



Assessment of energy parameters of biomass and biochars, leachability of heavy metals and phytotoxicity of their ashes

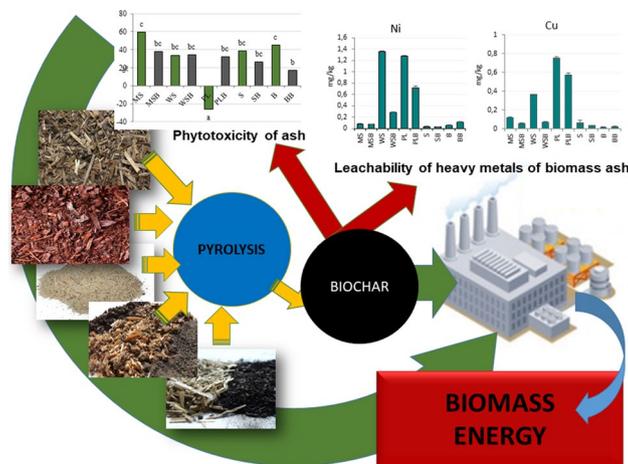
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Abstract

The aim of this study was to determine selected energy parameters, leachability of heavy metals and phytotoxicity of biomass ash for different types of plant biomass (wheat straw, miscanthus straw, bark and sawdust) and poultry manure, as well as biochars produced from them. Based on data from proximate and ultimate analysis of the investigated materials, fuel value index (FVI) was calculated to determine their suitability for energy production. The ashes were analyzed for both chemical composition and leaching behavior. The phytotoxicity test of aqueous ash extracts was performed for *Lepidium sativum* L. It was found that the calorific value of biochars was higher on average by 36% than the value determined for feedstocks used in the pyrolysis process. The pyrolysis of organic materials resulted in the reduction of the volatile matter content. The gross calorific value was determined in biochars formed from miscanthus straw and sawdust which were 26.6 and 23.4 MJ kg⁻¹, respectively. Leachability of heavy metals of biomass ash was highly diverse and depended on the analyzed element and the material type. The phytotoxicity analysis showed that, in general, each of the ash extracts tested had a positive effect on the growth of *Lepidium sativum* L. compared to the control. The use of ash, fertilizer, or sorbents can be an interesting alternative for materials with high ash content. In all these cases, biochars seem to be very attractive materials that can be used not only in energy production. Given the high carbon content of biochar obtained in the pyrolysis process, it has a high-energy potential and can be used as a biofuel.

Graphical abstract



Keywords Biochar · Biomass · Fixed carbon · Heat of combustion · Calorific value · Heavy metals · Phytotoxicity

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Introduction

Nowadays, biomass is considered one of the most promising sources of the renewable energy, especially in the case of small-scale boilers used for municipal heating. It is worth mentioning that biomass is also widely used in the production of electricity and district heat, reducing the emission of carbon dioxide [1–4]. The worldwide technological development accompanied by a continuous increase of energy consumption as well as the need to implement provisions of the Kyoto Protocol cause a steadily increasing interest in the use of energy from renewable sources [5]. The depletion of conventional fossil fuels (coal, oil or natural gas) observed in recent years is also significant. Worse still, conventional power plants that use traditional energy carriers pollute the environment. For this reason, it is so important to obtain renewable energy sources which could reduce harmful impacts on the natural environment. This strategy of diversified energy production will require rapidly developing technologies of biomass combustion, as well constant monitoring of the use of different types of biomass.

In contrast to conventional fossil fuels, biomass is an energy carrier mainly with local potential, which is caused by its low (compared to coal) bulk density. Moreover, biomass requires not only special boilers and burners, but also specially designed storage and transportation equipment, and this is probably a more complex problem. In many cases, efficient processing of this fuel requires special preparation techniques, mostly due to its high moisture content, heterogeneity, and the relatively low energy content per unit volume [6–8]. Nevertheless, the prevalence and the overall availability of biomass make this feedstock very popular among manufacturers and potential customers. Another benefit of processing of biomass for energy purposes is development of companies which can utilize local feedstocks and sell it to local clients.

Biomass as a source of energy can be either the waste from the wood processing and farming (e.g., bark, sawdust, and straw) or a product obtained intentionally (energy crops) [3, 9]. Another branch of production from which significant amounts of energy can be received is the poultry industry [10]. In the recent years, this sector has been considered the most rapidly growing part of the economy in many countries, able to provide significant amounts of energy. High amounts of solid waste produced by the poultry industry and the emission of greenhouse gases are two major problems of the poultry production. It is believed that the use of poultry litter as a feedstock for bioenergy production or its conversion into biochar is a promising alternative to waste management and utilization [10]. Another important issue is the pyrolysis process, in which that material undergoes hygienisation due to the use of high temperatures.

However, it should be noted that during combustion, solid by-products (ashes) are formed, the number of which increased significantly in the last decade [11]. Although their use for fertilization is widely known (high macroelement content, high pH values), ashes are usually stored in landfills. This is due to the potential content of heavy metals, which rises concern related to soil environment pollution. The chemical and physical properties of the ash can vary considerably depending on the type of biomass and combustion technology used. Therefore, the availability of nutrients and heavy metals can differ significantly between individual ashes. For this reason, leaching tests can provide more information on the release of components from the ash and their potential toxicity, including effects on plants. Additionally, it should be emphasized that the storage of these materials may pose a serious threat especially to water purity, as minerals (including toxic heavy metals) are leached and infiltrated.

The composition and structure of biomass play a key role in the generation and emission of heat from installations for the combustion of alternative fuels, but, at the same time, they often cause technological problems. High carbon content and relatively low degradability make biochar obtained in the pyrolysis process usually a high-energy fuel [8, 12, 13]. Depending on the biomass type and process parameters such as temperature, time, and pressure, one can obtain a product of different quality and, consequently, requiring different management methods. The product quality is a common subject of research available in the literature. Undoubtedly, biochar, in contrast to feedstocks from which it is produced, has a greater homogeneity hydrophobicity, and energy density (concentration) [12, 14].

The evaluation of the possibility of using certain types of biomass for energy purposes requires application of the same principles as in the case of traditional fuels. Therefore, the investigations were conducted with the aim to determine (i) the energy potential of feedstocks and biochars produced from them, estimated on the basis of: elemental composition, moisture content, ash content, volatile matter, fixed carbon, heat of combustion, and lower heating value; (ii) bulk and absolute densities and porosity. To assess the possible effect of combustion residues on the environment, the following were analyzed: (iii) leachability of heavy metals; and (iv) phytotoxicity of biomass ash for feedstocks, as well as biochars produced from them.

Materials and methods

Experimental design

Feedstocks used in the study were the representative samples of wheat straw (WS), *Miscanthus giganteus* straw (MS), sawdust (S), coniferous trees bark (B) and poultry litter (PL),

as well as biochars derived from these materials: wheat straw biochar (WSB), Miscanthus straw biochar (MSB), sawdust biochar (SB), bark biochar (BB), and poultry litter biochar (PLB). These feedstocks came from a farmstead (straw and poultry litter) or were obtained as sawmill waste (sawdust and bark). All materials were collected in the area of Lesser Poland. Due to their different humidity, materials were conditioned at 65 °C for 24 h. Then, the samples were ground in a laboratory mill to fractions of less than 5 mm for thermal conversion. The analysis of the effect of particle size on the process was omitted.

