

ANALYSIS OF THE ENERGY PARAMETERS OF SELECTED BIOMASS AND BIOCHAR TYPES AND THE ENVIRONMENTAL IMPACT OF THEIR ASHES

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A b s t r a c t

The study determined the similarities and differences between the fuel properties of different types of biomass (triticale and oat straw; bark: oak, alder, hornbeam, pine) and biochar (municipal waste biochar, composting biochar, pellet biochar and Fluid's biochar). Bulk and actual densities and moisture contents, ash amounts, elemental composition (C, H, N) were determined, and the calorific value, heat of combustion and porosity of the substances studied were calculated. In addition, the physico-chemical properties of the ashes were determined.

All the substances tested have high energy potential and can be used as biofuel. Fluid's biochar had the best energy properties due to the highest calorific value and heat of combustion, as well as carbon content, with a small amount of ash. Varying composition of the ashes obtained still poses a problem in developing methods for their management.

Keywords: energy parameters, biochair, biomass

1. INTRODUCTION

The demand for energy is increasing with the progressing economic development, which adversely affects the environment [1]. In addition, the current geopolitical situation has intensified the energy problems in Europe. Conventional energy

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remains the primary source from which energy is generated; this includes the energy from fossil fuels, i.e. coal, oil, or natural gas. Fossil fuel resources are being depleted, and an additional threat is environmental pollution from the products of natural fuel combustion: dust, sulfur oxides, nitrogen oxides and coal [2]. Therefore, in order to reduce the rate of consumption of natural resources, renewable energy sources are increasingly being used, which, unlike non-renewable energy sources, are inexhaustible and environmentally friendly [3]. In addition, the unstable situation in the fuel market contributes to the fact that countries strive to become independent of raw material suppliers and produce energy themselves. One of the most important solutions for mitigating the energy problems, is the use of biomass materials as an energy feedstock [4]. Because of social resistance to burning crop plants, mixtures and pellets made from or including waste materials are a good alternative [5].

Biomass is all organic matter existing on Earth, i.e. substances of plant or animal origin, which are biodegradable [6]. The concept of biomass is defined in Directive 2009/28/EC of the European Parliament and of the Council of April 23, 2009 on the promotion of the use of energy from renewable sources (together with amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC) biomass denotes the biodegradable fraction of products, wastes or residues of biological origin from agriculture (including plant and animal substances), forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. Biomass can be used to produce biochar. Recent studies showed that the latter can be successfully used in the energy sector [7].

In Poland, the economic potential of biomass in 2020 is expected to be 600 168 TJ. However, the market potential is estimated at 533 118 TJ (data according to the Institute of Renewable Energy – Possibilities of using RES in Poland until 2020). The energy potential of biomass consists of, among others, energy plantations, waste wood, organic waste and vegetable waste [8]. Biomass materials can be used, depending on their processing, to generate electricity, produce heat, or transport fuels [9, 10].

However, the conversion of biomass materials into fuels is a technologically demanding process. Their variability and diversity necessitates constant control of their physico-chemical composition [11]. The physical and chemical properties of biomass are influenced by the timing of biomass harvesting, the genetic characteristics of the plants from which it is produced, and the conditions of plant cultivation [12]. The most rational solution seems to be co-firing biomass with coal and lignite in large power boilers. However, the different physical and chemical properties of biomass from coals cause serious operational problems. The main differences between biomass and coal are: higher moisture content in raw biomass, which adversely affects: combustion efficiency and

increases transportation costs, higher volatile content, (which changes ignition and combustion conditions), lower calorific value of biomass and higher content of alkaline elements [13, 14].

Therefore, the use of biomass materials necessitates the evaluation of their physical and chemical properties. Conducting further research on the energy properties of biomass materials will enable to create databases to promote greater use of biomass in the energy industry.

The purpose of this article is to evaluate the energy parameters of biomass: triticale and oat straw; bark: oak, alder, hornbeam, pine, as well as biochar produced by the Fluid company, i.e.: municipal waste biochar, composting biochar, pellet biochar and Fluid's biochar. In addition, the physical and chemical properties of the ashes of selected biomass materials were determined, as well as the effect of residues from the combustion of selected biomass on the phytotoxicity of *Lepidium sativum* L. (cress) growth.

2. MATERIALS AND METHODS

The following materials were used in the study: triticale straw (TS), oat straw (OS), barks: oak bark (OB), alder bark (AB), pine bark (PB) and hornbeam bark (HB). All materials were collected from a farm located in the Lublin Province, Biała district, Janów Podlaski municipality, Werchliś village. In addition, four biochars produced by Fluid were used in the study: Fluid's biochar (FB), municipal waste biochar (MB), composting biochar (CB), and pellet biochar (PK). Fluid's Biochar is obtained from plant biomass by pyrolysis, at 300°C. The municipal waste biochar is produced from municipal waste and composting biochar is produced from compost in a reactor that combines the operations of desiccation, degassing, thermolysis and pyrolysis gas combustion, at a temperature of about 650°C. Pellet biochar is formed from coal dust, with the addition of biomass in the form of pellets, and was obtained in reactors at 600°C [15]. Table 1 specifies the methods and standards used during the research.

