.1
	W	RM	544.2	1238.5	286.1	2279.5	35.5	9.4	0	164.7	105.1
	W	170°C	495.7	1208.6	257.2	2181.8	28.8	8.8	0	137.7	63.2
	W	270°C	807.9	1549.9	419.6	3331.3	51.8	11.5	0	196.2	145.6
	W	370°C	1532.9	1602.5	762.8	5950	58.9	14.4	0	253	228.5
	BW	RM	1047.5	1295.1	439.8	4277.6	40.7	13.9	0	158.6	116
	BW	170°C	903.6	1109.7	402.7	3761.3	40.2	13.2	0	149.6	66.2
	BW	270°C	1322.2	1511.1	584.8	5139.6	56.5	16	0	216.8	171.3
	BW	370°C	2674.1	1584	1119.3	9833	90.4	24.8	0	247.4	221.7

B, bark; W, wood; BW, bark and wood; P, phosphorus; Na, sodium; Mg, magnesium; K, potassium; Fe, iron; Mn, manganese; Zn, zinc; Al, Aluminium; B, Boron; RM, …

from wood. At 370°C, the respective percentages were 6.8-12.7% (bark-based biochar) and 2.04-2.7% (wood-based biochar). A similar trend of changes in the above chemical parameters in biomass submitted to carbonisation has been demonstrated by Medic *et al.* (2012), Tsai *et al.* (2012), Al-Wabel *et al.* (2013), and Zhao *et al.* (2013). Changes in the content of volatile substances followed a different course depending on the analysed fraction of biomass. The initial content of volatile particles in dry matter of biochar produced *via* pyrolysis of bark at a temperature of 170°C was 71.0-74.5% and did not undergo significant alteration, although when a change did occur, it was a rapid one, for example, the content of volatile substances decreased to 55.3-62.2% at 270°C, and then to 32.8-40.0% at 370°C. When wood biomass was submitted to pyrolysis at 170°C, the initial content of volatile substances was significantly higher than in bark equalling 79.2-79.6%. At 270°C, the content of volatile substances was distinctly lower, 55.6-

Table 5. Changes in the content of total carbon, hydrogen, oxygen, nitrogen, sulfur and the following mol ratios hydrogen to carbon, oxygen to carbon, carbon to nitrogen, (oxygen+nitrogen)/carbon in biochars depending on the species, type of biomass, and pyrolytic temperature (mean value±standard deviation, n=3).

