

Article

The Effect of *Carpinus betulus* Ash on the Maize as an Energy Crop and the Enzymatic Soil Properties

Edyta Boros-Lajszner , Jadwiga Wyszowska*  and Jan Kucharski 

Department of Soil Science and Microbiology, University of Warmia and Mazury in Olsztyn, Plac Łódzki 3, 10-727 Olsztyn, Poland; edyta.boros@uwm.edu.pl (E.B.-L.); jan.kucharski@uwm.edu.pl (J.K.)

* Correspondence: jadwiga.wyszowska@uwm.edu.pl

Abstract: Maize can easily adapt to changing weather conditions, has moderate soil requirements, and offers high green mass productivity. The goals of this study were to assess the possibility of using ash from *Carpinus betulus* aided by soil amendment with compost and HumiAgra in *Zea mays* cultivation and to determine the energy potential of maize. Wood ash had a relatively minimal effect on the combustion heat and calorific value of maize biomass. It increased the contents of C, H, S, N, O, and ash in the aerial parts of the maize. In addition, it positively affected the contents of organic carbon, total nitrogen, soil pH, sum of exchangeable base cations, total exchangeable capacity of soil, and degree of soil saturation with alkaline cations. In contrast, it strongly decreased the yield of maize, negatively affected the biochemical activity of the soil, and reduced the hydrolytic acidity of the soil. Soil amendment with compost and HumiAgra had positive effects on the heat of combustion; calorific value; the contents of C, H, S, N, O, and ash in the aerial parts of maize; and on the properties of the soil. In addition, they mitigated the adverse effects of wood ash on maize biomass and the enzymatic properties of the soil.

Keywords: renewable energy; maize; heat of combustion; energy value; ash



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1. Introduction

Today, there is a growing interest in new, renewable energy sources that are available locally and across each country to respond to the ever-increasing energy consumption demand and ensure energy supply both locally and globally [1]. Therefore, there is a growing interest in the research, production, and application of energy from biomass, as well as biogas as fuels of renewable origin, which can replace fuels of nonrenewable origin in the short term [2,3]. These transformations are expected to lead to significant technological progress, reflected in a greater capacity to produce clean, affordable, and nonpolluting energy, and to reduced production costs for the benefit of the population, which altogether follow the aims of Agenda 2030 [4]. Nevertheless, today's global energy demand has risen sharply due to rapid population growth and technology development. At the same time, an urgent need has emerged to reduce the emissions of greenhouse gases (GHGs), like CO₂ [5], methane, and nitrous oxide [6,7], which are severely harmful to the natural environment. In particular, the CO₂ emissions recorded in recent years have accounted for 50% of the global warming [5]. Some environmental damage is caused by the combustion of fuels, while other damage is due to various anthropogenic activities [8], e.g., mining, which causes environment pollution with heavy metals, thereby posing a common and severe problem affecting the elemental composition of the soil and its biological properties [9].

This requires the search for new sources of energy to replace these nonrenewable resources [10,11]. One such renewable source could be biomass to be used as a fuel, as there has recently been a growing interest in this waste's energy potential due to its several advantages such as its availability, neutral carbon dioxide emissions, and ease of

combustion [12]. In addition, plant biomass has lower sulfur and nitrogen contents and a higher oxygen content than fossil fuels. Furthermore, the burning of straw instead of wood results in lower emissions of polycyclic aromatic hydrocarbons [13,14]. Maize straw seems to be an interesting raw material among the broad range of biomass-derived fuels. Maize is one of the most widely grown cereals in Poland, and its straw is an interesting source of biomass to be used for energy purposes [15]. Maize (*Zea mays* L.) belongs to the *Poaceae* family. It is indigenous to the American continent, where it was cultivated already in ancient times. It is now one of the world's most popular and widely produced crops, including in the USA, China, India, and Brazil. Maize is an annual monocotyledonous plant, cultivated mainly for human and animal consumption [16], but, in recent decades, the purpose of its cultivation has been redefined by biofuel production. Brazil and the United States are currently the largest producers of biofuels, accounting for 44% of the global production and meeting 1.2% of the vehicle fuel demand [2]. At present, the share of maize in the production of biofuels, in particular bioethanol, has increased to levels equal to or greater than that of all energy crops [17]. Notably, maize should be cultivated for energy purposes on contaminated or degraded areas, not on agricultural land intended for food production [18], and this approach requires using fertilizers, e.g., wood ash [19–21]. Today, wood ash is treated as waste, being most commonly used as a fill for former mine shafts or simply as landfill. The increasing cost of landfill and the reluctance to open new landfills have led to a growing interest in alternative disposal methods. These entail the use of wood ash in horticulture, agriculture, or forestry [22–25].

Soil biochemical activity can be harnessed as an indicator to assess the impact of wood ash on its biological life. Soil enzymes are direct mediators of the biological catabolism of the organic and mineral soil components. Thus, these catalysts enable a reliable assessment of the rates of important soil processes. The enzyme activity in soil is often closely linked to the soil's or biomass's organic matter content, properties, and microbial activity. Changes in enzyme activity appear much earlier than those of other parameters, thus providing early signs of the transformations taking place in the soil environment [26–28].

The above information led us to perform an experiment, the main objectives of which were to evaluate the possibility of using ash from *Carpinus betulus*, aided with the addition of compost and HumiAgra, in *Zea mays* cultivation and to determine the energy potential of the maize, measured using parameters such as calorific value and heat of combustion. *Carpinus betulus* L. (European hornbeam) is a deciduous tree that is widespread in Europe and Asia Minor [29]. It is a long-lived tree, not demanding in terms of soil conditions, and its wood is hard. The wood of *Carpinus betulus* L., known as hornbeam, is suitable for instrument making (pianos, violins) and carpentry [30]. *Carpinus betulus* L. is considered one of the best species for firewood due to its properties [31]: it is a very hard and heavy wood and has the highest calorific value (14 MJ kg^{−1}). Another advantage is its fast drying time. Due to its low bark content, it is a low-smoking wood and leaves a small amount of ash [32,33]. Due to its hardness and density, hornbeam is very difficult to split. Another objective was to assess the impact of soil amendment with ash from *Carpinus betulus*, compost, and HumiAgra on the biochemical and physicochemical properties of the soil.