Pyrolysis process

Pyrolysis was carried out under laboratory conditions on a stand for thermal conversion of biomass, in the oxygen-free atmosphere [15, 16]. Nitrogen was used as an inert gas, since it is a most common and inexpensive medium. Samples of approx. 100 g were placed in a closed chamber at 300 ± 10 °C. Exposure time was 15 min. The analysis of biomass energy properties before and after the pyrolysis process included the determination of: moisture content, ash content, higher and lower heating values, as well as bulk and absolute densities. These parameters were used to determine the porosity of the material before and after the process. Based on these determinations, basic information on the structure and functional properties of the material, mainly in the context of its energy use, were obtained. These analyses were performed on the test apparatus in a certified laboratory, in accordance with the applicable European standards, as well as using their own procedures. The samples were analyzed in duplicate to ensure accuracy required by a corresponding standard.

Energy potential of feedstocks and biochars

The moisture content (M_{ar}) before and after pyrolysis was determined based on PN-EN 14774-3:2010 [17]. The oven-drying method was applied: a small amount of material (1 g sample) was dried in a dryer (SLN 160, POLEKO) in an air atmosphere at 105 °C. The moisture content was determined as a difference between sample weights before and after drying [17].

The ash content (A_d) was determined according to PN-EN 14775:2010 [18], by calculating the mass of the residue after sample combustion in a furnace (SNOL 3/1100, SNOL) in an air atmosphere, under rigidly controlled conditions of time and temperature (550 ± 10 °C). The mass of the residual ash in the crucible was then compared with the initial mass of the sample [18].

The volatile matter content (V_d) was determined according to PN-EN 15148:2009 [19]. A test portion of the whole sample used in the analysis was heated with ambient air at

900 ± 10 °C for 7 min. The percentage of volatile matter was calculated based on the loss in mass of the test portion after deducting the loss in mass due to moisture.

Gross calorific value (higher heating value, $q_{v,dr,d}$) was determined according to PN-EN 14918:2010 [20]. The sample of 1 ± 0.05 g was placed in an isoperibol calorimeter (C 6000 Isoperibol, IKA). Then, the sample was combusted in the form of a compressed pellet in a bomb calorimeter in pure oxygen and at high pressure (3 MPa). The sample was ignited using a cotton thread with known heat of combustion value. The calorific value was calculated according to equations specified in the standard [20], and then entered into operational software of the device. Net calorific value (lower heating value, $q_{p,net,d}$) was calculated from the relation between the heat of combustion and gross calorific value. Gross calorific value was reduced by the value of heat used to evaporate water obtained from the fuel in the hydrogen combustion process as well as moisture present in the sample. This parameter was calculated using a computer program controlling operation of the calorimeter, according to the equations given in the standard [20].

The bulk density (BD) was determined according to PN-EN 15103:2010 [21]. Calibrated, constant volume vessel was filled with material and weighted. The bulk density was then calculated as a mass of the sample divided by the vessel volume. The absolute density (ρ_{abs}) was determined using our own procedure with helium pycnometry apparatus (AccuPyc 1340, Micromeritics). The device was equipped with 50 cm³ chamber. According to this technique, the sample mass is divided by the sample skeletal volume, measured by the apparatus. Skeletal volume is the volume of the solid sample (including closed pores, which are not accessible for helium). This parameter is determined based on the change of pressure resulting from variations in the helium volume. An important fact about this method is that helium atoms penetrate all open pores within the analyzed particle [21]. Normal procedure provides analysis of three samples in ten series of measurements [22]. Then, the average value is estimated for each material. Porosity of the material is estimated according to the following equation:

$$\varphi = \frac{BD}{\rho_{abs}} \quad (1)$$

Chemical analyses

The ultimate analysis (C_d , H_d , N_d , S_d) of samples was made using the CHNS analyzer (Vario EL Cube, Elementar) by specific standardized methods [23, 24]. Total O was determined by subtraction according to DIN 51733:2008–2012 [25], as follows:

$$O_d = 1 - C_d - N_d - H_d - S_d \quad (2)$$

The total contents of macroelements and trace elements were determined according to PN-EN ISO 16968:2015–2007 [26]. Organic material samples were placed in Teflon vessels and treated with 6 cm³ of concentrated HNO₃ (Suprapur 65%) and 2 cm³ of H₂O₂. Subsequently, the materials were mineralized in a closed system using a microwave oven (Multiwave 3000, AntonPaar). The contents of macroelements and trace elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES Optima 7300 DV, Perkin Elmer) [27].

Fuel value index

Based on data from proximate and ultimate analysis of the investigated materials, fuel value index (FVI) was introduced to determine their suitability for energy production. This parameter takes into account values obtained in the proximate analysis to determine the energy effect of combustion per bulk density of the material. Calculations were made according to the formula [28]:

$$FVI = \frac{q_{p,net,d} \times BD}{A_d \cdot M_{ar}}, \quad (3)$$

where *FVI* is the fuel value index (GJ/m³), *q_{p,net,d}* is the net calorific value (GJ/kg), *BD* is the bulk density (kg/m³), *A_d* is the ash content (%), and *M_{ar}* is the moisture content (%).

According to the literature, higher FVI can be obtained for good quality fuels and, usually, for such materials it should exceed 500 GJ/m³.

Leaching tests

The leaching test was conducted for the analyzed ashes at a liquid to solid ratio of 1:20 (material:redistilled water). Samples were placed on a shaker and shaken for 24 h. The contents of Cu, Cd, Pb, Zn, Mn, Ni, Cr, and Fe were determined in the obtained solutions by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 7300 DV). Additionally, the following parameters were determined in the tested extracts: pH—electrochemically using pH meter (CP-505) and electrical conductivity using conductometer (conductivity/oxygen meter CCO-501).

Phytotoxicity of ash water extracts

The phytotoxicity of the tested ash extracts (material:water = 1:20) was investigated for *Lepidium sativum* L. The experimental design included ten treatments carried out in three replicates: H₂O—redistilled water, *Miscanthus giganteus* straw (MS), *Miscanthus giganteus* straw biochar (MSB), wheat straw (WS), wheat straw biochar (WSB), poultry litter (PL), poultry litter biochar (PLB),

sawdust (S), sawdust biochar (SB), coniferous trees bark (B), and coniferous trees bark biochar (BB). The seeds of *Lepidium sativum* L. (20 pieces) were placed in extracts for 24 h. After that time, the seeds were placed on Petri dishes lined with tissue paper and moistened with redistilled water. Then, the seeds were placed in an incubator for 72 h at 25 °C ± 0.1. Subsequently, the length of the plant hypocotyl and root was measured. The inhibition/stimulation index value was calculated based on the results obtained, and the treatment in which test was carried out on redistilled water was adopted as a point of reference:

$$IG = [(A - B)/A] \times 100\%, \quad (4)$$

where *A* is the average for seed germination and root growth in control, while *B* is average for germination of seeds and root growth of *Lepidium sativum* L.

Statistical calculations

The standard deviation (SD) value was calculated for the results obtained. The phytotoxicity results were compiled using a one-way analysis of variance (ANOVA). The mean values of analyzed properties were compared using Duncan's multiple range test at *p* ≤ 0.05. All statistical calculations were made using the STATISTICA 10 package (Stat-Soft Inc.).