From the measurement data were calculated:

- moisture M_a [%] [16],

$$M_a = \frac{m_2 - m_3}{m_2 - m_1} \cdot 100 [\%],$$

where:

M_a – moisture [%],

m_2 – weight of the sample vessel [g],

m_3 – weight of the sample vessel after drying [g],

m_1 – weight of the empty vessel [g].

- volatile matter A_d [%] [17],

$$A_d = \frac{m_4 - m_1}{m_2 - m_1} \cdot 100 [\%],$$

where:

A_d – volatile matter [%],

m_2 – weight of the sample vessel [g],

m_4 – weight of the sample vessel after calcination [g],

m_1 – weight of the empty vessel [g].

- total oxygen content [%] [25],

$$O = 100 - C - N - H - S [\%],$$

where:

C, H, N, S – total carbon, hydrogen nitrogen and sulfur content.

- heat of combustion Q_s [26]

$$Q_s = 355.88 \cdot C + 1130.44 \cdot H + 104.67 \cdot S - 106.76 \cdot O$$

$$[\text{kJ} \cdot \text{kg}^{-1}],$$

where:

C, H, S, O – total carbon, hydrogen sulfur and oxygen content.

- higher heating value (HHV) [26]

$$\text{HHV} = 355.88 \cdot C + 1130.44 \cdot H + 104.67 \cdot S - 106.76 \cdot O - 24.95 \cdot (8.94 \cdot H - M_a)$$

$$[\text{kJ} \cdot \text{kg}^{-1}],$$

where:

M_a – moisture [%],

- the percent root growth inhibition (RI) [27] percent root growth inhibition and germination index:

$$\text{RI} = \frac{A - B}{A} \cdot 100$$

where:

RI – the percent root growth inhibition, %,

A – the mean root length in the control sample mm,

B – the mean root length in the analyzed sample, mm.

- The percent germination index (GI) [27]:

$$GI = 100 \cdot CD$$

where:

GI – the percent germination index, %,

C – the ratio of the number of germinated seeds in the test materials and the number of germinated seeds in the control,

D – ratio of the mean root length of the plants obtained in the test samples to the mean root length of the control.

Table 1. Research methods used during the research

Determined parameters	Device	Standard
Moisture Ma [%]	Laboratory dryer	PN-EN ISO 18134-2:2017-03 [16]
Volatile matter Ad [%]	FCF 2,5S electric muffle furnace made by Czylok with SM-946 electronic controller and temperature display (Warsaw, Poland)	PN-EN ISO 18122:2016-01 [17]
Determination of total carbon, hydrogen, and nitrogen [%]	CHNS Flash EA 1112 Series Elemental Analyzer (Thermo Finnigan, Waltham, USA)	PN-EN ISO 16948:2015-07 [18]
Preparation of the aqueous extracts from the ashes of the biomasses tested (1:10 ash:water ratio)	Laboratory equipment	PN-EN 12457-4:2006 [19]
The concentrations of selected metals in the ashes of the biomasses tested (1:10 ash:water ratio)	8900 ICP MS Triple Quad Agilent	PN-EN ISO 17294-2:2016-11 [20]
	Mineralization was carried out in a microwave mineralizer Topex Preekem	PN-EN 13656:2002 [21]
Phytotoxkit root test on the <i>Lepidium sativum</i> plant on ashes from the biomass samples tested	Laboratory equipment	Test był prowadzony zgodnie z metodyką firmy Microbiotest (Belgia)–producenta testu Phyttoxkit [22]
pH content of ash water extracts from the biomass samples	ORION multimeter model: VERSA STAR	PN-EN 10390:1997 [23]
Electrolytic conductivity (EC) and total dissolved solids (TDS) content of ash water extracts from the biomass samples	ORION multimeter model: VERSA STAR	PN-EN 27888:1999 [24]

3. RESULTS AND DISCUSSION

The chemical composition of biomass is primarily carbon, hydrogen and oxygen. The content of these elements affects the calorific value of the fuel. On the other hand, the elements nitrogen and sulfur affect the level of emissions produced in the combustion process. Table 2 shows the contents of carbon C, nitrogen N, sulfur S, hydrogen H, oxygen O as well as the H/C and O/C ratios for the materials tested. The proportion of each element in the tested samples varies and depends primarily on its type.