With the increasing use of biomass in the energy and heating sectors, it is considered necessary to develop a research model that will allow wood ash to be used in a natural and environmentally friendly way. The formulated research hypotheses assumed a positive effect of the applied dose of ash from *Carpinus betulus* on the growth and energy potential of maize and on the enzymatic properties of the soil. In addition, compost and HumiAgra were assumed to boost the positive effect of ash from *Carpinus betulus* on maize and soil enzymes.

2. Materials and Methods

2.1. Characteristics of Soil, Wood Ash, Compost, and HumiAgra

The soil used to establish this experiment was collected from a depth of 0.00–0.20 m of the arable humus in Tomaszkowo village, Olsztyn commune, Warmia and Mazury

Province, Poland (53.7161° N, 20.4167° E). Before the experiment as established, the soil was sieved through a screen with a mesh size of 0.5 cm. Then, the fraction size composition and basic chemical and physicochemical properties of the soil were determined (Figure 1). The characteristics of the *Carpinus betulus* L. ash, compost, and HumiAgra used in the experiment are given in Figure 1.

Soil			Component Additives		
% fraction			Basic chemical and physicochemical properties		
sand	silt	clay	Units		
69.41	27.71	2.88	Organic carbon content	g kg ⁻¹	6.18
			Total nitrogen content	d.m.	1.27
			pH _{Ca}		6.09
			Hydrolytic acidity		8.81
			Sum of exchangeable base cations	mmol (+)	24.00
			Cation exchange capacity	kg ⁻¹ d.m.	32.81
			Extent of saturation with base cations	%	73.14
			Composition		
			Units		
			Ash from <i>Carpinus betulus</i>	% of d.m.	C – 51.04
					H – 5.87
					S – 0.02
					N – 0.38
					Cl – 0.02
					P – 0.09
					K – 0.17
					pH 12.60
			Compost produced by Ekokonsorcjum-Effekt company (Cracow, Poland; license no. 21/02)	% of d.m.	C _{org} – 23.20
					N _{total} – 1.30
					P – 0.26
					K – 1.24
					Mg – 0.30
					Ca – 1.43
			HumiAgra (AgraPlant, Kielce, Poland)	%	pH 8.20
					Dark-brown powder containing 90% of humic acids (45% of humins and 45% of fulvic acids)
					K – 6.00
					S – 3.00
					Si – 1.00
					Ca – 0.70
					Fe – 0.20
					Mg – 0.25
					Zn – 0.12
					Cu – 0.04
					pH 8–10

Figure 1. Characteristics of the soil, ash, compost and HumiAgra used in this study.

2.2. Pot Experiment

This experiment was conducted in the greenhouse of the University of Warmia and Mazury (UWM) in Olsztyn, Poland, Central Europe. First, 3.5 kg of soil was weighed, and macroelements were added in all experimental variants in the following doses per pure compound (mg kg⁻¹ d.m. of soil): nitrogen—150 in the form of CO(NH₂)₂, phosphorus—70 in the form of KH₂PO₄, potassium—120 as KCl + KH₂PO₄, and magnesium—15 as MgSO₄ · 7H₂O. Ash from *Carpinus betulus* (20 g kg⁻¹ soil d.m.), compost (2.5 mg kg⁻¹ soil), and HumiAgra (2.5 mg kg⁻¹ soil d.m.) were then added to individual pots. This experiment involved six variants, each of which was performed in four replications. The scheme of the experiment was as follows:

1. Control soil;
2. Soil + ash from *Carpinus betulus*;
3. Soil + compost;
4. Soil + ash from *Carpinus betulus* + compost;
5. Soil + HumiAgra;
6. Soil + ash from *Carpinus betulus* + HumiAgra.

Doses of wood ash and soil additives were established based on the results of our previous study [34]. The soil, together with the macroelements, ash from *Carpinus betulus*, compost, and HumiAgra, was thoroughly mixed and placed in pots (capacity 3.7 dm³). The soil without the addition of wood ash, compost, and HumiAgra served as the control. Then, 7 maize grains (LG 32.58 cultivar) were sown into the pots, and the soil was moistened to 50% of the maximum water capacity. At the BBCH 10 stage of maize development, the seedlings were thinned, and 4 plants were left in each pot. During the vegetation period (60 days), soil moisture was monitored and maintained at a constant level (50% of the maximum water capacity). Soil moisture was checked 3 times a day, and water losses were systematically replenished with deionized water. According to the Biologische Bundesanstalt, Bundessortenamt and Chemical Scale (BBCH), when maize was at developmental stage BBCH 19, BBCH 31, and BBCH 33, the leaf greenness index was determined using a chlorophyll meter (KONICA MINOLTA, Inc., Chiyoda, Japan) and is expressed in relative units. Measurements were carried out in 4 replications. At the BBCH 39 developmental stage of maize, the fresh and dry weight of its aerial parts and roots were determined after green mass drying at 65 °C for 7 days. The biomass of the aerial parts of maize was additionally analyzed to determine the heat of combustion, calorific value, the elemental composition (C, H, S, N, O), and the ash content. At the same time, soil samples were collected for enzymatic and physicochemical analyses.

2.3. Chemical Analyses of Plants

The chemical properties of the plants were determined as follows (Figure 2): the procedure for performing the calculations are described in Wyszowska et al. [35].

Chemical analysis of plants		
Parameter	Abbreviation	Methods/References
Heat of combustion	Q	Calorimeter – C-2000 (IKA WERKE, USA), acc. (Hanau, Germany) [PN-EN ISO 18125:2017 IKA C2000]
Heating value	Hv	Automatic ELTRA CHS 500 analyzer (Carbon Hydrogen Sulfur Determinator, Neuss, Germany) [PN-G-04584 and PN-G-04517]
Carbon, Hydrogen, Sulfur	C, H, S	Digestion kit – K-424 mineralizer; and a distillation kit – B-324 nitrogen distiller (BUCHI Labortechnik AG, Flawil, Switzerland) [PN-EN ISO 20483]
Nitrogen	N	Has been estimated based on the total content of such elements as: C, H, S, N, and ash [Protásio et al. 2011]
Oxygen	O	Dry mineralization in an ELTRA THERMOSTEP muffle furnace (Thermogravimetric Analyser, Neuss, Germany)
Ash		

Figure 2. Methods of chemically analyzing plants used in this study [36–40].