Species	Type of biomass	Pyrolysis temperature	Elemental composition (% wt)					Molar ratio			
			C_t	H	O_a	N	S	H/C	O/C	C/N	(O+N) /C
Salix viminalis	B	RM	52.4±0.4	5.6±0.0	40.2	1.6±0.0	0.18±0.01	1.3	0.6	38.8	0.6
	B	170°C	53.7±0.2	5.9±0.1	38.6	1.7±0.0	0.10±0.00	1.3	0.5	37.7	0.6
	B	270°C	62.0±0.1	5.0±0.0	30.8	2.1±0.0	0.08±0.00	1.0	0.4	34.4	0.4
	B	370°C	71.4±0.3	4.0±0.0	22.2	2.3±0.0	0.06±0.00	0.7	0.2	36.1	0.3
	W	RM	54.9±0.2	6.0±0.0	38.6	0.4±0.0	0.07±0.00	1.3	0.5	160.5	0.5
	W	170°C	53.2±0.3	6.4±0.0	39.8	0.5±0.0	0.03±0.00	1.4	0.6	116.1	0.6
	W	270°C	63.7±2.1	5.1±0.2	30.5	0.6±0.0	0.04±0.02	1.0	0.4	124.3	0.4
	W	370°C	78.4±0.2	3.8±0.0	16.9	0.8±0.0	0.04±0.00	0.6	0.2	108.6	0.2
	BW	RM	53.7±0.5	5.7±0.0	39.8	0.7±0.0	0.12±0.00	1.3	0.6	93.6	0.6
	BW	170°C	50.9±0.2	6.0±0.0	42.2	0.7±0.0	0.07±0.01	1.4	0.6	79.7	0.6
	BW	270°C	64.7±0.2	5.0±0.0	29.2	1.0±0.0	0.05±0.00	0.9	0.3	79.1	0.4
	BW	370°C	78.4±0.2	3.7±0.0	16.6	1.2±0.0	0.04±0.00	0.6	0.2	73.2	0.2
Salix purpurea	B	RM	51.4±0.1	5.7±0.0	41.3	1.5±0.0	0.17±0.01	1.3	0.6	40.6	0.6
	B	170°C	54.3±0.1	6.1±0.0	37.8	1.7±0.0	0.10±0.00	1.3	0.5	37.1	0.5
	B	270°C	64.3±0.1	5.2±0.0	28.4	2.1±0.0	0.07±0.00	1.0	0.3	35.7	0.4
	B	370°C	69.9±0.0	4.3±0.0	23.4	2.3±0.0	0.08±0.00	0.7	0.3	35.3	0.3
	W	RM	55.8±0.2	6.1±0.1	37.6	0.5±0.0	0.10±0.00	1.3	0.5	130.2	0.5
	W	170°C	51.3±0.7	6.3±0.1	41.7	0.6±0.1	0.05±0.01	1.5	0.6	92.9	0.6
	W	270°C	63.7±0.2	5.5±0.0	30.1	0.7±0.0	0.04±0.00	1.0	0.4	109.4	0.4
	W	370°C	77.0±0.2	3.8±0.0	18.1	1.0±0.0	0.05±0.00	0.6	0.2	86.5	0.2
	BW	RM	54.8±0.4	5.9±0.0	38.5	0.6±0.0	0.10±0.00	1.3	0.5	100.0	0.5
	BW	170°C	51.3±0.3	6.1±0.0	41.7	0.7±0.0	0.06±0.01	1.4	0.6	81.8	0.6
	BW	270°C	65.5±0.0	5.2±0.0	28.4	0.9±0.0	0.05±0.00	1.0	0.3	82.8	0.3