Table 2. Elemental composition for the materials tested

Analyzed materials	N [%]	C [%]	H [%]	S [%]	O [%]	H/C	O/C
CB	0.38	45.50	4.22	0.73	49.16	0.09	1.08
MB	0.66	55.36	0.18	0.33	36.47	0.03	0.66
FB	0.22	61.54	5.16	0.42	28.84	0.08	0.47
PEB	0.12	53.85	4.57	0.62	35.21	0.08	0.65
OB	0.83	41.20	3.73	0.14	40.08	0.09	0.98
PB	0.17	36.41	3.51	0.21	38.85	0.09	1.07
HB	0.23	31.47	2.89	0.12	52.9	0.09	1.68
AB	0.38	44.85	4.16	0.19	31.09	0.09	0.69
OS	0.51	42.20	3.80	0.13	39.99	0.95	4.99
TS	0.63	43.26	4.03	0.19	32.77	0.09	0.76

The analyzed materials contained from 61.54% to 31.47% carbon. The biochars tested contain more carbon than straw or oak bark. However, the carbon content of the composting biochar is ~40% and is not significantly different from alder bark, hornbeam bark, oak bark and the tested straw.

The mass share of nitrogen shows the highest value for oak bark and this value is 0.84%, while the lowest value is for pine – 0.17% and pellet biochar – 0.12%.

The hydrogen content of the tested materials ranged from 5.16% for Fluid's biochar to 0.18% for municipal waste biochar.

The sulfur content of the samples ranged from 0.12% to 0.73%, where the lowest value was recorded for hornbeam, while the highest value was recorded for the composting biochar. In the case of oxygen content, the highest mass share is for hornbeam – 52.10%, while the lowest is for Fluid's biochar – 28.84%. In hard coal, the mass shares of elements are as follows: N – from 1 to 2%, C – from 75 to 92%, H – from 4 to 6%, S – from 0.3 to 1.5%, O – from 2 to 16% [28]. The mass shares of nitrogen, carbon, sulfur and hydrogen in biomass materials are lower than the mass share of these elements in hard coal. In contrast, the mass share of oxygen is higher for biomass materials. The proportions in which carbon, hydrogen and oxygen are present in biomass have a decisive impact on its energy

values. The nitrogen (N) and sulfur (S) contents of fuels are of particular concern due to their transformation into gaseous pollutants in the form of NO_x (nitrogen oxides) and SO₂ (sulfur dioxides), respectively [29]. High N and S content in biomass results in the formation of high-energy bonds. In contrast, low N and S contents in biomass is more favorable from an ecological point of view, since they do not contribute to acid rain and greenhouse gas emissions [30]. In the biomass samples studied, the sulfur content is low and ranged from 0.12 to 0.21%, which is much less than in hard coal (S – 0.3 to 1.5%). Low sulfur content is one of the most favorable characteristics of biomass, from an environmental point of view, as it reduces the emission of its compounds in the flue gas [31].

Considering H/C and O/C ratios, the best energy properties are those of raw materials for which the O/C ratio is the lowest, simultaneously with the highest H/C ratio [32]. In the bark and straw biomass samples studied, the H/C ratios reach low values (0.09-0.1). The O/C ratio is higher than H/C and ranges from 0.69 for alder to 1.68 for hornbeam.

The H/C and O/C ratios are the more important parameters when studying biochar. They enable to determine the chemical structure of biochar and its variation [33]. Biochar is produced by pyrolysis, which leads to a series of chemical reactions, and as a result, there is an increase in condensation and degree of aromatization, which translates into: changes in the molar ratios of O/C (degree of carbonization) and H/C (degree of aromatization) [34]. The H/C ratio helps determine the aromatization and maturation of the biochar with which it is associated to their long-term stability in the environment [35]. For the biochar samples tested, the H/C ratio for most materials was similar, at 0.08. The lowest H/C ratio value was obtained for municipal waste biochar (0.003) (Table 2). All biochar samples in this study had an H:C ratio < 0.12 indicating a graphite-like structure in biochar [31]. On the other hand, knowing what the O/C ratio is, it is possible to compare the abundance of biochar in oxygen functional groups. For the biochar studied, this ratio is virtually identical for composting biochar, municipal waste biochar and pellet biochar, at 0.66. Only in the case of the Fluid's biochar, it equals 0.47. Spokas noted that most biochar types have an O:C ratio in the range of 0.2-0.6, and an O:C ratio within such limits indicates the least stable biochar [36].

The moisture and ash contents of biomass materials are key parameters in the selection of technical parameters in the combustion process. In the case of plant materials, the moisture content can reach up to 50%. In the literature it has been described the optimal moisture characteristic of biomass in real conditions; less than 10% is practically unobtainable in the real energy plants [37]. The moisture content of the biomass samples tested ranged from 3.54 to 10% (Fig. 1).