2.4. Soil Biochemical Analyses

The activity of the following soil enzymes was determined in the experiment described in Figure 3.

Biochemical analysis of soil

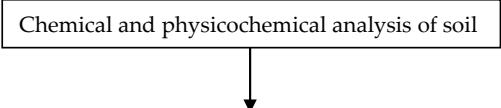
Enzymes	Abbreviation	Methods/References	Equipment
Dehydrogenases	Deh	Lenhard in Öhlinger's modification [1996]	Perkin-Elmer Lambda 25 spectrophotometer (Waltham, MA, USA)
Urease	Ure	Alef i Nannipieri [1998]	
Acid phosphatase	Pac		
Alkaline phosphatase	Pal		
Arylsulphatase	Aryl		
β-glucosidase	Glu	Tehrani and Moosavi-Movahedi [2018]	Measured by potassium permanganate titration method
Catalase	Cat		

Figure 3. Soil enzyme analysis methods used in this study [41–43].

The determination of the activity of the individual soil enzymes, the substrates used, the units of activity, and the test conditions are described in detail in a previous publication by Wyszowska et al. [44].

2.5. Soil Chemical and Physicochemical Analyses

The basic chemical and physicochemical properties of the soil were determined as show in Figure 4.



Parameter	Abbreviation	Methods/References
Organic carbon	C _{org}	Vario MaxCube CN elemental macroanalyser (Hanau, Germany)
Total nitrogen	N _{Total}	
Granulometric composition		Aerometric method PN-R-04032 [1998] and ISO 11464 [2006]
Soil pH _{KCl}		Potentiometric in 1 mol dm ³ aqueous KCl solution [ISO 10390]
Hydrolytic acidity and	HAC	Kappen [1993]
Sum of exchangeable base cations	EBC	
Exchange capacity	CEC	Klute [1996]

Figure 4. Soil chemical and physico-chemical analysis methods used in this study [45–49].

2.6. Statistical Analysis

Data were statistically processed using the Statistica 13.1 package [50]. Results were compared using ANOVA followed by Tukey's post hoc test (HSD). Subsets of the averages were identified at a significance level of $p = 0.05$. The results had a normal distribution and similar variance. Principal component analysis (PCA) of elemental content (carbon,

hydrogen, sulfur, nitrogen, oxygen) and ash in maize ear tips was performed using multivariate exploration techniques. To better assess the effects of ash, compost, and HumiAgra on maize biomass and soil enzyme activity, we determined the percentage contribution of each independent variable to the dependent variables. For this purpose, we used an analysis of variance (ANOVA) to measure the effect η^2 . Standard deviations were also counted, which provide information on how widely the values of a given quantity are spread around its mean.

3. Results

3.1. Response of Maize to Ash from *Carpinus betulus*

The application of *Carpinus betulus* ash into the soil reduced the biomass of the aerial parts and roots of maize. In turn, soil amendment with compost (KO) and HumiAgra (HA) alleviated these adverse effects. The yield of the aerial parts and roots of maize depended, to the greatest extent, on the wood ash used, as indicated by the percentage of the factors of the observed variability, reaching 84.36% and 50.65%, respectively Figure 5. In turn, KO and HA contributed to 12.84% of the variability in the root biomass yield.

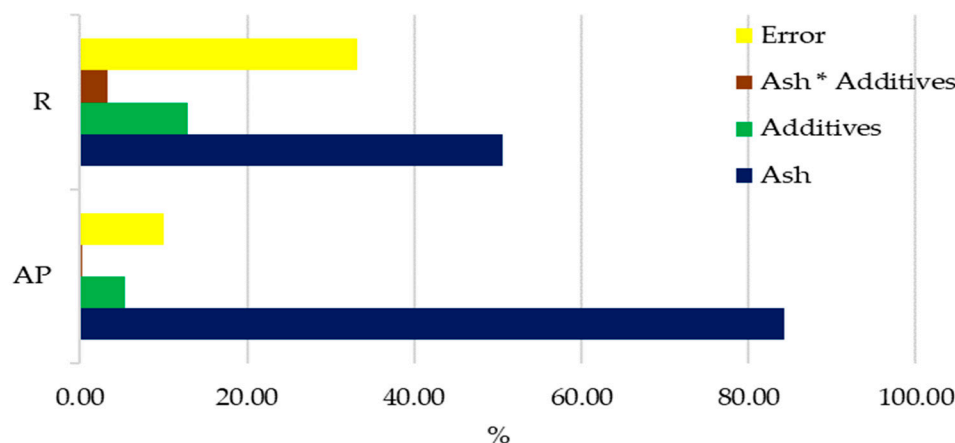


Figure 5. Coefficient of observed variation η^2 (%). AP—yield of aerial parts; R—yield of roots.

The ash from *Carpinus betulus* negatively affected the growth and development of the maize (Figures 6 and 7). The 20 g kg⁻¹ soil d.m. dose applied to the soil resulted in a statistically significant reduction in the yield of the dry weight of the aerial parts and roots of the maize compared to the control soil, regardless of KO and HA addition. The aerial parts and roots of the plants were the longest in the soil fertilized with KO, followed by that amended with HA, and the shortest in the soil samples without additives.

The application of wood ash, KO, and HA to the soil had no significant effect on the leaf greenness index (SPAD) of the maize (Figure 8). The SPAD values determined in the first two developmental stages of maize remained at similar levels. The maize's SPAD decreased significantly only in the third stage of its development, i.e., the highest value was recorded in BBCH 19 and BBCH 31 and the lowest one in BBCH 33. These relationships were recorded in both unfertilized soil and soil fertilized with KO and HA.

The values of the heat of combustion of maize were similar in the samples from soils without and with the addition of KO and HA (Table 1). The highest Q value, reaching 18.453 MJ kg⁻¹ p.d.m. of plants, was determined for the maize grown in the soil with compost but without the addition of *Carpinus betulus* ash. The differences noted in the other soil variants were not statistically significant. This study's results indicate that the soil amendment with wood ash had no significant effect on the heat of combustion of maize. The calorific value values were similar across all experimental variants. As was the case for the combustion heat, the highest calorific value was also found for the plants grown in the soil amended with KO but without wood ash and amounted to 16.594 MJ kg⁻¹ p.d.m. of plants. In soil fertilized with KO and HA, the energy obtained from the maize biomass

produced from 1 kg of soil was higher than that from the maize produced from the soil without these additives. This correlation was determined for maize from both the control soil and from the soil amended with *Carpinus betulus* ash.