Results and discussion

Elemental analysis

The analysis of the tested materials revealed an increase in the contents of carbon and nitrogen after pyrolysis. Furthermore, the contents of hydrogen, sulfur, and oxygen were reduced, as shown in Table 1. Such a change in the elemental composition can be attributed to the fact that, during pyrolysis, light organic fractions are being decomposed. These are mainly substances that break down to release compounds with significant amounts of hydrogen (light hydrocarbons and simple structure polymers). The carbon content in materials ranged from 34 to 68%. However, higher values (exceeding 60% of the C content) related to biochars were produced from miscanthus straw, sawdust, and wheat straw. According to Tripathi et al. [29], the proportions in which carbon, hydrogen, and oxygen occur in biomass have a decisive effect on its calorific value. The authors stated that the high content of N and S in biomass can result in the formation of high-energy C–N, H–N, C–S, and H–S bonds. On the other hand, the low content of N and S in biomass is more environmentally friendly when the biomass is combusted, because it does not contribute to the formation of acid rains and greenhouse gas emissions. What is more, the ash content seems to be an

Table 1 The ultimate analysis of plant materials, poultry litter and biochars

| Material | N_d % | C_d | H_d | S_d | O_d | H/C | O/C |
|---------------|-----------------|-----------------|------------------|------------------|-----------------|------|------|
| Raw materials | | | | | | | |
| B | 0.43 ± 0.02 | 34.2 ± 0.15 | 4.09 ± 0.17 | $0.03 \pm <0.01$ | 19.7 ± 0.20 | 0.12 | 0.58 |
| S | 0.09 ± 0.01 | 47.5 ± 0.10 | 6.70 ± 0.08 | $0.01 \pm <0.01$ | 44.8 ± 2.15 | 0.15 | 0.94 |
| WS | 0.25 ± 0.02 | 47.2 ± 1.12 | 6.63 ± 0.11 | $0.03 \pm <0.01$ | 40.3 ± 3.29 | 0.16 | 0.85 |
| MS | 0.37 ± 0.01 | 46.1 ± 0.19 | 6.39 ± 0.12 | 0.55 ± 0.01 | 41.0 ± 2.87 | 0.16 | 0.89 |
| PL | 2.67 ± 0.11 | 35.8 ± 0.20 | $0.61 \pm <0.01$ | 0.65 ± 0.02 | 28.6 ± 0.20 | 0.20 | 0.80 |
| Biochars | | | | | | | |
| BB | 0.57 ± 0.02 | 34.2 ± 1.11 | 2.48 ± 0.19 | $0.03 \pm <0.01$ | 14.0 ± 1.12 | 0.18 | 0.41 |
| SB | 0.10 ± 0.05 | 67.1 ± 2.18 | 4.72 ± 0.08 | $0.01 \pm <0.01$ | 27.2 ± 2.00 | 0.17 | 0.41 |
| WSB | 0.50 ± 0.02 | 67.7 ± 0.89 | 4.67 ± 0.03 | $0.02 \pm <0.01$ | 15.4 ± 0.59 | 0.30 | 0.23 |
| MSB | 1.00 ± 0.07 | 62.9 ± 0.92 | 4.58 ± 0.12 | $0.06 \pm <0.01$ | 18.0 ± 1.14 | 0.25 | 0.29 |
| PLB | 3.36 ± 0.06 | 39.0 ± 0.35 | 3.55 ± 0.09 | 0.53 ± 0.05 | 10.7 ± 0.98 | 0.33 | 0.27 |

B—bark, S—sawdust, WS—wheat straw, MS—miscanthus straw, PL—poultry litter, BB—bark biochar, SB—sawdust biochar, WSB—wheat straw biochar, MSB—miscanthus straw biochar, PLB—poultry litter biochar

important factor having impact on the dynamics of changes in the elemental composition. Its high value, usually combined with a low volatile matter content, significantly limited variations in the elemental composition [30]. The content of sulfur in the tested materials ranged from 0.01% (S) to 0.65% (PL). Smaller variations were found for the hydrogen content. The highest contents of hydrogen were determined in sawdust and miscanthus straw and were over 6%. These are the most typical values for these types of biomass. In these cases, the pyrolysis resulted in the creation of a material which is more similar to lignite or low-quality coal and it means that it can be used as a fuel.

The pyrolysis process leads to a series of chemical reactions as a result of which the increase of the condensation and aromatization degree takes place, which translates into the change in mol relations O/C (carbonization degree) and H/C (aromatization degree) [31]. It is generally recognized that the O/C ratio in biochar should not exceed 0.4, and the H/C ratio below 0.6, which is also confirmed by our results. The results of Do et al. [32] showed that the pyrolysis temperature increase from 300 to 800 °C increases the losses of O and H, which result from the removal of water, CO, and CO₂ from biomass. Finally, biochars become highly carbonaceous at higher temperatures, and the H/C and O/C ratios of biochars decrease gradually with increasing temperatures of pyrolysis. Our study revealed the H/C ratio for all biochars of below 0.6. The O/C ratio of below 0.4 was obtained in WSB, MSB, and PLB biochars. This ratio was slightly higher (0.41) in BB and SB biochars produced from woody biomass. This indicates that the aromatic C structures were more stable. The theory is confirmed by the study of Kim et al. [33], who argued that there is a relationship between the H/C and O/C ratios and the pyrolysis temperature and

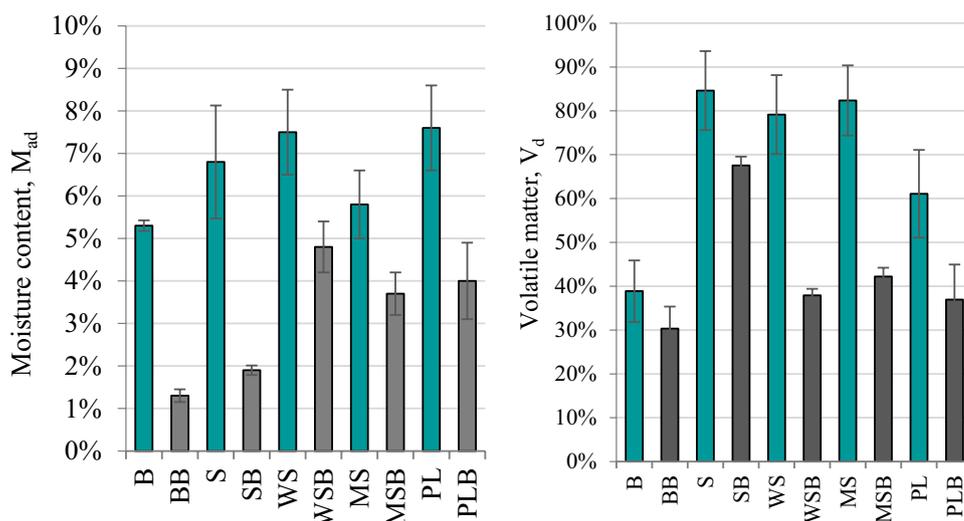
the biomass type. The authors stated that dehydration and decarboxylation reactions significantly depend on the type of biomass (e.g., carbon content, humidity level) and the temperature. Tripathi et al. [29] argued that the calorific value of biochar increases with increasing temperature and with the decreasing H/C and O/C molar ratios. This thesis was not fully confirmed by our results, as we did not discover such a dependency. This was particularly evident for PL and PLB treatments.