	BW	370°C	75.0±0.4	3.7±0.0	20.0	1.2±0.0	0.06±0.00	0.6	0.2	70.7	0.2
Populus nigra x P. Maximowiczii	B	RM	57.4±0.2	6.0±0.0	34.9	1.6±0.0	0.08±0.01	1.2	0.5	41.9	0.5
	B	170°C	55.0±0.2	6.1±0.1	37.0	1.8±0.0	0.08±0.00	1.3	0.5	35.2	0.5
	B	270°C	64.3±0.2	5.5±0.0	28.0	2.1±0.0	0.07±0.00	1.0	0.3	35.0	0.4
	B	370°C	71.6±0.4	4.3±0.1	21.8	2.3±0.0	0.06±0.00	0.7	0.2	36.2	0.3
	W	RM	57.8±0.0	5.4±0.2	36.4	0.5±0.0	0.02±0.00	1.1	0.5	141.6	0.5
	W	170°C	56.4±0.1	6.5±0.0	36.5	0.6±0.0	0.02±0.00	1.4	0.5	102.1	0.5
	W	270°C	63.7±0.2	5.7±0.0	29.9	0.6±0.0	0.03±0.00	1.1	0.4	118.1	0.4
	W	370°C	77.5±0.2	3.7±0.0	17.7	1.0±0.0	0.03±0.00	0.6	0.2	89.8	0.2
	BW	RM	55.2±0.2	5.5±0.0	38.5	0.7±0.0	0.04±0.00	1.2	0.5	86.2	0.5
	BW	170°C	54.7±0.3	6.2±0.0	37.9	1.1±0.0	0.05±0.00	1.4	0.5	58.0	0.5
	BW	270°C	62.6±0.0	5.8±0.0	30.4	1.1±0.0	0.04±0.00	1.1	0.4	64.8	0.4
	BW	370°C	74.1±0.2	3.9±0.0	20.3	1.7±0.0	0.05±0.00	0.6	0.2	51.3	0.2
Robinia pseudoacacia	B	RM	52.4±0.1	5.8±0.1	38.6	3.0±0.0	0.10±0.00	1.3	0.6	20.3	0.6
	B	170°C	53.3±0.1	6.1±0.1	36.9	3.6±0.0	0.09±0.01	1.4	0.5	17.3	0.6
	B	270°C	60.7±0.2	5.9±0.0	29.1	4.3±0.0	0.08±0.00	1.2	0.4	16.6	0.4
	B	370°C	66.7±0.1	4.4±0.1	24.5	4.3±0.0	0.08±0.00	0.8	0.3	18.2	0.3
	W	RM	55.3±0.4	5.8±0.1	38.5	0.5±0.0	0.03±0.00	1.2	0.5	129.9	0.5
	W	170°C	54.2±0.0	6.2±0.1	39.0	0.6±0.0	0.02±0.00	1.4	0.5	111.0	0.5
	W	270°C	60.5±0.8	5.6±0.0	33.2	0.7±0.0	0.03±0.00	1.1	0.4	97.1	0.4
	W	370°C	77.5±0.2	3.9±0.0	17.5	1.0±0.0	0.03±0.00	0.6	0.2	88.8	0.2
	BW	RM	55.5±0.4	6.1±0.0	37.5	0.9±0.0	0.04±0.00	1.3	0.5	73.9	0.5
	BW	170°C	54.1±0.2	6.3±0.0	38.5	1.1±0.0	0.04±0.00	1.4	0.5	59.6	0.6
	BW	270°C	61.5±0.1	5.9±0.0	31.1	1.5±0.0	0.04±0.00	1.2	0.4	49.0	0.4
	BW	370°C	76.6±0.2	4.1±0.0	17.3	2.0±0.0	0.05±0.00	0.6	0.2	45.3	0.2