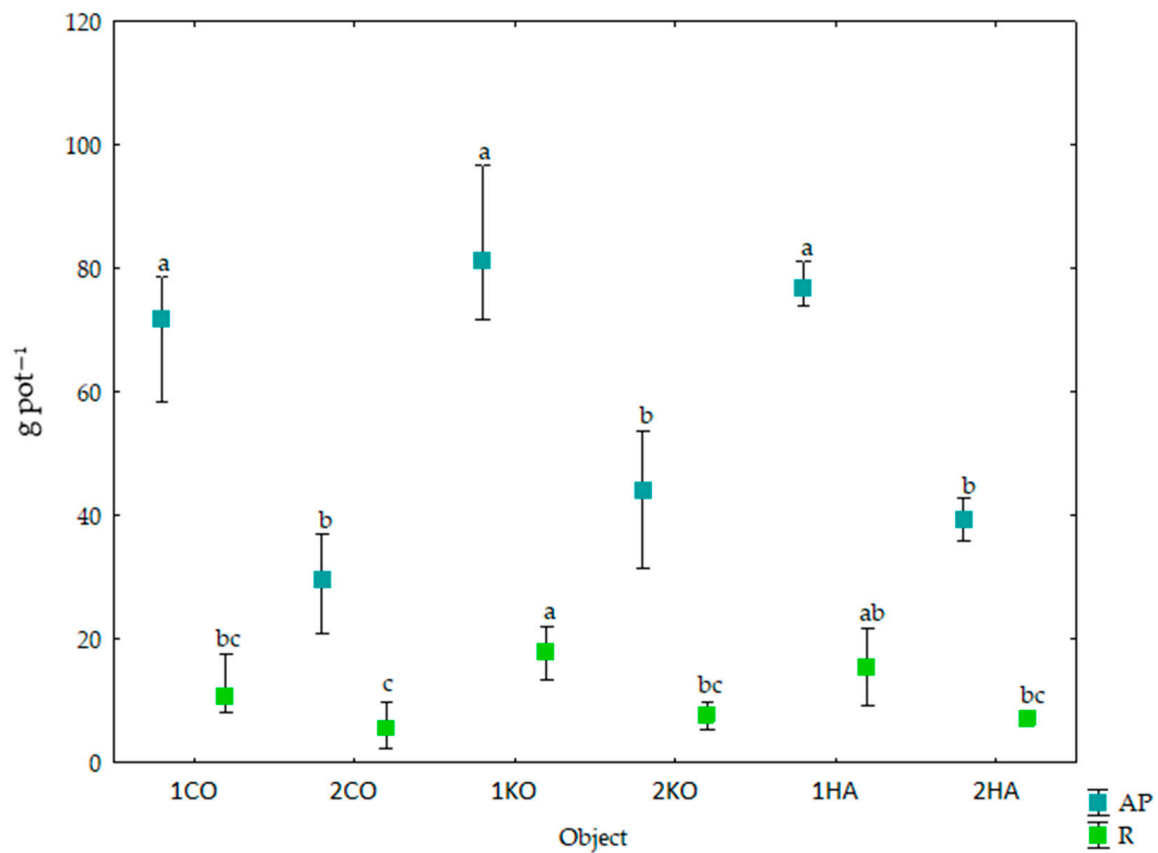


Figure 6. Dry weight of aerial parts and roots of maize from soil to which ash of *Carpinus betulus* was added in g pot⁻¹. Explanations: 1—0 ash kg⁻¹ of soil; 2—20 ash kg⁻¹ of soil; CO—soil without additives; KO—soil with compost; HA—soil with HumiAgra. The same letters (a–c) denote homogeneous groups separately for aerial parts and roots.

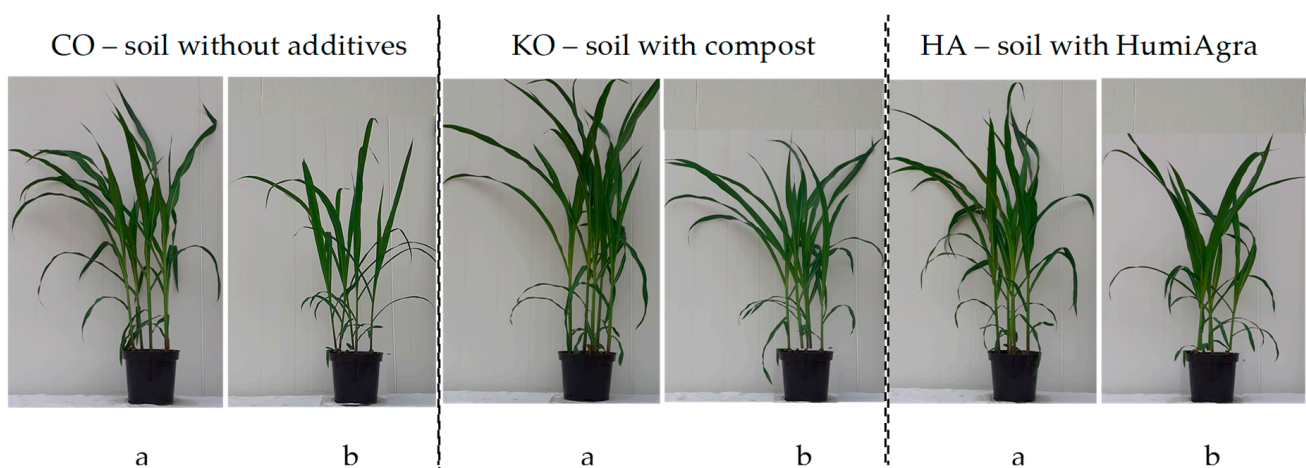


Figure 7. View of *Zea mays* L. BBCH 39 (stage 9 or more knees) in soil containing ash from *Carpinus betulus*. Definitions are given in the Figure 6 caption, a—0 g ash kg⁻¹ of soil; b—20 g ash kg⁻¹ of soil.