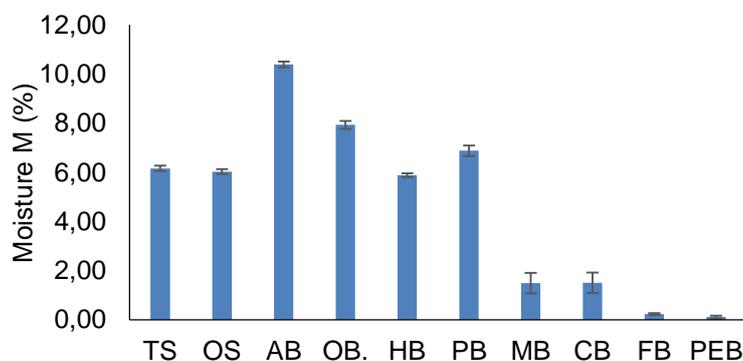


Fig. 1. Moisture of the analyzed materials

The moisture content of biochar is significantly lower than that of the straw and bark samples tested. However, the moisture contents of the straw and bark samples are low, compared to those known from the literature, the moisture content of straw can reach up to 25%, whereas that of bark – up to 82.2 [38, 39]. The low moisture content of the samples tested can be explained by the time and location of biomass sample collection. In addition, the acquired samples were protected from moisture. Since moisture content reduces the calorific value, due to the loss of heat used for heating and evaporation of water, the best raw materials for energy generation purposes are those with the lowest possible moisture content.

The suitability of biomass for energy purposes is determined by the heating value and heat of combustion. The graphs show the higher heating value (HHV) (Fig. 2.) and heat of combustion heat of combustion (Fig. 3) for the biomass samples tested.

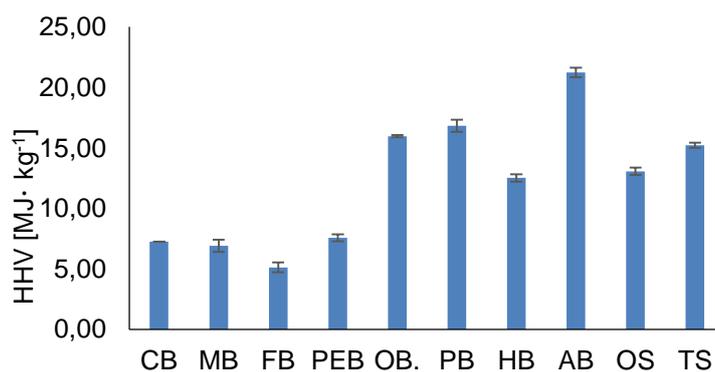


Fig. 2. Higher heating value (HHV) of the analyzed materials

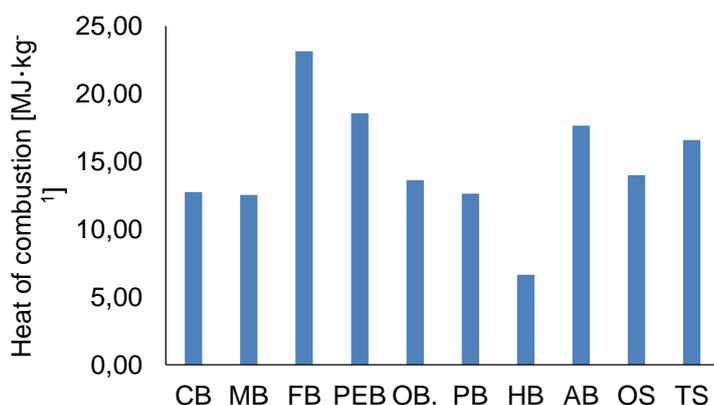


Fig. 3. Heat of combustion of the analyzed materials

The analyzed biochars achieved higher calorific values than the straw and bark samples tested, allowing more efficient energy production from biochar than from the other materials tested. Fluid's biochar achieved the highest value among the tested biochar samples at 24.03 MJ·kg⁻¹. It was the closest to the average calorific value of hard coal, which is about 27 MJ·kg⁻¹, depending on its origin. Other biochars achieved lower parameters, but all remained around 20 MJ·kg⁻¹. The calorific value of the remaining materials ranged from 9.63 MJ·kg⁻¹ to 18.72 MJ·kg⁻¹. Alder bark had the highest value, followed immediately by triticale straw with a calorific value of 17.72 MJ·kg⁻¹. The values for oat straw and oak bark are at a similar level of more than 15 MJ·kg⁻¹. The lowest value is indicated by hornbeam bark 9.63 MJ·kg⁻¹. On the basis of the research performed, it can be concluded that the range of combustion heat values for the biomass materials studied is in the range of combustion heat values for lignite, for which the combustion heat value ranges from 5.9 to 23 MJ·kg⁻¹ [40].