C_t, total carbon; B, bark; W, wood; BW, bark and wood; RM, …; H, hydrogen;, nitrogen; S, sulfur; H/C, hydrogen to carbon; O/C, oxygen to carbon; C/N, carbon to nitrogen.

65.5%, declining to 28.7-30.7% when the temperature rose to 370°C, being much lower than its content following the pyrolytic treatment of bark at the same process temperature.

Losses in the content of volatile particles and an increase in the ash content reflect the ongoing decomposition of organic matter and release of volatile organic compounds during pyrolysis (Bergman and Kiel, 2005; van der Stelt *et al.,* 2011; Lee *et al.,* 2013; Mohan *et al.,* 2014; Zhao *et al.,* 2018). The content and quality of ash broadly define the potential use of biochar. A high ash concentration might mean that the biochar in question cannot be used industrially; it may also implicate difficulties in the thermochemical conversion of biomass (*e.g.*, low melting point) (Weber

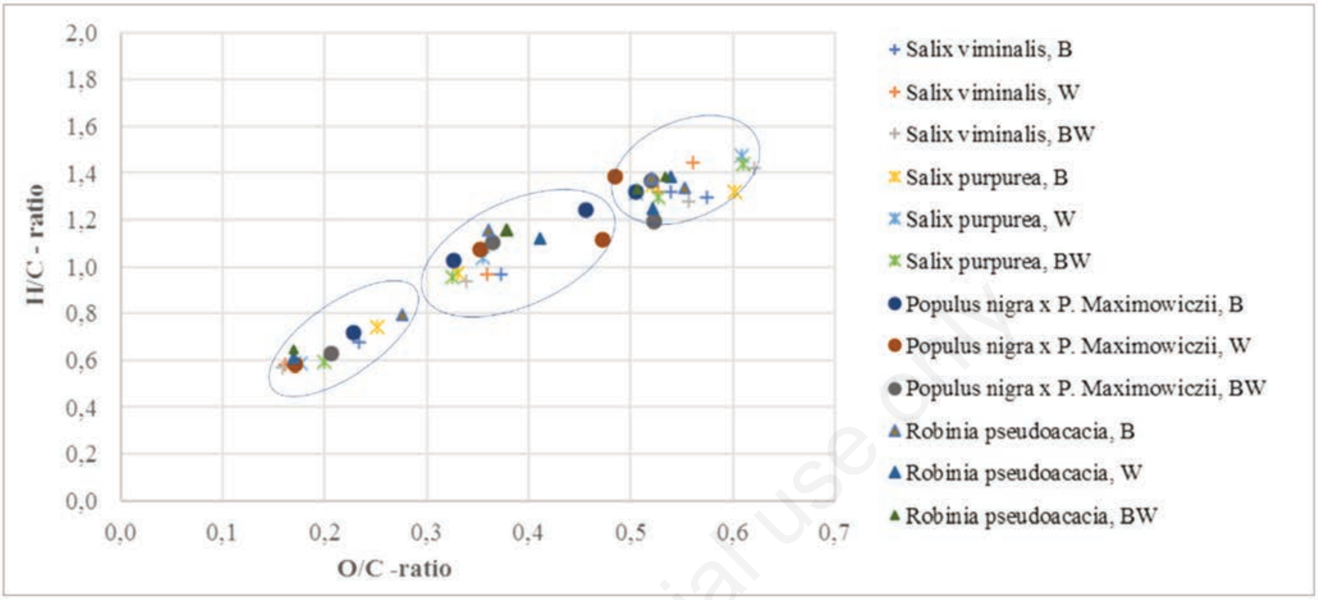

Figure 3. Relationships between changes in the O/C and H/C ratios in biochars depending on the species, type of biomass, and pyrolytic temperature (B, bark; W, wood; BW, bark, and wood).

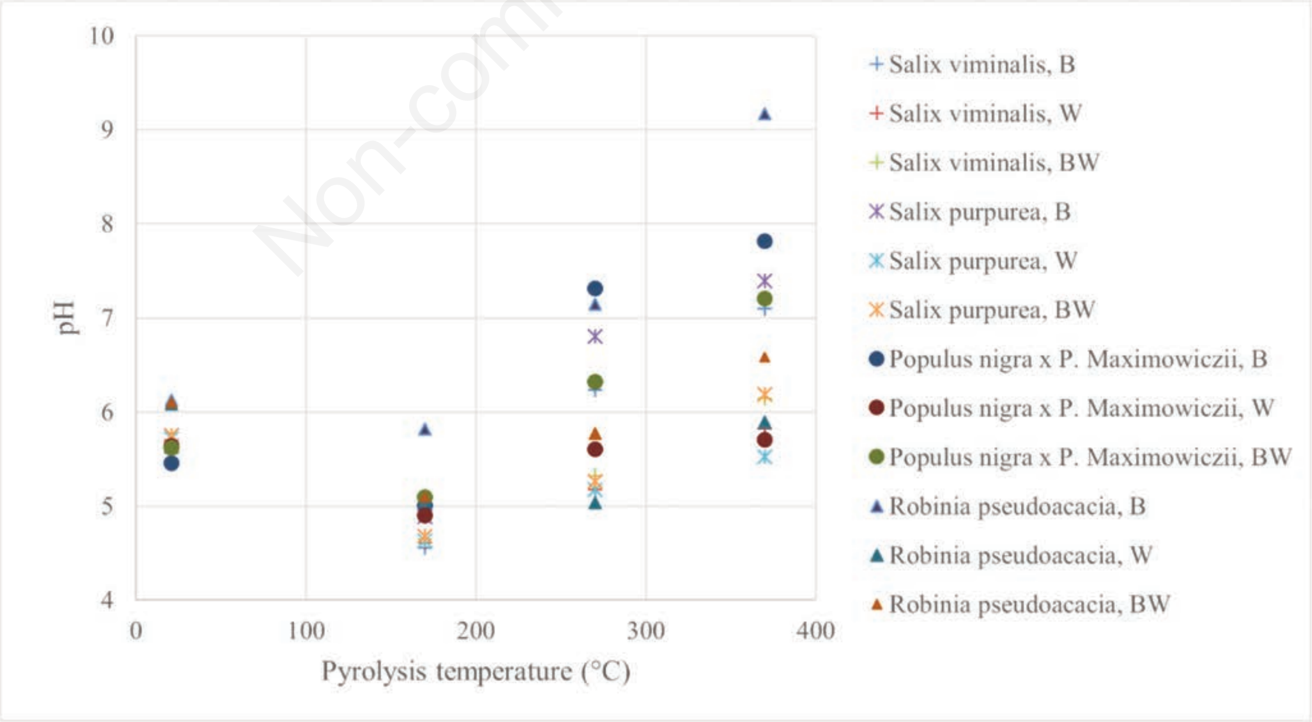

Figure 4. The pH of biochars in relation to species, type of biomass, and pyrolytic temperature. B, bark; W, wood; BW, bark and wood. B, bark; W, wood; BW, bark and wood.

and Quicker, 2018). On the other hand, a high ash content can be a source of valuable micro- and macronutrients in fertilisation products essential for obtaining high yields of crops.