Moisture content in feedstocks and biochars

Humidity is an important problem related to the combustion of biomass, which, in the case of plant feedstocks, can reach even 50% [32, 34]. The high moisture level makes the biomass combustion less profitable, not only because of the process itself, but also due to high transportation costs (low energy density). As in the case of all combustion fuels, moisture significantly affects the lower calorific value and plays an important role in the combustion process. Combustion of fuels having a high moisture content increases the volume of exhaust gases and, consequently lowers the combustion temperature [35]. Additionally, increased losses related to partial and incomplete combustions can be observed, as the temperature in the combustion chamber will not be sufficient to combust all flammable substances in flue gases [36].

Moisture content in feedstocks was similar and ranged from 5.3 to 7.6% (Fig. 1). It is worth mentioning that, before pyrolysis, feedstocks were pre-dried at 65 °C. The main objective of this operation was to limit the influence of feedstock moisture on the process. This approach allowed to evaluate the process effect on the specific material. Therefore, the humidity may be considered analytical

Fig. 1 Change in moisture and volatile matter contents (as analyzed in air-dried state). *B* coniferous trees bark, *BB* coniferous trees bark biochar, *S* sawdust, *SB* sawdust biochar, *WS* wheat straw, *WSB* wheat straw biochar, *MS* miscanthus straw, *MSB* miscanthus straw biochar, *PL* poultry litter, *PLB* poultry litter biochar. Results are the mean of three replicates and error bars indicates standard deviation of triplicates



(air-dry state). Given that pyrolysis was carried out at above 280 °C, in all cases, we expected to observe reduction in the moisture content. The highest moisture reduction compared to feedstocks was achieved for bark biochar (BB) and sawdust biochar (SB). Among all the tested biochars, the lowest humidity was determined for bark biochar (1.3%), and the largest in miscanthus straw (4.8%) (Fig. 1).

Volatile matter content

Volatile matter content is an important parameter that significantly affects the combustion process [28]. Literature data indicate that biomass contains up to 2.5 times more volatile matter than coal, which has a major effect on the conditions of its ignition and combustion [37]. During combustion of high volatile fuels, large amounts of flammable substances (mainly CO, low hydrocarbons, and monocyclic aromatic hydrocarbons) are released, which reveals itself by higher flames. This requires the introduction of additional air to ensure complete burnout of these products [34, 37]. Higher volatile matter content than in the case of hard coal requires specially designed solutions for biomass combustion. Our results revealed that the thermal conversion of organic materials by pyrolysis reduced the volatile matter content (Fig. 1), which is fully consistent with information given in the literature. In this case, volatile matter content ranged from 37.0% (WSB) to 84.6% (S) (Fig. 1). The thermal process was found to reduce the volatile matter content in all materials, as shown in Fig. 1. According to this data, the intensity of raw material devolatilization during pyrolysis was relative to changes in the volatile matter content. The most intense release of volatiles was observed for straws of wheat and miscanthus, as almost 50% of them were released from these materials. As stated by Mitchual et al. [38], when biomass is heated to 400–500 °C, volatile gases are released,

giving the so-called volatile matter. Volatile matter (flammable gas and smoke) is created when biomass is heated up under sufficient air, time, temperature, and turbulence conditions. According to Patel and Gami [39], the higher the volatile matter content in the fuel, the larger the amount of high-pressure secondary air is required for effective combustion. On the other hand, incomplete combustion of volatile matter leads to dark smoke, heat loss, pollution hazard, and soot deposition on boiler surfaces [39].

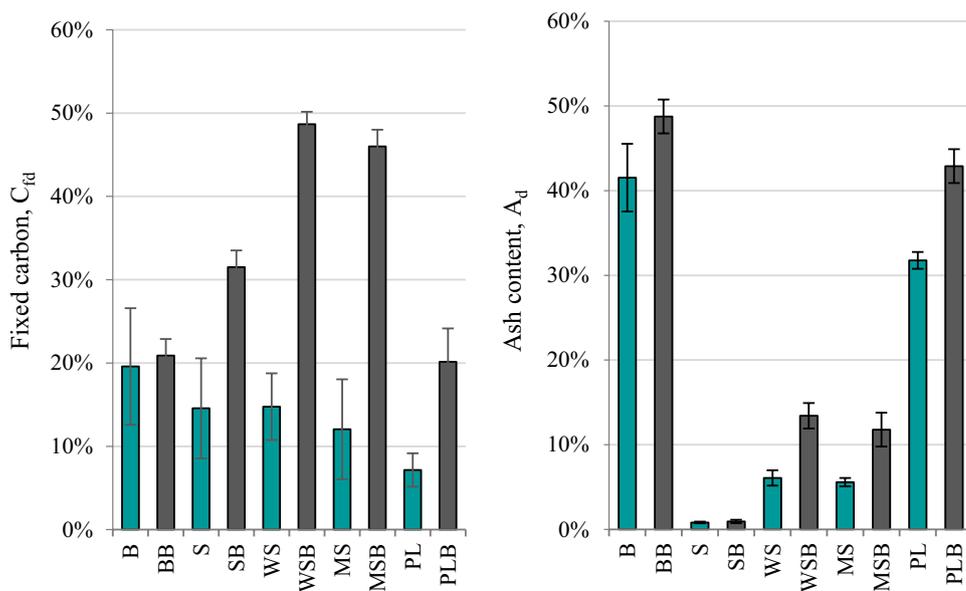
Fixed carbon content

Fixed carbon content (C_{fd}) represents the amount of matter which will form coke during combustion. A high value of this parameter indicates that fuel will be burned in two steps: pyrolysis and coke combustion; however, the latter will last longer. These fuels tend to combust in the form of embers. Sadiku et al. [28] noted that the fixed carbon of any material gives a rough estimate of the heating value of a fuel and acts as the main heat generator during the combustion. For the analyzed materials, fixed carbon content ranged from 7.2% (PL) to 48.7% (WSB) (Fig. 2). In all cases, pyrolysis increased the carbon content. The largest increase in this parameter was found for biochar produced from poultry litter (280%), and the lowest in bark biochar (6.7%). Such properties of biochar favor its use as fuel similar to coal. Similar changes in fixed carbon content were also obtained by other researchers [10, 30, 40].