The classification and quality requirements for fuels produced from waste, named SRF (Solid Recovered Fuels), were used to assess the energy suitability of the biomass samples tested. According to the qualification, the fuel is classified as Class 3 fuel when the dry calorific values are ≥ 18 MJ·kg⁻¹, and for Class 4 these values are ≥ 12 MJ·kg⁻¹, whereas for Class 5 – HHV ≥ 3 MJ·kg⁻¹ [41]. The straw and bark samples tested, with the exception of hornbeam bark, can be classified as Class 3 fuel. In turn, the hornbeam bark and tested biochars can be classified as Class 4 fuel.

For the biomass samples tested, the heat of combustion value ranged from 6.65 MJ·kg⁻¹ for hornbeam to 23.14 MJ·kg⁻¹ for Fluid's biochar. The heat of combustion value for hard coal is variable, ranging from 16.7 to 29.3 MJ·kg⁻¹, while for lignite it ranges from 5.9 to 23 MJ·kg⁻¹ [40].

Physicochemical and chemical properties of ashes from the analyzed biomass samples

Biomass fly ash is a product of thermal conversion of biomass. In recent years, in addition to forest biomass, straw of cereals, rapeseed is increasingly used for energy purposes. According to the Polish legislation, ashes must be subjected to the process of disposal. The physicochemical properties of ashes vary and depend on the composition of the biomass; they are characterized by high values of loss on ignition and alkaline compounds. These properties determine their application; they are most often used in the construction sector or as fertilizers and soil improvers. Researchers attempt to modify the ashes for example in the magnetic activator or adding bentonite [42, 43]. Identification of biomass ash composition is therefore necessary for its correct management.

Ash contains harmful substances, so the lower amount ash, the better. Compared to straw and bark, biochars have a higher ash content. The biochars tested, with the exception of the pellet biochar, contained more than 15% ash, while straw contains about 4% and tree bark about 1% (Fig. 4). In comparison, the ash content of hard coal averages 19.1%, showing that straw and bark have much lower ash content [39].

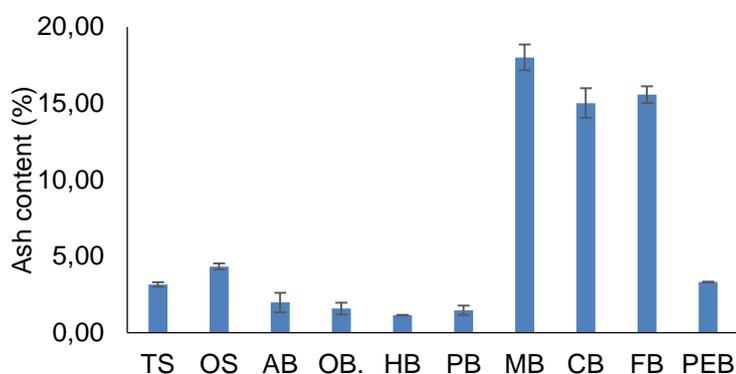


Fig. 4. Ash contents of the analyzed materials

The main problem in the management of ash is its salinity. Table 3 shows the pH, electrolytic conductivity (EC) and total dissolved solids (TDS) content of ash water extracts from the biomass samples.

All tested ashes were alkaline, total dissolved solids (TDS) describes all chemical compounds that are dissolved in water. High solubility of salts in water entails higher electrical conductivity, which is confirmed by the results obtained from ash samples. Both TDS and electrolytic conductivity characterize the salinity of the substance [44] The highest value of total dissolved substances was recorded

for straw ash, where oat straw ash obtained 3910 ppm and triticale straw ash obtained 2504 ppm. The least amount of total dissolved substances was found in oak bark ash, at 504 ppm, as well as in biochar and pellet biochar ashes.

Table 3. Elemental composition

Analyzed materials	pH	EC [mS·cm ⁻¹]	TDS [ppm]
CB	9.96	37.65	1771
MB	10.26	33.67	1578
FB	4.62	16.01	750
PEB	7.37	14.14	651
OB	9.67	10.55	504
PB	9.99	27.95	1288
HB	10.10	23.45	1111
AB	10.45	25.85	1225
OS	10.28	83.70	3910
TS	10.27	52.66	2504

Oat straw ash had the highest salinity with a value equal to 8.3 mS·cm⁻¹, followed by triticale straw ash with a slightly lower value of 5.2 mS·cm⁻¹. The EC values for wood bark ash are more than twice as low as those of straw ash and biochar ash. In contrast, the lowest value was obtained by oak bark ash – 1.0 mS·cm⁻¹.

In practice, the high salinity of the ashes limits their use in agriculture. Most of the tested ashes, with the exception of oak bark ashes, show EC>2 mS·cm⁻¹. Comparing the obtained EC values of the tested ash samples with the soil salinity scale according to Jackson, the tested ashes should be considered toxic to almost all species (EC>2 mS·cm⁻¹). The ashes of oak bark, biochar and pellet biochar are characterized by EC=1 mS·cm⁻¹, which, according to the Jackson scale, is considered a salinity limit only for sensitive plants [45].