Strong positive correlations were determined between the total carbon content, the fixed carbon content, and the calorific value of biochar. Negative correlations were identified between the above variables and the content of volatile substances. The remaining correlations tested were statistically insignificant.

Micro- and macronutrients

The content of macro- and micronutrients, particularly of Ca, Mg, P, and K, is essential for the suitability of biochars as fertilisation products (Tan *et al.,* 2017). Biomass also contains large quantities of alkaline metals and alkaline earth metals, mainly K, Na, Ca, and Mg (Weber and Quicker, 2018). Moreover, ash from biomass contains considerable amounts of Si and Al. Several studies have shown that micro- and macronutrients are partly released to the gaseous phase during thermochemical conversion, and they can be detected over the entire range of pyrolytic temperatures. However, most of the release occurs below 500°C or very high temperatures, over 800°C (Weber and Quicker, 2018). Lower temperatures during the pyrolysis process prevent the loss of valuable micro- and macroelements thus ensuring their higher concentration in the final product – biocarbon.

Changes in the content of macro- and micronutrients and heavy metals in biochars in this study are specified in Table 4. The concentration of phosphorus in the dry matter of bark extraction mass was 1899 mg/kg, three-fold higher than in wood extraction mass, where it equalled 572 mg/kg. At 170°C, changes were minimal, but phosphorus content increased considerably at higher temperatures, reaching 3918 mg/kg in bark-based biochar and 1728 mg/kg in wood-based biochar at 370°C. A similar trend was noted for the other macronutrients: sodium, magnesium, and potassium. At all temperatures, the input biomass in the form of bark and the biochars obtained from bark contained much higher concentrations of the above elements. The results were similar for the analysed metals (Fe, Mn, Zn, Al, B), which appeared in much higher concentrations in bark-based biochars than in biochars produced from wood biomass. However, heavy metals, such as Pb, Cd, Cu, and Cr, were not detected in any of the samples.

Elemental composition and molar ratios

Biochar consists mainly of the following elements: C, H, O, N, and S, while other elements occur in trace amounts. The elemental composition of the biochars in this study is specified in Table 5. During the pyrolytic process, due to the removal of functional groups containing oxygen and hydrogen atoms and the oxygen and hydrogen concentrations decrease while the carbon content increase (Weber and Quicker, 2018; Zhao *et al.,* 2018). At higher temperatures of pyrolysis, the molar ratios decline. This confirms the ongoing decrease in polarity and the simultaneous increase in aromaticity of the material (Fischer and Glaser, 2012; Schimmelpfennig and Glaser, 2012; Jining *et al.,* 2014; De Bhowmick *et al.,* 2018).