Ash content

As in the case of hard and brown coal, combustion of biomass generates solid waste, mostly in the form of the bottom ash. The amount of that waste depends mainly on the type of biomass used [37]. Usually, the ash content after combustion

Fig. 2 Fixed carbon and ash contents. *B* coniferous trees bark, *BB* coniferous trees bark biochar, *S* sawdust, *SB* sawdust biochar, *WS* wheat straw, *WSB* wheat straw biochar, *MS* miscanthus straw, *MSB* Miscanthus straw biochar, *PL* poultry litter, *PLB* poultry litter biochar. Results are the mean of three replicates and error bars indicates standard deviation of triplicates



of biofuels is significantly lower than for fossil fuels like hard coal or lignite. This has some operating advantages, i.e., longer periods between ash removal. The analysis of feedstocks showed that the ash content ranged from 0.80 to 41.5%. It was found that bark biochar (BB) and poultry litter biochar (PLB) had the highest ash contents among the tested biochars (Fig. 2). For these materials, the ash content was 48.8% and 42.9%, respectively. Its high value determined for BB sample was mainly related to the high amount of mineral impurities (mainly sand) sourced from the wood harvesting process. This was also the case for thermally unconverted bark (B). On the other hand, the ash content of less than 1% was marked for sawdust (S) and biochar produced from it (SB). Such a low ash content is normal for pure organic materials, devoid of impurities. Nevertheless, as we expected, pyrolysis caused the ash content decrease in all materials. Higher ash content for biochars could have either positive or negative results, depending upon utilization methods. He et al. [36] stated that feedstocks such as cotton stalk biochar and rape straw with low ash content should be used in fuel production, whereas materials such as rice straw biochar, due to their high ash content, should be used as fertilizers. With this in mind, in our study, S, WS, MS and biochars obtained from them would be the best fuels. On the other hand, B, BB, PL, and PLB should be used as fertilizers.

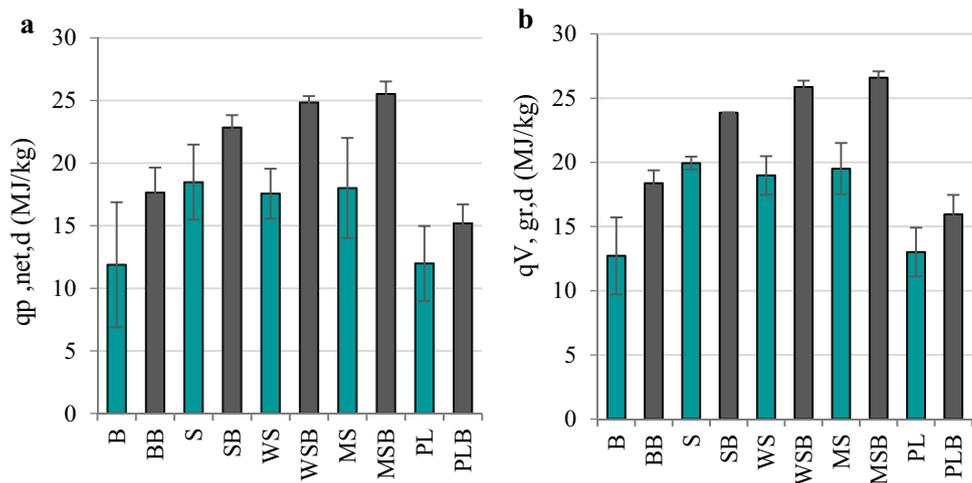
Compared to the A_d feedstock, the highest change in the ash content was observed for straw materials (WS and MS). In the case of materials with either low (S) or high (B, PL) ash content, the change was not so intensive and was below 40% for all these three materials. It is crucial to select the right type of biomass for combustion, as it can affect not only the amount of the ash formed, but also the chemical

composition and leaching of important compounds (e.g., heavy metals, sulfate ions, chlorides) [34]. Ashes from the combustion of biomass have higher contents of CaO, SO_3 , Cl and lower contents of SiO_2 , Al_2O_3 and Fe_2O_3 than residues after burning of coal [7, 37, 41, 42]. That is why, many literature sources report that bottom ash remaining after biomass combustion can be used as an additive in the production of fertilizers [43–46]. In that case, it is important to assess the concentration of heavy metals, as they cannot exceed the permissible values.

Net and gross calorific values

Net calorific value ($q_{p,net,d}$) is one of the most important thermo-physical parameters describing energy potential of materials. This parameter constitutes a basis for assessing the quality of fuel as an energy source. Net calorific value is associated with moisture and strongly depends on the fuel chemical composition [30]. In this study, the highest gross calorific value ($q_{v,gr,d}$) was determined for miscanthus straw biochar and sawdust biochar and reached 26.59 and 23.42 MJ kg^{-1} , respectively (Fig. 3). The calorific value of WSB and MSB was 29% and 28%, respectively, higher than the calorific value of feedstocks. Also, Ul Saqib et al. [47] indicated a 21% increase in the calorific value of leaf biochar compared to the raw biomass. The lowest $q_{p,net,d}$ was determined for untreated bark (11.88 MJ kg^{-1}) and poultry litter (11.98 MJ kg^{-1}). Lower heating values of sawdust, wheat straw, and miscanthus straw were similar, which finds confirmation in the literature [31, 43, 44]. Gross calorific value of biochars was higher on average by 36% than calorific value of feedstocks used in the pyrolysis process, which suggests that they are a better solid fuel. This is due to the

Fig. 3 The net calorific value (dry state) (a) and the gross calorific value (b). *B* coniferous trees bark, *BB* coniferous trees bark biochar, *S* sawdust, *SB* sawdust biochar, *WS* wheat straw, *WSB* wheat straw biochar, *MS* miscanthus straw, *MSB* miscanthus straw biochar, *PL* poultry litter, *PLB* poultry litter biochar. Results are the mean of three replicates and error bars indicates standard deviation of triplicates



fact that pyrolysis results in the release of volatile matter and increase of fixed carbon and thus a higher carbonization degree. Additionally, according to He et al. [36], the higher the C content, the lower the O content and, consequently, the gross calorific value undergoes a constant increase. However, these authors demonstrated that when the pyrolysis was carried out at 300 °C, 75–84% of primary energy of plant biomass was retained in biochars. On the other hand, at 600 °C, 47–51% of energy was stored in biochars and the remaining 20% was retained in gases. In turn, Tsai et al. [33] stated that in the case of biochars, the gross calorific value increases at up to 500 °C and then remains relatively constant. Similar results were obtained by Poudel et al. [48] for empty fruit bunches and palm kernel shell and by Wróbel et al. [49] for woody biomass.

Fuel value index (FVI)

Analysis of the FVI (Fig. 2) showed that materials' applicability for energy production was different. Only for three samples, the value of this parameter exceeded 100 which seems to be a threshold value for application as fuel. What is also important, not in all cases values for biochar were more favorable. In the case of wheat and miscanthus straws, there was a decrease in the FVI value, which was probably caused by lower bulk density of these materials. The highest value was obtained both for raw sawdust and biochar obtained from it. More importantly, the value for biochar was two times higher than for untreated material, 1037 and 2334 GJ/m³, respectively. The highest increase was observed for biochar from bark, which was five times higher than for untreated feedstock (25 and 127 GJ/m³, respectively). Our results showed that one of the biochars produced can be considered a potentially valuable material for energy production. The FVI of biochar produced from bark showed that, due to its high ash content, this material can create threats,

as it can cause fouling and slugging problems during combustion. It needs to be mentioned that FVI gives only general information about the application ability of the fuel, that is why further tests should be made to determine fouling or slagging factors. The study of Sadiku et al. [28] proved that the FVI is positively correlated with the fixed carbon content and negatively correlated with volatile matter content (Table 4). Our results also confirmed that the FVI increases with the increasing fixed carbon content and decreases with the increasing volatile matter content. These correlations are mainly related to the ash content change. When ash content rises, the volatile and fixed carbons lower.