The alkaline ash, high salinity and total dissolved matter content of straw ash can pose a threat to environmental elements such as soil, water.

Leaching tests are performed to assess the risk of groundwater contamination. The results of leaching tests give an approximate knowledge about the potential environmental impact of the waste, but much more valuable data for the assessment of environmental risk. Figures 5-15 show the concentrations of selected metals in the aqueous extracts from the ashes of the biomasses tested (1:10 ash:water ratio).

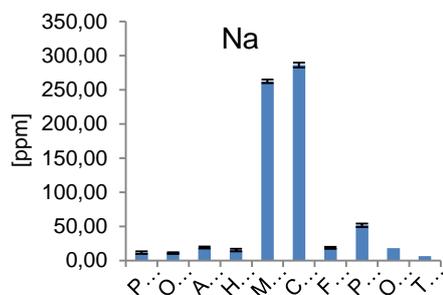


Fig. 5. The concentrations of Na in the aqueous extracts from the ashes of the biomasses tested

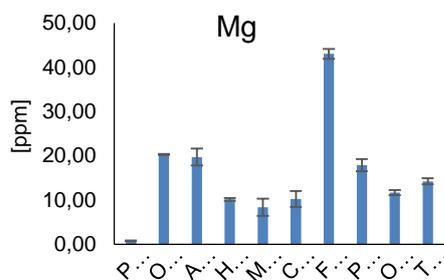


Fig. 6. The concentrations of Mg in the aqueous extracts from the ashes of the biomasses tested

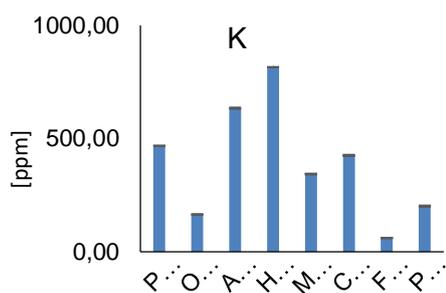


Fig. 7. The concentrations of K in the aqueous extracts from the ashes of the biomasses tested

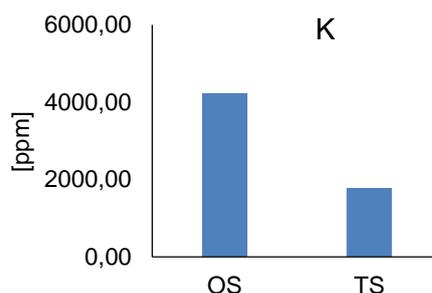


Fig. 8. The concentrations of K in the aqueous extracts from the ashes of the biomasses tested

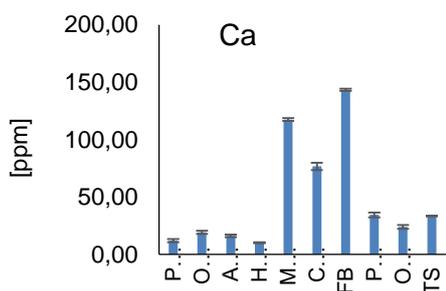


Fig. 9. The concentrations of Ca in the aqueous extracts from the ashes of the biomasses tested

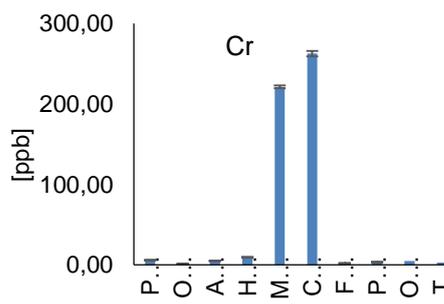


Fig. 10. The concentrations of Cr in the aqueous extracts from the ashes of the biomasses tested

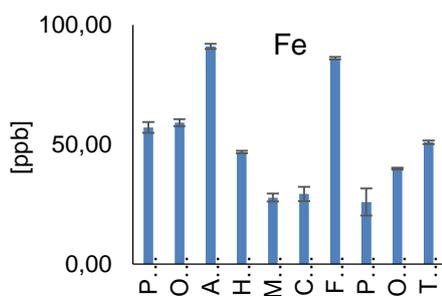


Fig. 11. The concentrations of Fe in the aqueous extracts from the ashes of the biomasses tested

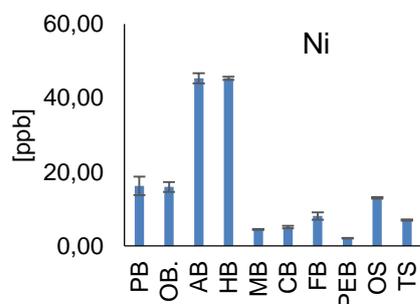


Fig. 12. The concentrations of Ni in the aqueous extracts from the ashes of the biomasses tested