The ongoing process of carbonisation reflected by changes in the H/C and O/C molar ratios is illustrated by van Krevelen's diagram (Weber and Quicker, 2018). The H/C molar ratio is considered an indicator of aromaticity, while the O/C, (O+C)/N molar ratios indicate carbonisation and polarity (Jining *et al.,* 2014; De Bhowmick *et al.,* 2018). As such, they are also used as indirect indicators of the stability of biochar in soil (Tan *et al.,* 2017). It is assumed that biochar should have an O/C mol ratio below 0.4 and, depending on references, the H/C molar ratio should be below 0.6 (Fischer and Glaser, 2012; Schimmelpfennig and Glaser, 2012; Jining *et al.,* 2014;) or below 0.7 (De Bhowmick *et al.,* 2018). The O/C indicator is used to estimate the half-life of biochar in soil. Within the O/C≥0.7 range, the half-life of biochar is estimated to last from a few up to one hundred years, while at the O/C in the range of 0.2-0.6, it can continue for 100-1000 years, and when the O/C mol ratio is ≤0.2 the biochar's half-life is estimated to exceed 1000 years (Spokas, 2010). The degree of aromaticity of biochars indirectly influences the functional properties of the substance. Aromatic structures are characterised by high resistance to decomposition; hence biochars possessing a considerable degree of aromaticity are highly stable and resistant to the geochemical decomposition in soil. Two types of aromatic structures are distinguished in biochar. One consists of aromatic rings forming an amorphous structure, and the other is composed of condensed polyaromatic structures that create a regular crystalline network. Research results prove that aromaticity increases dramatically in temperatures between 200 and 500°C, reaching the peak at 500-800°C (Weber and Quicker, 2018). The biggest changes in the mol ratios mentioned here during the process of pyrolysis appear within the temperatures of 250-350°C when they are contained in a range of 0.7-0.3 for the O/C ratio and 1.5-0.8 for the H/C mol ratio, the said changes are milder at higher temperatures (Weber and Quicker, 2018). In the research reported herein, the H/C mol ratio declined from 1.12-1.34 to 0.57-0.80, while the O/C mol ratio decreased from 0.46-0.60 to 0.16-0.28 (Figure 3 and Table 4). The H/C mol ratio of less than or equal 0.7 was achieved at the pyrolytic temperature of 370°C, except for the substrate of false acacia bark. Based on the O/C ratio=0.2, it can be predicted that the half-life time for the biochars produced at 370°C will be over one-thousand years (except the biochars from the bark of *Salix purpurea* and *Robinia pseudoacacia*). The decreased values of the molar ratios achieved in this experiment align with the results reported by De Bhowmick *et al.* (2018). Similar results were obtained by de Caprariis *et al.* (2017), where the H/C molar ratio fell from 0.035 to 0.025 within the range of process temperatures of 550-750°C, thus verifying an increase in aromaticity, while the decrease in the O/C molar ratio from 0.16 to 0.11 suggested a decrease in the share of polar function groups in the chemical structure of the produced biochar.

pH

Biochars can affect soil pH; therefore, pH of biochars is particularly important when used for fertilisation (Tan *et al.,* 2017). Pyrolysis increases the pH of biochar (Weber and Quicker, 2018, Zhao *et al.,* 2018). Nowadays, most soils worldwide are acidic or slightly acidic in pH (FAO, 2019). The high acidity of soils has negative consequences for the soil microbial community, in addition to which highly acidic soils (pH<5.5) are characterised by having toxic amounts of aluminium and manganese. Most agricultural crops yield the best on mineral soils with pH=6.5 (FAO, 2019). In the long term, soil enrichment with neutral or alkaline biochar can contribute to higher soil pH.

Raw biomass typically has a slightly acidic pH. During pyrolysis, acidic functional groups, that is, carboxyl, hydroxyl, or formyl groups, are cut off, thereby biochars typically have neutral or slightly acidic pH (Tan *et al.,* 2017; De Bhowmick, 2018; Weber and Quicker, 2018; Zhao *et al.,* 2018). pH depends on the relative content of ash – a higher concentration of ash leads to higher pH of biochar (Tan *et al.,* 2017; Weber and Quicker, 2018). Furthermore, some research indicates that most acidic functional groups are released relatively early during the carbonisation process. Therefore, the impact of the termination time and the heating rate on pH are limited (the first 15 minutes are the most important) (Angin, 2013; Conti *et al.,* 2014; Wang *et al.,* 2018; Weber and Quicker, 2018).

The input biomass used in this study had a relatively low pH. It increased under the influence of carbonisation (Figure 4), and a neutral pH was obtained only for the bark fraction submitted to pyrolysis at a temperature of 270-370°C for all of the analysed species, which suggests their potentially positive influence on soil pH should these biochars be used as a soil improver. The remaining biochars produced at 270 and 370°C reached a pH above 5, suggesting that they could be applied to very acidic soils.