Bulk density, absolute density, and porosity of the analyzed materials

The measurement results bulk and absolute densities were summarized in Table 2. A slight decrease in bulk density was determined for all materials. However, this is normal, because the overall shape of the material is preserved during pyrolysis conducted at relatively low temperatures. On the other hand, the absolute density increases, because new pores are formed in the process and this affects the material volume. The highest absolute density value was determined in poultry litter biochar (1.91 g/cm³), and the lowest in miscanthus straw (1.43 g/cm³). It is expected that high density will affect the fuel value index of biomass for energy generation, as these parameters show a positive correlation (Table 4). High-density materials show a higher mass in relation to volume and thereby they have a higher combustion yield. In our study, the highest bulk density was determined in bark and sawdust, and the lowest in maize straw. According to Mitchual et al. [38], higher material density at room temperature and low pressure allows for the production of higher density briquettes.

Table 2 Density, porosity and fuel value index of analyzed materials

| Material | | Bulk density (g/cm ³) | Absolute density (g/cm ³) | Porosity (%) | Fuel value index (FVI) |
|----------|---------------|-----------------------------------|---------------------------------------|--------------|------------------------|
| B | Raw materials | 0.460 ± 0.021 | 1.766 ± 0.561 | 73.9 | 24.83 |
| S | | 0.313 ± 0.072 | 1.502 ± 0.235 | 79.2 | 1037 |
| WS | | 0.143 ± 0.013 | 1.464 ± 0.314 | 90.3 | 54.95 |
| MS | | 0.152 ± 0.015 | 1.430 ± 0.152 | 89.4 | 84.64 |
| PL | | 0.270 ± 0.032 | 1.672 ± 0.193 | 83.8 | 13.41 |
| BB | Biochars | 0.456 ± 0.041 | 1.817 ± 0.123 | 74.9 | 126.8 |
| SB | | 0.183 ± 0.032 | 1.516 ± 0.162 | 88.0 | 2334 |
| WSB | | 0.075 ± < 0.01 | 1.558 ± 0.091 | 95.2 | 28.74 |
| MSB | | 0.081 ± < 0.01 | 1.565 ± 0.050 | 94.8 | 43.64 |
| PLB | | 0.295 ± 0.011 | 1.909 ± 0.020 | 84.6 | 26.10 |

± standard deviation, $n=3$

As it results from the literature data [46, 50–52], in all cases, the porosity of biochars increased after pyrolysis. This was directly connected to the volatile matter content decrease and thereby the formation of a free space in the material structure. Our results showed a slight increase in porosity for materials with high ash content, i.e., those in which the amount of the released volatiles was small relative to their dry weight. This phenomenon finds its confirmation in literature [52, 53]. Porosity is a particularly important parameter when using biochars for anything other than energy purposes. For example, when using biochars as sorbents or fertilizers, porosity is directly related with the material's effect on the biological, chemical, and physical properties of soil.

Our investigations proved that it is advisable to use pyrolytic biochars (produced at 300 °C) for energy purposes. The volatile matter content is an important aspect and, in the cases analyzed by us, it was similar to that typical for lignite [53, 54]. This can increase the popularity of using this type of fuel in conventional coal boilers. In some materials (except for bark biochar and poultry litter), the ash content was less than 10%. This result is very advantageous from the operational point of view and allows to reduce the necessary boiler maintenance. The calorific value as a main criterion in the assessment of energy potential of raw fuel, was also more promising in the case of biochars. However, one should take into account the energy consumption of the pyrolysis process, having a direct impact on the final costs of acquiring energy from this medium, and which was omitted in this study. It is also worth mentioning that pyrolysis of biomass can significantly reduce its moisture content, affecting its quality in terms of energy production [54]. Since the ash content in the analyzed materials can be very different, it is important to determine the future destination of the ash produced during combustion. High amounts of heavy metals in the analyzed materials (e.g., in poultry litter) can prevent these materials from being used as fertilizers, but, in some

cases, they can be applied for the production of sorbents [55].

Heavy metal concentration in feedstocks and biochars

The potential utilization of ash is influenced by contaminants such as heavy metals and the extent to which the ash is sintered. Clean biomass contains minerals and important trace elements and, therefore, can be recycled to forest grounds; however, these trace metals must be clearly quantified and their impacts studied if they are to be applied to soils [56]. Results of the trace element analysis, presented in Table 3, show that heavy metal contents varied to a large extent for both feedstocks and biochars. In general, all biochars had increased contents of the tested metals compared to feedstocks used in their production, as shown in Table 2. This relation was foreseeable, because thermal conversion affects the combustible matter, and ash remains in biochar. Pels et al. [46] and Hossain et al. [47] reported that increased pyrolysis temperature increases the content of trace elements, which is a consequence of a more intense discharge of flammable substances. The temperature used in our study (300 °C) was selected considering not only the further heavy metal content, but also the possibility of using the resulting biochars as fertilizers. The highest contents of heavy metals were observed in samples related to poultry litter (PL and PLB). Very high concentrations of zinc, iron, and copper can reduce the applicability of their ashes as fertilizers. The correlation analysis confirmed that there is a strong relationship between the content of ash and the content of the tested heavy metals in materials used for the study (Table 4). According to Demirbas [55], the composition of ash is dependent on the plant species, growth conditions, and ash fraction. For example, Vamvuka [56] suggested that the high concentration of Ni and Cr present in the tested olive kernel ash was most likely due to the soil parent material.

Table 3 Analysis of heavy metals content in raw materials and biochars

| Material | | Cd | Cu | Cr | Fe | Mn | Ni | Pb | Zn |
|----------|---------------|--------------|-------------|-------------|------------|-------------|--------------|-------------|--------------|
| | | mg/kg DM | | | | | | | |
| B | Raw materials | 0.47 ± 0.01 | 8.18 ± 0.31 | 7.00 ± 0.59 | 4534 ± 377 | 243 ± 1.98 | 4.07 ± 0.35 | 11.1 ± 0.22 | 47.6 ± 4.39 |
| S | | 0.32 ± <0.01 | 2.01 ± 0.07 | 1.03 ± 0.04 | 121 ± 21 | 138 ± 1.77 | 0.62 ± <0.01 | 1.58 ± 0.65 | 15.5 ± 0.41 |
| WS | | 0.56 ± <0.01 | 1.32 ± 0.11 | 2.22 ± 0.95 | 128 ± 8.80 | 41.2 ± 1.78 | 1.12 ± 0.57 | 0.73 ± 0.07 | 32.9 ± 4.07 |
| MS | | 0.14 ± 0.01 | 1.77 ± 0.92 | 1.89 ± 0.32 | 200 ± 26 | 34.6 ± 3.04 | 0.82 ± 0.37 | 1.15 ± 0.49 | 14.4 ± 1.08 |
| PL | | 0.39 ± 0.01 | 16.1 ± 0.91 | 2.82 ± 0.17 | 800 ± 51 | 132 ± 8.13 | 3.42 ± 0.12 | 2.02 ± 0.25 | 111 ± 4.45 |
| BB | Biochars | 0.66 ± 0.06 | 9.36 ± 0.23 | 9.04 ± 1.44 | 3033 ± 159 | 323 ± 3.39 | 5.89 ± 0.24 | 14.5 ± 0.67 | 63.91 ± 3.13 |
| SB | | 0.73 ± 0.01 | 2.14 ± 0.08 | 3.61 ± 0.30 | 195 ± 8.50 | 269 ± 13.9 | 2.40 ± 0.02 | 1.48 ± 0.06 | 29.87 ± 5.58 |
| WSB | | 1.20 ± 0.07 | 3.19 ± 0.34 | 4.01 ± 0.65 | 326 ± 46 | 72.9 ± 8.69 | 1.97 ± 0.31 | 1.62 ± 0.08 | 48.8 ± 2.67 |
| MSB | | 0.31 ± <0.01 | 4.14 ± 0.03 | 4.29 ± 0.58 | 505 ± 16 | 74.2 ± 3.12 | 1.78 ± 0.07 | 2.44 ± 0.21 | 32.0 ± 2.51 |
| PLB | | 0.55 ± 0.02 | 57.6 ± 1.20 | 16.4 ± 0.82 | 1577 ± 263 | 419 ± 12 | 10.8 ± 0.67 | 3.91 ± 0.36 | 280 ± 4.56 |