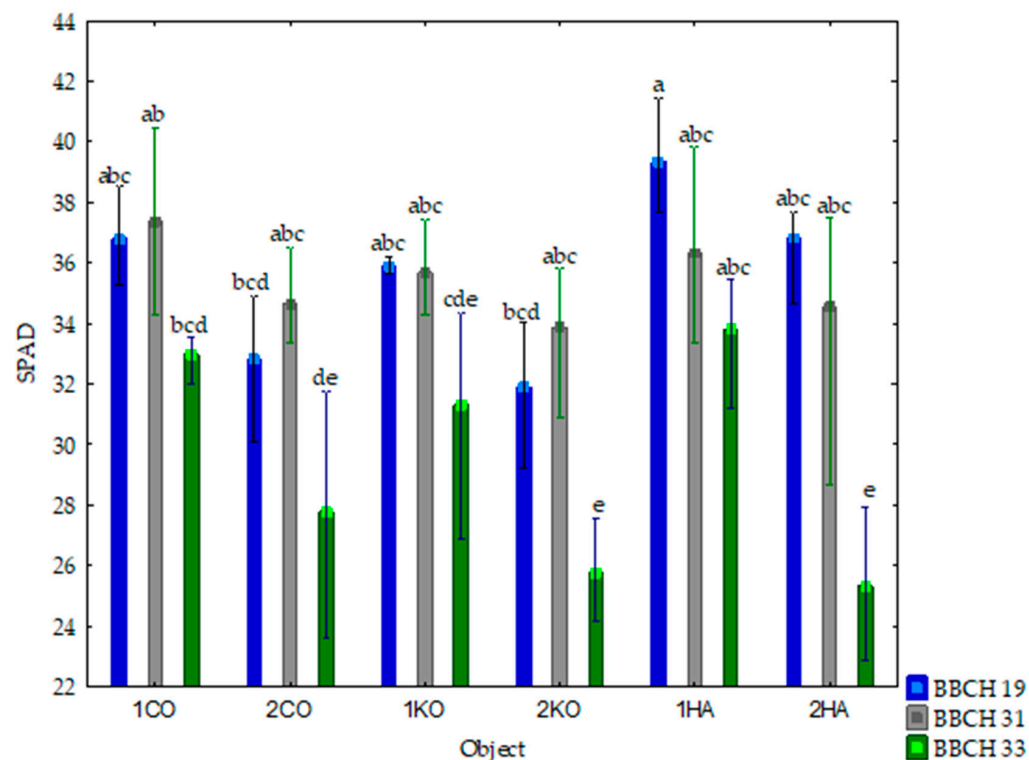


Figure 8. Leaf greenness index in maize. Definitions are given in the Figure 6 captions. Subsets of the averages are indicated by the same letters in columns (a–e).

Table 1. Heat of combustion, calorific value, and energy production of *Zea mays* L. grown in soil supplemented with *Carpinus betulus* ash.

Ash g kg ^{−1} d.m. Soil	Heat of Combustion	Heating Value	Energy Production
	MJ kg ^{−1} Air-Dried Plant Matter		
Control			
0	18.189 ^b ± 0.014	16.291 ^b ± 0.200	0.333 ^b ± 0.020
20	18.065 ^c ± 0.001	16.066 ^c ± 0.100	0.136 ^c ± 0.010
Compost			
0	18.453 ^a ± 0.004	16.594 ^a ± 0.200	0.384 ^a ± 0.020
20	18.162 ^b ± 0.035	16.339 ^b ± 0.100	0.205 ^b ± 0.010
HumiAgra			
0	18.218 ^b ± 0.037	16.462 ^b ± 0.200	0.360 ^b ± 0.020
20	18.186 ^b ± 0.015	16.402 ^b ± 0.100	0.184 ^b ± 0.010

Subsets of the averages are indicated by the same letters in columns (a–c).

Statistical analysis of the PCA results showed the stimulating effect of ash from *Carpinus betulus* and the use of KO and HA on the C, H, S, N, and O as well as ash contents in the aerial parts of the maize (Figure 9). The PCA revealed that the first two PCs explained 84.94% of the total variability in the input data, dividing the data into two groups. The first group constituted carbon, hydrogen, and oxygen, whereas the second one constituted sulfur, nitrogen, and ash. The vectors of most of the analyzed elements were of similar length, except for hydrogen, whose vector was shorter, indicating its weaker contribution to data variability. The dispersion of the points suggests that the use of KO and HA had a positive effect on the content of the analyzed elements and ash in the aerial parts of the maize.