Conclusions

This research explored the parameters of biochar obtained from bark, wood, and wood and bark residues of four woody species after supercritical CO_2 extraction of bioactive substances. The parameters were discussed in the context of biochar functionality as an energy source and soil improver. Concerning raw material, biochar has a significantly higher content of total carbon (by 77.0-78.4%) and calorific value (by 25.8-30.1 MJ/kg), which confirms a high energy potential of biochar. The energetic value of biochars from bark residues is slightly decreased due to a 1.1-2.5-fold increase of ash, but at the same time, the 1.7-7.2-fold higher content of ash in relation to wood and bark and wood increases the value of this biochar as a soil improver. Moreover, biochars had a significantly higher fixed carbon by 64.7-66.7% and lower H/C and O/C molar ratios, which suggests their greater stability and resistance to geochemical decomposition; hence they can increase the reservoir of organic carbon in the soil. Concerning their application for soil fertilisation and their sequestration role, the biochars contain more macronutrients (P, Na, Mg, K) and metals (Fe, Mn, Zn, Al, B) than the extraction remains, being free from heavy metals (Pb, Cd, Cu, Cr).

Generally, biochars obtained from bark supercritical extraction waste have a much higher concentration of micro- and macronutrients. In contrast, wood extraction mass reaches higher concentrations of total carbon and fixed carbon, although this is achieved at the expense of a lower mass and energy yield. The results indicate that lignocellulose biomass extraction waste can be a valuable input raw material for the production of biochar and depending on the temperature regime of pyrolysis and the type of biomass processed, the biochar produced can serve different functions.

References

Al-Wabel M.I., Al-Omran A., El-Naggar A.H., Nadeem M., Usman A.R.A. 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. Bioresour. Technol. 131:374-9.

Angin D. 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. Bioresour. Technol. 128:593-7.

Bai M., Wilske B., Buegger F., Bruun E.W., Bach M., Frede H.G., Breuer L. 2014. Biodegradation measurements confirm the predictive value of the O:C-ratio for biochar recalcitrance. J. Plant Nutr. Soil Sci. 177:633-7.

Bergman P.C.A., Kiel J.H.A. 2005. Torrefaction for biomass upgrading. Proceedings of the 14th European Biomass Conference and Exhibition, Paris, France.

Białowiec A., Pulka J., Stępień P., Manczarski P., Gołaszewski J. 2017. The RDF/SRF torrefaction: an effect of temperature on characterization of the product – carbonized refuse derived fuel. Waste Manag. 70:91-100.

Conti R., Rombolà A.G., Modelli A., Torri C., Fabbri D. 2014. Evaluation of the thermal and environmental stability of switchgrass biochars by Py-GC-MS. J. Anal. Appl. Pyrolysis 110:239-47.

De Bhowmick G., Sarmah A.K., Sen R. 2018a. Production and characterization of a value added biochar mix using seaweed, rice husk and pine sawdust: a parametric study. J. Clean. Prod. 200:641-56.

De Bhowmick G., Sarmah A.K., Sen R. 2018b. Lignocellulosic biorefinery as a model for sustainable development of biofuels and value added products. Bioresour. Technol. 247:1144-54.

de Caprariis B., De Filippis P., Hernandez A.D., Petrucci E., Petrullo A., Scarsella M., Turchi, M. 2017. Pyrolysis wastewater treatment by adsorption on biochars produced by poplar biomass. J. Environ. Manage. 197:231-8.

EBC. 2019. Guidelines of the European biochar certificate. Available from: https://www.european-biochar.org/media/doc/2/version_en_10_3.pdf. Accessed on: 21 January 2020.

European Commission. 2015. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Closing the loop - an EU action plan for the circular economy. Available from: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52015DC0614. Accessed: 21 January 2020.

FAO. 2019. FAO soils portal. Available from: http://www.fao.org/soils-portal/soil-survey/soil-classification/numerical-systems/chemical-properties/. Accessed: 21 January 2020.

Fischer D., Glaser B. 2012. Synergisms between compost and biochar for sustainable soil amelioration. In: Kumar S., Bharti A. Management of Organic Waste. IntechOpen, London, UK.

Jining Z., Lü F., Luo C., Shao L., He P. 2014. Humification characterization of biochar and its potential as a composting amendment. J. Environ. Sci. 26:390-7.

Kan T., Strezov V., Evans T.J. 2016. Lignocellulosic biomass pyrolysis: a review of product properties and effects of pyrolysis parameters. Renew. Sustain. Energy Rev. 57:1126-40.

Knowles O.A., Robinson B.H., Contangelo A., Clucas L. 2011. Biochar for the mitigation of nitrate leaching from soil amended with biosolids. Sci. Total Environ. 409:3206-10.