±standard deviation, $n = 3$

Table 4 Spearman's correlation coefficients between ash and heavy metals contents

| | Cd | Cu | Cr | Fe | Mn | Ni | Pb | Zn |
|-----|-------|---------|---------|----------|-------|---------|---------|---------|
| Ash | 0.260 | 0.818** | 0.842** | 0.915*** | 0.478 | 0.866** | 0.830** | 0.866** |

*Significant at the $p \leq 0.05$ level

**Significant at the $p \leq 0.01$ level

***Significant at the $p \leq 0.001$ level

According to the author, the soil type is laden with Ni/Cr which is transferred to the plant [56].

Leachability, pH and EC of heavy metals in biomass ash

With view of using ashes in the nature, the analysis of the heavy metal content in the obtained ashes was carried out. Due to the possible leaching into underground and surface waters, heavy metals contained in ash residue may have negative environmental impacts if irrationally managed and disposed [57]. The chemical composition and leaching behavior of biomass ashes were analyzed. As shown in Fig. 4, leachability of heavy metals of biomass ash was highly diversified and conditioned by the analyzed element and material type. Our investigations showed that ashes produced from thermally unconverted biomass had higher leachability of heavy metals. The cadmium content was determined only in WS, WSB, and S ash extracts and ranged from 0.006 mg to 0.022 mg/kg. The highest Cu content was determined in the extracts: PL (0.75 mg/kg), PLB (0.57 mg/kg), and WS (0.37 mg/kg). The contents of other elements ranged as follows: for Cu from 0.01 mg/kg (MS) to 0.75 mg/kg (PL), for Fe from trace contents (PLB, BB) to 4.84 mg/kg (MS), for Ni from 0.03 mg/kg (S) to 1.35 mg/kg (WS), for Pb from 0 mg/kg (PLB) to 0.13 mg/kg (MS), for Zn from 0.05 mg/kg (BB) to 2.14 mg/kg (S), for Cr from 0.03 mg/kg (B) to 0.53 mg/kg (PLB), and for Mn from 0.17 mg/kg

(PLB) to 87 mg/kg (S). After analyzing the literature data on the heavy metal content in extracts from ashes of various biomasses, one can conclude that the mean content of individual elements is, usually: 3.5 mg/kg for Cr, 0.052 mg/kg for Ni, <0.0014 mg/kg for Cd, and 0.0027 mg/kg for Pb [3, 11, 58]. On the other hand, taking into account regulatory limits (2003/33/EC), the not-hazardous limits for leachates for Cr, Ni, Cd, and Pb are: 4 mg, 5 mg, 0.6 mg, and 5 mg/kg, respectively. It should be emphasized that the content of these elements in the analyzed extracts was lower than that given in the literature and in regulatory limits (2003/33/EC).

Extracts derived from leaching of ashes had a wide range of pH values, i.e., from 5.50 to 11.40 (Table 5). High pH values of ash extracts confirm the possibility of using ashes for fertilizing purposes (liming). However, it is necessary to monitor the solubility of individual minerals in ashes from various types of biomass to avoid the potential risk of uncontrolled disturbances of soil and groundwater pH.

The EC measured in the resulting extracts ranged from 0.33 to 5.51 mS/cm (Table 5). This parameter value indicates that easily soluble salts were present in extracts. This is of particular importance when it comes to the plant's response to any possible increase in the substrate salinity, which may result in a limited availability of water [59, 60]. According to Ribeiro et al. [59], amendment with biomass fly ash slightly elevated soil pH, to values within the most adequate range for plant growth. Results showed small raises in the availability of essential plant macronutrients—Ca, K, and Mg—especially