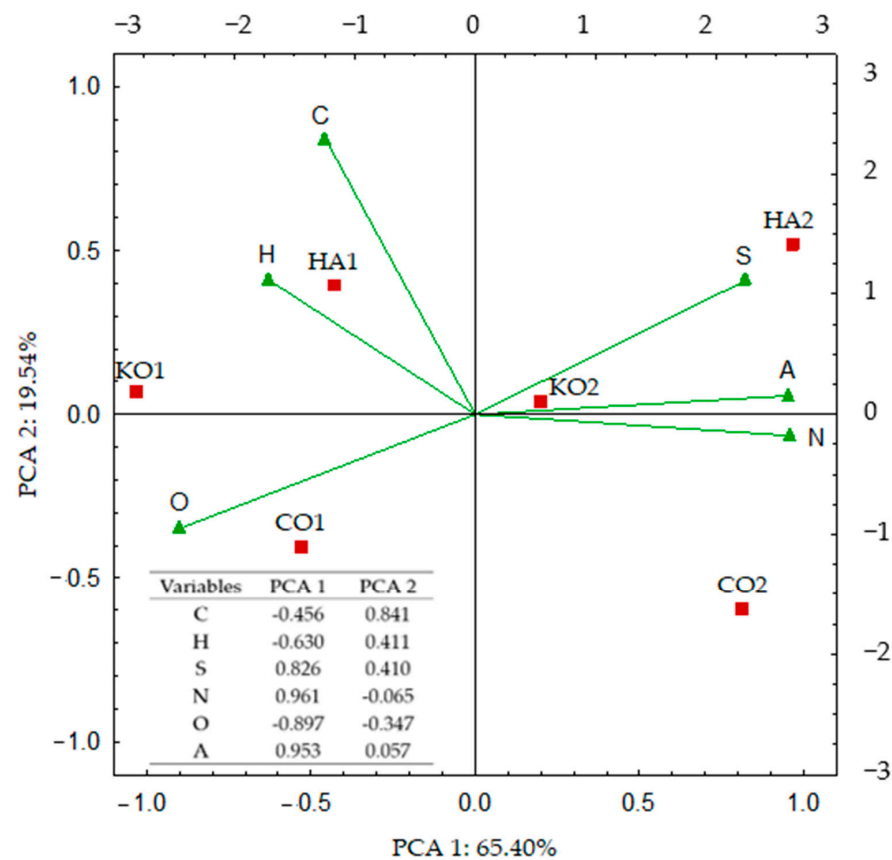


Figure 9. Elemental and ash contents of aerial parts of maize plotted according to PCA. Definitions are given in Figures 2 and 6 captions.

3.2. Response of Soil Enzymes and Certain Chemical and Physicochemical Properties of the Soil to Its Amendment with Ash from *Carpinus betulus*

The activity of the analyzed soil enzymes depended most strongly on the dose of *Carpinus betulus* ash, as indicated by the percentage share of the factors of the observed variability, expressed as the η^2 coefficient values, which was as follows: Deh—95.30%, Cat—94.76%, Pac—91.04%, Glu—87.32%, Pal—83.92%, Aryl—63.60%, and Ure—62.87% (Figure 10). The effect of the soil additives on its enzymatic properties was weaker. KO and HA elicited a stronger effect on the activity of three enzymes: arylsulfatase (26.85%), catalase (20.00%), and alkaline phosphatase (11.66%).

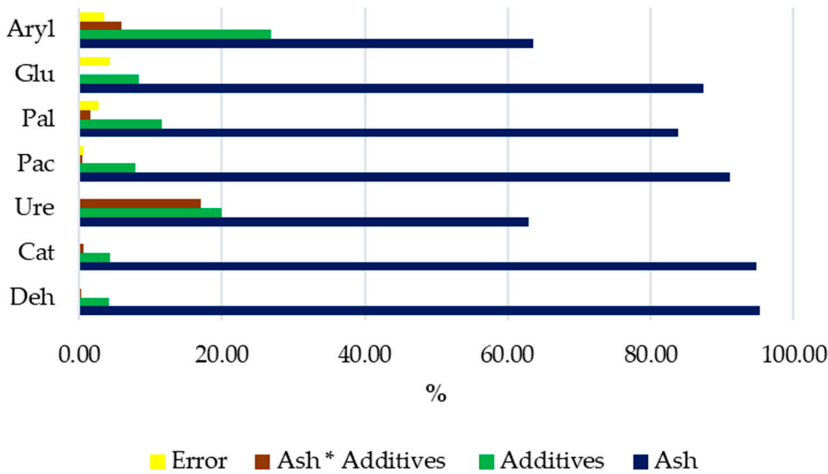


Figure 10. Coefficient of observed variation η^2 (%). Definitions are given in the Figure 3 caption.

The response of the enzymes to soil amendment with ash from *Carpinus betulus* was unequivocally negative Figure 11. Wood ash significantly inhibited the activities of Deh, Cat, Ure, Pal, Pac, Glu, and Aryl compared to their activities in the control soil. In the soil variants without the addition of *Carpinus betulus* ash, the highest activity of soil enzymes was found after soil fertilization with KO, followed by HA, and the lowest in the soil without their addition. This was particularly evident in the cases of Deh and Pal. In the soil samples amended with ash, Pal was the most sensitive enzyme, and Aryl was the most resistant one. KO and HA alleviated the negative effects of ash from *Carpinus betulus*.

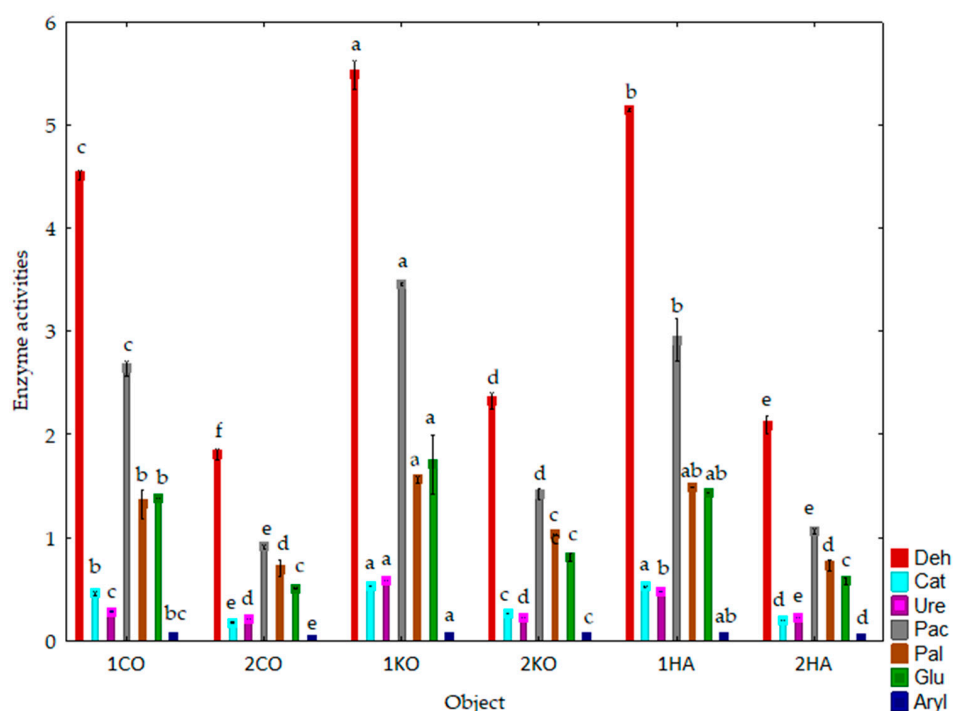


Figure 11. Enzyme activity in soil to which *Carpinus betulus* ash was added. Definitions are given in Figure 6 caption. Deh—dehydrogenases in $\mu\text{mol TFF kg}^{-1} \text{ d.m. h}^{-1}$; Cat—catalase in $\text{mol O}_2 \text{ kg}^{-1} \text{ d.m. h}^{-1}$; Ure—urease in $\text{mmol N-NH}_4 \text{ kg}^{-1} \text{ d.m. h}^{-1}$; Pac—acid phosphatase in $\text{mmol PNP kg}^{-1} \text{ d.m. h}^{-1}$; Pal—alkaline phosphatase in $\text{mmol PNP kg}^{-1} \text{ d.m. h}^{-1}$; Glu— β -glucosidase in $\text{mmol PNP kg}^{-1} \text{ d.m. h}^{-1}$; Aryl—arylsulfatase in $\text{mmol PNP kg}^{-1} \text{ d.m. h}^{-1}$. Subsets of the mean values are indicated by the same letters for each enzyme (a–f).