Kopetz H., Jossart J.M., Ragossnig H., Metschina C. 2007. European biomass statistics 2007: a statistical report on the contribution of biomass to the energy system in the EU 27. European Biomass Association, Brussels, Belgium.

Lee Y., Park J., Ryu C., Gang K.S., Yang W., Park Y.K., Jung J., Hyun S. 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500°C. Bioresour. Technol. 148:196-201.

Lehmann J., Rillig M.C., Thies J., Masiello C.A., Hockaday W.C., Crowley D. 2011. Biochar effects on soil biota - a review. Soil Biol. Biochem. 43:1812-36.

Liu Z., Quek A., Kent Hoekman S., Balasubramanian R. 2013. Production of solid biochar fuel from waste biomass by hydrothermal carbonization. Fuel. 103:943-9.

Mašek O., Budarin V., Gronnow M., Crombie K., Brownsort P., Fitzpatrick E., Hurst P. 2013. Microwave and slow pyrolysis biochar - comparison of physical and functional properties. J. Anal. Appl. Pyrolysis. 100:41-8.

Medic D., Darr M., Shah A., Potter B., Zimmerman J. 2012. Effects of torrefaction process parameters on biomass feedstock upgrading. Fuel. 91:147-54.

Mohan D., Sarswat A., Ok Y.S., Pittman C.U. 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent - a critical review. Bioresour. Technol. 160:191-202.

Mumme J., Srocke F., Heeg K., Werner M. 2014. Use of biochars in anaerobic digestion. Bioresour. Technol. 164:189-97.

Nelissen V., Saha B.K., Ruysschaert G., Boeckx P. 2014. Effect of different biochar and fertilizer types on N_2O and NO emissions. Soil Biol. Biochem. 70:244-55.

Ostolski M., Adamczak, M., Brzozowski B., Wiczkowski W. 2021. Antioxidant activity and chemical characteristics of supercritical CO_2 and water extracts from willow and poplar. Molecules. 26:545.

Radawiec W., Dubicki M., Karwowska A., Żelazna K., Gołaszewski J. 2014. Biochar from a digestate as an energy product and soil improver. Agric. Eng. 18:149-56.

Schimmelpfennig S., Glaser B. 2012. One step forward toward characterization: some important material properties to distinguish biochars. J. Environ. Quality. 41:1001-13.

Sigua G.C., Novak J.M., Watts D.W., Cantrell K.B., Shumaker P.D., Szögi A.A., Johnson M.G. 2014. Carbon mineralization in two ultisols amended with different sources and particle sizes of pyrolyzed biochar. Chemosphere. 103:313-21.

Spokas K.A. 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon Manag. 1:289-303.

Tan Z., Lin C.S.K., Ji X., Rainey T.J. 2017. Returning biochar to fields: a review. Appl. Soil Ecol. 116:1-11.

Tang J., Zhu W., Kookana R., Katayama A., 2013. Characteristics of biochar and its application in remediation of contaminated soil. J. Biosci. Bioeng. 116:653-9.

Troy S.M., Lawlor P.G., O' Flynn C.J., Healy M.G. 2013. Impact of biochar addition to soil on greenhouse gas emissions following pig manure application. Soil Biol. Biochem. 60:173-81.

Tsai W.T., Liu S.C., Chen H.R., Chang Y.M., Tsai Y.L. 2012. Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as a soil amendment. Chemosphere. 89:198-203.

van der Stelt M.J.C., Gerhauser H., Kiel J.H.A., Ptasinski K.J. 2011. Biomass upgrading by torrefaction for the production of biofuels: a review. Biomass Bioener. 35:3748-62.

Weber K., Quicker P. 2018. Properties of biochar. Fuel. 217:240-61.

Zhao B., Connor D.O., Zhang J., Peng T., Shen Z., Tsang D.C.W., Hou D. 2018. Effect of pyrolysis temperature , heating rate , and residence time on rapeseed stem derived biochar. J. Clean. Prod. 174:977-87.

Zheng H., Wang Z., Deng X., Herbert S., Xing B. 2013. Impacts of adding biochar on nitrogen retention and bioavailability in agricultural soil. Geoderma. 206:32-9.