Fig. 4 Leachability of heavy metals of biomass ash

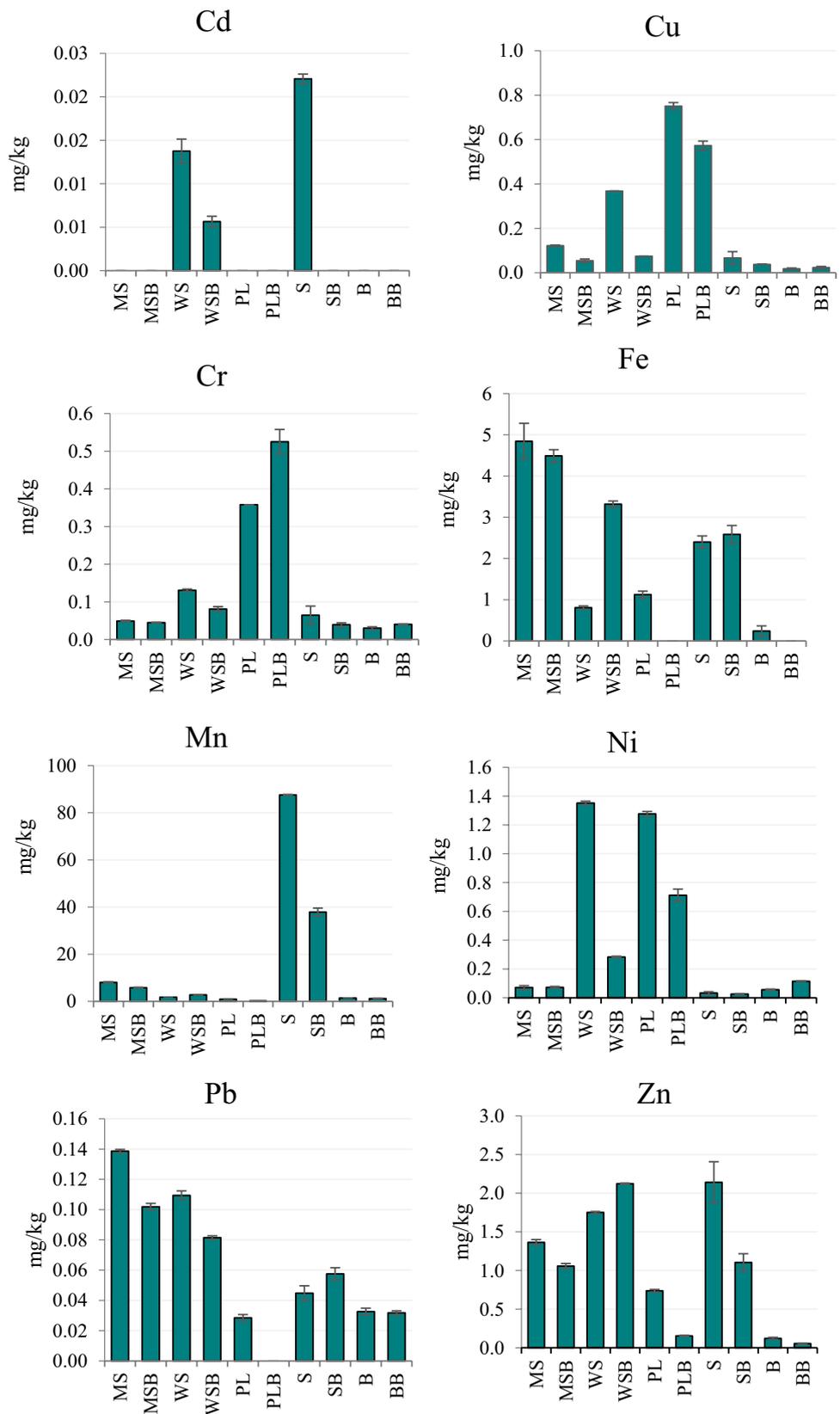


Table 5 pH and EC values of extracts from analyzed ashes

| Material | | pH | EC (mS/cm) |
|----------|---------------|-------------|-------------|
| B | Raw materials | 7.21 ± 0.15 | 0.38 ± 0.02 |
| S | | 7.69 ± 0.11 | 0.80 ± 0.01 |
| WS | | 10.0 ± 0.09 | 3.72 ± 0.03 |
| MS | | 6.97 ± 0.10 | 1.26 ± 0.01 |
| PL | | 11.1 ± 0.19 | 4.22 ± 0.15 |
| BB | Biochars | 8.29 ± 1.02 | 0.48 ± 0.11 |
| SB | | 5.50 ± 0.15 | 0.33 ± 0.08 |
| WSB | | 9.19 ± 0.12 | 2.77 ± 0.11 |
| MSB | | 6.90 ± 0.13 | 0.91 ± 0.06 |
| PLB | | 11.4 ± 0.19 | 5.51 ± 0.14 |

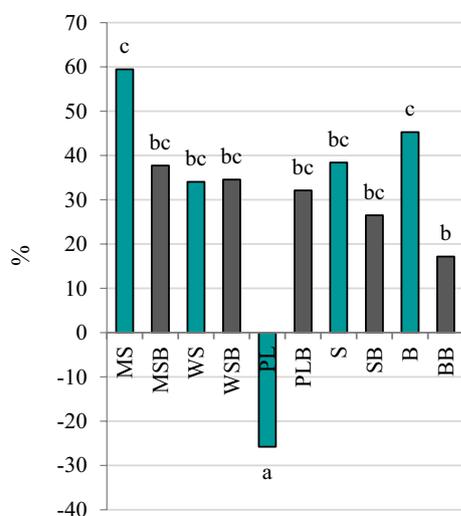
± standard deviation, $n = 3$ 

Fig. 5 Phytotoxicity (% inhibition/stimulation compared to the control) of extracts from ashes for *Lepidium sativum* L. B coniferous trees bark, BB coniferous trees bark biochar, S sawdust, SB sawdust biochar, WS wheat straw, WSB wheat straw biochar, MS miscanthus straw, MSB miscanthus straw biochar, PL poultry litter, PLB poultry litter biochar. Results are the mean of three replicates and error bars indicates standard deviation of triplicates

in the top layer of the soils, where the amendment materials were applied. The mobilization of cations to the groundwater was always minimal, which is promising, since it means little contamination of groundwater [59].

Phytotoxicity of biomass ash

Phytotoxicity analysis showed that, in general, each of the tested ash extracts had a beneficial effect on the growth of *Lepidium sativum* L. compared to the control treatment (Fig. 5). Our results suggest that the extracts contained substances that not only did not inhibit the germination of *Lepidium sativum* L., but also stimulated the growth of the plant at a very early stage. This

is important information, especially given the fact that plants are susceptible to adverse environmental factors in the early stages of growth. The highest plant growth stimulation was determined after the application of MS (59%) and B (45%) extracts. Compared to the control, the growth inhibition of *Lepidium sativum* L. of 26% was noted only after using the PL ash extract. The comparison of the effect of ashes from feedstocks and biochars revealed that PL showed significantly higher phytotoxicity to *Lepidium sativum* L. than PLB. In the case of other treatments, no significant changes in the phytotoxicity were found between the feedstock ash extract and the biochar ash extract. In addition to the highest Cu content in extract, PLB also had the highest pH and EC values. On the other hand, the results obtained by Lu et al. [61] showed that the effect of pyrolysis temperature on chemical speciation distribution, leaching toxicity, and bioavailable contents of heavy metals in biochar was inconsistent, and the potential risk of soil and groundwater contamination after the application of biochar was lower than in the case of sewage sludge. In the study of Rombola et al. [60] on relationships between chemical characteristics and phytotoxicity of biochar from poultry litter pyrolysis, it was found that higher phytotoxicity of poultry litter than of corn biochars was tentatively attributed to hydrophilic biodegradable substances derived from lipids or proteins removed by water leaching or microbial treatments. The combustion process could release active forms not only of trace elements, but also microelements, which, in turn, caused a negative response of *Lepidium sativum* L. The investigations conducted by Gondek et al. [62] showed that the thermal conversion of mixtures of sewage sludge and plant biomass significantly inhibited sprouting and growth of *L. sativum* roots. The inhibition of *L. sativum* root growth ranged from 13 to 59% for thermally unconverted materials and from 9 to 38% for biochars. In the study, Oleszczuk et al. [63] reported slightly different relationships—the tested biochars were more toxic to *V. fischeri* than to *L. sativum*. Other studies by Mierzwa-Hersztek et al. [64] showed that the type of feedstock from which biochars were produced has a significant effect on the toxicity of biochars. According to Ribeiro et al. [59], ash amendment and ash + sludge amendment resulted in similar *Lolium perenne* growth compared to the control. However, biomass grown in Cao-amended pots showed the highest root size.

Conclusions

The production of energy from biomass is a crucial way to limit greenhouse emissions whose permissible values are set by the environmental protection program. The fuel (such as straw) can be combusted directly or processed to obtain biochar and utilized in this form. Our results clearly showed that not every biochar produced for this study can be used as fuel. Some materials have such a high amount of mineral impurities (e.g., bark) that it will increase even

more during pyrolysis. Also, we also discovered an issue of low bulk density, which can also cause transportation and storage problems. Therefore, some biochars, fertilizers, or sorbents can be an interesting alternative for such materials. In all these cases, biochars seem to be very attractive materials that can be used not only in energy production. Our investigations clearly indicate that the type of biomass used in the process has an important effect on the energy parameters as well as chemical and biological parameters of the resulting ashes, which are decisive for their potential utilization. It should also be emphasized that ashes are a waste whose characterization is particularly difficult due to the variability of feedstocks and conditions of the combustion process. Moreover, biochar applied as biofuel limits the emissions of greenhouse gases, as it reduces the amount of waste and increases the share of energy generated from renewable sources. Additionally, the thermal process (such as pyrolysis) may constitute a stage that preconditions further processes such as gasification and production of the second-generation biofuels.

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