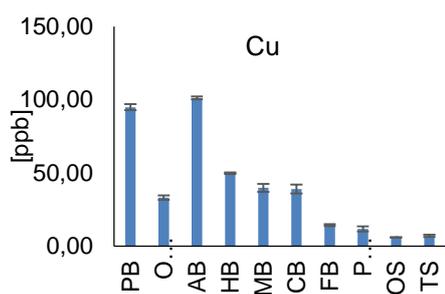


Fig. 13. The concentrations of Cu in the aqueous extracts from the ashes of the biomasses tested

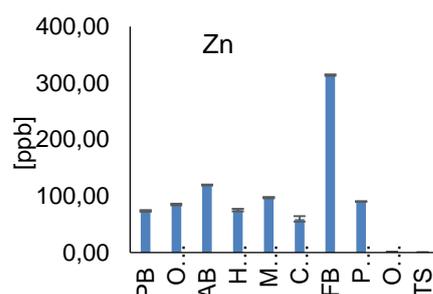


Fig. 14. The concentrations of Zn in the aqueous extracts from the ashes of the biomasses tested

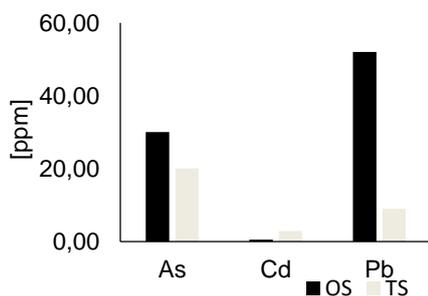


Fig. 15. The concentrations of As, Cd, Pb in the aqueous extracts from the ashes of the biomasses tested

The metal content of the aqueous extracts from the biomass ashes tested can be ranked as follows:

- oat straw: K>P>Ca>Na>Mg>Mn>Fe>Zn>Cu>Pb>As>Ni>Cr >Co>Cd,
- triticale straw: K>P>Ca>Mg>Na>Fe>Mn>Zn>Cu>As>Pb>Ni>Cr>Co>Cd,
- horbeam bark: K>Na>Mg>Ca>Zn>Cu>Fe>Ni>Cr,
- alder bark: K>Mg>Na>Ca>Zn>Cu>Fe>Ni,
- pine bark: K>Na>Ca>Mg>Cu>Zn>Fe>Ni>Cr,
- oak bark: K>Mg>Ca>Na>Zn>Fe>Cu>Ni,
- municipal waste biochar, composting biochar: K>Na>Ca>Mg>Cr>Zn>Cu>Fe>Ni,
- biochar: Ca>K>Mg>Na>Zn>Fe,
- pellet biochar: K>Na>Ca>Mg>Zn>Fe>Cu.

Ashes from biomass materials contain much more alkali metals than heavy metals in aqueous extracts. Literature studies have shown that leaching of elements from biomass combustion ash can be ranked as follows: K > Na > Sr > Ni > Mn > Cd > Cr > Zn > Co > Si > Mo > - Li > (Mg, Pb) > Ca > Cu > Ba > P > Se > Sb > Al > Fe > (Br, Hg) > (W, B, Sn, Ti, V), and the high leaching is due to the presence of easily soluble compounds in the ashes such as: chlorides (sylvite, halite), sulfates (syngenite, ettringite, gypsum), oxides (CaO), hydroxides (portlandite), nitrates, carbonates and bicarbonates [46].

In the ash extracts of the materials studied, with the exception of Fluid's biochar, potassium ions constituted the most leached element. High concentrations of leached potassium ions from ashes are a characteristic of most biomass ashes, as confirmed by studies by Vassilev et al. (2013) and Uliasz et al. (2015) [46, 47]. The concentration of leached potassium from the ashes of the biomass types studied ranged from 164.82-4393.37 ppm, and these values are much higher than the content of leached potassium ions in coal ashes. Uliasz et al. reported that the content of leached potassium ions from coal ash was only 6.46 ppm. The opposite is true for sodium ions, their content in water extracts from coal ashes is 35.58 ppm, while the concentration of sodium ions in water extracts from the ashes studied ranged from 10.98 ppm to 18.11 ppm. These two elements that can be described as "troublesome" in the biomass tarification process. They cause slagging, agglomeration and corrosion of plants in combustion processes [47]. The presence of these metals is a serious environmental problem. Storage of ashes with a high content of alkali metals poses a threat of leaching of these ions into surface and groundwater [48].

The content of heavy metal ions in water extracts from biochar ash is higher than that of the other ashes tested. In addition, higher concentrations of lead (9-52 ppb), chromium (3-6 ppb) and cadmium (4-10 ppb) were obtained in water extracts from straw ashes compared to the concentrations of these metals in water

extracts from tree bark ashes. Water extracts from tree bark ashes had the least content of heavy metals.