An increase in C_{org} content was observed in the control soil samples, as well as in those with KO and HA and with *Carpinus betulus* ash applied compared to that in the soil samples without its addition (Table 2). The highest C_{org} content was found in the soil samples fertilized with organic substances and the lowest one in the control sample. Wood ash addition also increased the N_{Total} content in the soils without and with the addition of KO and HA. The highest total nitrogen content was recorded in the soil fertilized with KO, followed by that fertilized with HA, and the lowest one in the control soil. Regardless of soil fertilization with the above organic substances, the soil pH and the EBC increased, whereas the soil HAC decreased under the influence of treatment with ash from *Carpinus betulus* (Table 2). Similar observations were made for CEC and BS; namely, their values were higher in the soil variants with wood ash. Soil fertilization with KO and HA positively affected the physicochemical soil properties.

Table 2. Properties of soil with the addition of *Carpinus betulus* ash.

Ash g kg ⁻¹ d.m. Soil	pH _{KCl}	Total Organic Carbon	Total Nitrogen	Hydrolytic Acid	Total Exchangeable Base Cations	Total Cation Exchange Capacity of the Soil	Base Cation Saturation Ratio in the Soil
		(g kg ⁻¹)			(mmol ⁽⁺⁾ kg ⁻¹ Soil)		%
Control							
0	4.200 ^e ± 0.02	7.896 ^d ± 0.179	1.311 ^f ± 0.001	17.213 ^b ± 0.037	43.700 ^f ± 0.300	60.913 ^f ± 0.337	71.742 ^d ± 0.095
20	7.800 ^c ± 0.05	12.039 ^b ± 0.097	1.453 ^c ± 0.004	2.363 ^c ± 0.038	310.000 ^c ± 0.200	312.363 ^c ± 0.238	99.244 ^a ± 0.011
Compost							
0	4.550 ^d ± 0.02	8.617 ^c ± 0.135	1.432 ^d ± 0.001	18.038 ^a ± 0.039	71.000 ^d ± 0.300	89.038 ^d ± 0.237	79.726 ^b ± 0.077
20	8.000 ^a ± 0.01	12.992 ^a ± 0.112	1.734 ^a ± 0.002	2.438 ^c ± 0.033	322.000 ^a ± 1.000	324.438 ^a ± 0.113	99.249 ^a ± 0.034
HumiAgra							
0	4.500 ^d ± 0.05	7.965 ^d ± 0.075	1.373 ^e ± 0.002	17.325 ^b ± 0.035	49.000 ^e ± 0.300	66.325 ^e ± 0.317	73.875 ^c ± 0.031
20	7.900 ^b ± 0.05	12.854 ^a ± 0.226	1.522 ^b ± 0.008	2.400 ^c ± 0.037	315.000 ^b ± 1.000	317.400 ^b ± 0.925	99.244 ^a ± 0.026

Subsets of the averages are indicated with the same letters in columns (a–f).

4. Discussion

4.1. Response of Maize to Ash from *Carpinus betulus*

Plant biomass, characterized by widespread availability, renewability, and relatively low sourcing costs, seems to be a promising feedstock for energy purposes [51]. Maize represents one of the target crops with high yield potential, particularly for the production of high-quality biofuels [52,53]. It is highly adaptable to changing weather conditions, has moderate soil requirements, and ensures high-efficiency photosynthesis [54,55] and high green matter productivity per unit area [54,56].

Soil amendment with wood ash can have a twofold effect on maize biomass. According to Gao and DeLuca [57], Hale et al. [58], and Saletnik et al. [59], it has a positive effect on plant growth and development and increases yield. In the study by Wyszowski et al. [60], coal ash and sewage sludge ash were used as substances to reduce soil contamination with diesel oil. Romdhane et al. [19] used willow biomass ash as a soil amendment. In these studies, ash amendments increased the biomass of maize. In contrast, the present study's results showed a negative effect of ash from *Carpinus betulus* on the biomass of the aerial parts and roots of maize. Such extremely different effects of ash application recorded between the present study and the above-mentioned studies are mainly due to differences in the chemical composition of the ash [61]. Zajac et al. [62] compared ashes according to their origin, namely, wood and woody biomass, energy crops (herbs and grasses), agricultural biomass (straw and hay), forest residues (bark), and agrifood industry waste (husks and peels). According to Lehmann et al. [63], excessive ash doses do not increase, and may even adversely affect, the yield of plants. The overapplication of wood ash can damage plants because it contains certain toxic elements, such as radioactive cesium-137, and certain metals, such as As, Pb, Zn, Ni, Co, and Cu, which can be toxic to plants and pose a threat to the environment [64]. These toxic substances, from excess wood ash doses, may interfere with the nutrient circulation and microbiological processes in the soil, which adversely affect plant growth [65]. Nabeela et al. [65] reported that the use of wood ash increased the bioaccumulation of trace elements in the seedlings of *Brassica napus* L.

In the present study, the use of ash from *Carpinus betulus* and soil fertilization with KO and HA, aimed to boost the effect of the ash, did not cause significant changes in the combustion heat, calorific value, or energy yield of maize biomass. The obtained results are comparable to the findings from our previous research [34] and those reported by other authors [66–68] regarding the influence of ash from *Salix viminalis* on the analyzed parameters. In a study by Xiong et al. [66], the average calorific value of the aerial maize parts was 18.46 MJ kg⁻¹; in the study by Lizotte et al. [67], it was 17.36 MJ kg⁻¹; and in that by Wojcieszak et al. [68], it was 18.2 MJ kg⁻¹.

In our experiment, soil enrichment with *Carpinus betulus* ash, KO, and HA triggered differences in the elemental composition and ash content of the maize. The carbon content of the maize biomass ranged from 47.54% from the soil with ash from *Carpinus betulus*

(control) to 49.51% in the soil without wood ash but with fertilization with HA. The sulfur content ranged from 0.05% (biomass from the soil without wood ash and fertilized with compost) to 0.11% (biomass from the soil with wood ash and fertilized with HA). The highest nitrogen content was found in the biomass harvested from the soil amended with wood ash and fertilized with HA, and the lowest ones in the biomass harvested from the soil not amended with *Carpinus betulus* ash but fertilized with HumiAgra. The oxygen content was the highest in the maize biomass harvested from the control soil without the addition of KO or HA (40.93%) and the lowest in the biomass from the soil amended with wood ash and fertilized with HA (35.59%). Wood ash, KO, and HA fertilization had no effect on the hydrogen content of the maize biomass. The highest ash content (8.64% soil d.m.) was found in the maize grown on the control soil amended with ash from *Carpinus betulus*. Maize cultivated in areas enriched with wood ash and fertilized with KO and HA could contribute to the biological reclamation of soils; since its biomass cannot be used for food purposes, its use for energy purposes is justified.

4.2. Response of Soil Enzymes and Certain Chemical and Physicochemical Properties of the Soil to Soil Amendment with Ash from *Carpinus betulus*

Soil biological activity, determined by its enzymatic activity, is a measure of soil fertility and productivity [26,28]. In the present study, adding *Carpinus betulus* ash to the soil suppressed the activities of all soil enzymes analyzed (Deh, Cat, Ure, Pac, Pal, Glu, and Aryl). This is consistent with findings from our previous study regarding ash from *Salix viminalis*, which also diminished soil biochemical activity when applied at a dose of 20 g kg⁻¹ soil d.m [34]. The finding that wood ash suppressed activities of the analyzed enzymes can stem from at least two reasons: Firstly, the wood ash could have adsorbed the substrate used by enzymes and inhibited the course of the enzymatic reaction. Secondly, the high pH of the wood ash could also have triggered changes in microbial biodiversity, resulting in suppressed enzyme secretion [69,70]. Soil fertilization with KO and HA alleviated the adverse effects of *Carpinus betulus* ash on soil enzymatic activity.

The results obtained in this study confirm the extensively described potential of wood ash for soil applications [22,71–74]. First of all, the positive effects of soil treatment with ash on EBC, HAC, CEC, and BS were noted in the studies by An and Park [74] as well as Meller and Bilenda [75]. Rolka et al. [76,77] used ash from the combustion of mixed wood chips, mainly Scots pine (*Pinus sylvestris* L.), and, similar to our own research, a positive effect of wood ash on the soil properties was observed. Meller and Bilenda [75] showed that soil fertilization with ash increased the soil's EBC and BS and decreased HAC. Likewise, a three-year study by Park et al. [63] using wood ash showed a relative increase in soil alkaline cation concentration of between 30 and 90 percent compared to that of the control site. The more significant increase in the BS reported by Park et al. [78] may have been due to the duration of the experiment, its nature, and the crop species analyzed. The positive effect of ash from *Carpinus betulus* on sorption properties observed in this study and in prior studies [75,78] indicates an increase in the cation exchange capacity, which has not always been confirmed in the literature. An example of this is the study by An and Park [74], which showed that the application of wood ash did not increase the CEC value. In addition to improving the structure of the sorption complex, including the reduction in the HAC, the addition of *Carpinus betulus* ash to the soil increased its pH, as in the studies of other authors [22,71–73]. Depending on the type of wood burnt, the pH of wood ash reported in the literature [79] ranges from 9.60 to 13.70. A high ash pH is often associated with a high calcium content [74]. The wood ash used in this study had a pH_{KCl} = 12.60, which could be attributed to a high content of not only calcium but also potassium. An increase in soil pH was also found in the studies by Szostek et al. [72] and Füzesi et al. [22]. In contrast, in the study by Stankowski et al. [80], the soil pH did not increase despite the fact that this material was more alkaline than that in our study. This effect may have been due to the granulometric composition of the soil and its buffering properties. The ash of *Carpinus betulus*, which is characterized by an alkaline reaction, could protect plants from the effects

of absorbing heavy metals from the soil. This is because most of them are immobilized in an alkaline environment. Light soils react much more to ash than heavy soils, which have a higher buffer capacity. The long-term use of wood ash can lead to salinization and heavy metal contamination of the soil and water [81–84]. According to Paramisparam et al. [84], between 5 and 30% of the heavy metals contained in ash are leached into the soil. Therefore, ash should be used carefully, as about 20% of the world's arable land is saline and degraded [81,83]. The use of ash is justified for energy crops on marginal land.

Compost and HumiAgra supported the positive effect of *Carpinus betulus* ash on the physicochemical properties of the soil, as they increased the content of its organic matter. They both represent an important link in the global carbon cycle [85,86]. The effect of *Carpinus betulus* ash on maize and soil properties has also been reported elsewhere [57–59,71–73,87,88].

5. Conclusions

Ash from *Carpinus betulus* did not affect the heat of combustion or the calorific value of maize biomass. It increased the contents of C, H, S, N, O, and ash in the aerial parts of the maize. In addition, it positively affected the contents of organic carbon, total nitrogen, soil pH, sum of exchangeable base cations, total exchangeable capacity of soil, and degree of soil saturation with alkaline cations. In contrast, it adversely affected the biomass of the aerial parts and roots of the maize and the biochemical activity of the soil. Soil amendment with compost and HumiAgra had a positive effect on the heat of combustion; calorific value; the contents of carbon, hydrogen, nitrogen, sulfur, oxygen, and ash in the aerial parts of the maize; and on the chemical and physicochemical properties of the soil. In addition, both fertilizers mitigated the adverse effects of the wood ash on the maize biomass and the enzymatic properties of the soil. The present study's results indicate the need for further research under field conditions aimed at establishing wood ash doses that would provide adequate nutrients to plants, improve the biochemical properties of the soil, and would not be toxic to either soil or plants.

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