The obtained results of leached heavy metal ions were compared with the results of leaching from ashes of coal combustion in a conventional boiler obtained by Uliasz et al. The concentrations of zinc (0.27 - 119.59 ppb), copper (6- 101.18 ppb), nickel (7-45.37 ppb), chromium (3-262.69 ppb), cadmium (0.44 -2.82 ppb) in the aqueous extracts from the ashes of the biomass types studied were higher than in the aqueous extracts from the ashes of hard coal reported by Uliasz et al. of: for zinc: 10 ppb; copper: 16 ppb; lead: 2 ppb; nickel: 1 ppb, chromium: 38 ppb; and cadmium: 2.4 ppb [47].

***Lepidium sativum* root test on ashes from the biomass samples tested**

Performing the Phytotoxkit root test on the *Lepidium sativum* plant, known as cress, allows the determination of two parameters: percent root growth inhibition and germination index. These parameters determine the plants' response to changes in the substrate. They are presented in Figures 16 and 17.

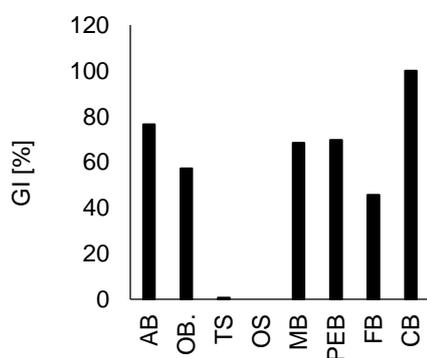


Fig. 16. The percent root growth inhibition on the ashes from the biomasses

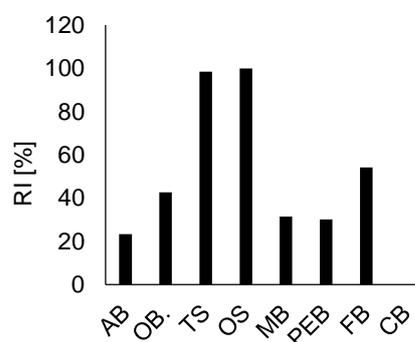


Fig. 17. The percent germination index on the ashes from the biomasses

The germination index (GI) is an indicator of the effect of the substrate on plants. The *Lepidium sativum* test showed that straw ashes completely inhibited seed germination and root development. Biochar ash proved to have lesser effect on the growth of *Lepidium sativum* than the other biomass ashes tested. The germination index (GI) had the highest value for composting biochar, reaching 100%. The values of municipal waste biochar and pellet biochar have similar values corresponding to 68.46% and 69.77%, respectively. In the case of alder bark ashes, 50% of the seeds germinated and a 23% inhibition of root development

was observed. A worse result was obtained for seeds germinated on biochar, as only 45.75% of seeds germinated.

4. CONCLUSION

The geopolitical situation is forcing an increase in the share of renewable energy sources in the power industry. In Poland, among renewable energy sources, biomass shows the greatest potential. Recently, there has been growing interest in the use of biochar as a fuel. The increase in the share of these materials in combustion processes requires its appropriate selection, both in quantity and quality.

1. The biomass materials analyzed were characterized by good technical parameters. The biochars tested had high calorific values ranging from 16.86 MJ·kg⁻¹ for the composting biochar, to 24.03 MJ·kg⁻¹ for the Fluid's biochar. In contrast, the straw and bark samples tested showed an average calorific value of 12 MJ·kg⁻¹. The calorific values of the analyzed biomass materials can ensure their energetic use in combustion and co-firing processes, and this value qualifies the fuels as a valuable energy source.

2. The analyzed biochars are characterized by a high elemental carbon content (more than 50%), while in the bark of the studied trees it averages 35%, and in the case of straw – about 42%. The materials studied contain low concentrations of nitrogen and sulfur, which makes it possible to reduce the emissions of nitrogen and sulfur oxides in the combustion and co-combustion processes of biochar.

3. The tested biochars have higher ash content (up to 15%) than the tested tree bark (~1%) and straw (~3%), while there is almost three times more ash in hard coal, compared to biochar.

4. Among the biomass materials tested, the biochar produced at the lowest temperature (300°C) by pyrolysis exhibited the best energy properties. It had the highest calorific value (24.03 MJ·kg⁻¹ MJ/kg), heat of combustion (25.09 MJ·kg⁻¹ MJ/kg), and carbon concentration (61.54%) while simultaneously having a low ash content (3.54%).

5. It is necessary to strictly control the produced biomass materials. Given their variable composition, it is desirable to study the correlation between the different properties of biomasses and the energy parameters of biochars.

6. The eluates from the studied ashes are characterized by high variability depending on the biomass material studied. The main ions leached are potassium and sodium ions. The water solubility of heavy metals is negligible.

7. The variable elemental composition in the aqueous extracts of ash from biomass materials makes it difficult to develop an universal type of management of their ash.

ADDITIONAL INFORMATION

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