

Article

Evaluation of the Properties and Usefulness of Ashes from the Corn Grain Drying Process Biomass

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Received: 25 January 2020; Accepted: 5 March 2020; Published: 10 March 2020



Abstract: The paper presents the results of a study on chemical composition of ashes from three types of waste biomass in terms of fertilizer usefulness. Waste from the process of corn grain drying, including corn cobs, corn grains and corn husk and their mixtures in the ratio 4:1 (*v/v*) were examined. The study proved that corn grain was the material with the highest concentration of macroelements among those studied (P—21,452 ppm, K—25,970 ppm, S—5911 ppm) and the mixture of corn cobs with corn grains (Ca—81,521 ppm). When microelements were considered, the highest concentration was recorded for corn cobs (Cu—207 ppm, Mn—844 ppm, Zn—857 ppm) and corn husk (Fe—15,100 ppm). The analysis of toxic elements in the ashes of the biomass studied showed their highest concentration in corn husk ash (Ni—494 ppm, Cr—301 ppm, Pb—42.7 ppm, As—4.62 ppm). The analysis showed that regardless of the type of biomass studied, all ashes were strongly enriched (in relation to the average soil content) with phosphorus and corn husk ash with calcium in particular. A slight enrichment in copper and lead was recorded for all ashes, and moderate or low for the other elements. It was found that the examined ashes from biomass, which is a residue from the drying of maize grain, have a high fertilizer usefulness.

Keywords: ash composition; biomass; corn; environmental and mechanical engineering

1. Introduction

The need to reduce the environmental impact of traditional fossil fuels, as well as the depletion of these resources and the sharp rise in fossil fuel prices, is the reason for the growing use of renewable energy sources, including biomass. Biomass can be used in conversion processes in various ways to produce gaseous and liquid fuels, and as a solid fuel [1]. One of the simplest ways is direct combustion. However, the large-scale use of biomass for energy generation faces some challenges in terms of biomass availability, processing and compaction [2,3], technical problems, as well as the management of ashes after combustion. The combustion of biomass fuels for electricity generation is accompanied by the formation of a significant amount of solid waste (ash and slag). It is important to know the composition of trace elements in ash from biomass combustion and their respective harmful or beneficial properties in order to determine the potential possibilities of their management (e.g., as fertilizer for agricultural and forestry purposes) [4,5]. In all cases of waste reuse, its possible disposal should be determined in order to avoid adverse effects on the environment [6]. The content of trace elements in ash depends on the type of fuel. The directions which are considered primarily when selecting the technology of

ashes management are the possibility of fertilizer use. Moreover, they can be used in the production of building materials [7], road construction [8], and mining [9]. However, the choice of the direction of use must be preceded by an examination of basic properties of ashes in order to specify the direction of analysis of the selected solutions.

Biomass ash contains large quantities of nutrients such as Ca, K, and P, which can partially replace mineral fertilizers and improve the properties of agriculturally used soils [10]. However, ash also contains trace elements in quantities sometimes high enough to cause concern. The content of toxic elements may be so high that waste products from biomass combustion will require special attention during their disposal and management [6].

The food life cycle is a complex, multi-stage process in which waste is produced at each stage. The generation of food waste includes all stages during production, processing, retail sale and distribution, and consumption of food, including all processes related to the disposal and treatment of waste [11]. The current trend in the management of agri-food products is a closed-loop economy, which focuses on the use of the resulting byproducts and waste [11,12]. Increasingly often, agri-food waste is used in energy systems and chemical syntheses [13,14], which increases energy efficiency and is a way to solve problems related to the management of waste biomass in accordance with the sustainable development principles. Organic waste can be transformed into energy by means of various thermochemical processes, the selection of which depends on the type and quantity of available waste biomass, the expected form of energy, as well as environmental protection regulations and economic conditions [15,16].

Corn is one of the most important feed and industrial crops in the world. Unlike other raw material crops, it has enormous yield potential and is characterised by a wide range of uses [17,18]. The growth of corn production in recent years has been mainly stimulated by an increase in demand from the industrial processing sector related to biofuel production [19].

Corn grains are considered as biological material sensitive to temperature and long storage in high humidity conditions [20]. After harvesting, the grain has a moisture content of 30%–40%, which must be reduced to 14% [21,22]. Due to the high initial moisture content, only thermal drying is recommended as this is the only way to achieve the required final moisture content. Drying costs can represent 40%–60% of the total cost of corn cultivation [22]. Corn shows a large variety of grain shapes, and additionally, when harvesting grain with a combine harvester, it contains a large percentage of damaged grains and impurities. Fungal spores find favorable conditions for development in contaminants such as soil, dust, and plant residues. Cleaning and drying the grain after harvesting is therefore an important stage in grain production [23]. It consists of bringing the grain to the desired moisture and purity. The cleaning and drying process therefore generates waste in the form of residues (i.e., corn cobs, parts of the grain (damaged grain), and husks).

The aim of this study is to evaluate the chemical composition of ashes from the combustion of waste biomass from corn grain drying and analysis of the concept of its use for fertilizing purposes, as well as to estimate the potential risk associated with its introduction into the environment. The paper presents the results of the study on ashes from waste biomass combustion, and an analysis of the basic properties of ashes resulting from its chemical composition (i.e., the content of macro-, microelements, and toxic elements).

Knowledge of the elemental composition of ash produced during biomass combustion is required for future studies on the possibility of using ashes from biofuel blends containing other agricultural waste so that biomass fuels can be a complete source of renewable energy with respect to a full life cycle assessment.

2. Materials and Methods

2.1. Material

The waste biomass used in the study originated from a corn grain drying plant located in the Lublin Province (51°08' N, 22°50' E) and came from the 2018 harvest. Detailed characteristics of the material are presented in the paper [24]. The material was initially cleaned from mineral impurities (dust and soil) using a laboratory sieve shaker Retsch AS200 (Retsch GmbH, Haan, Germany) with a sieve made of metal with 1 mm square mesh according to EN ISO 3310-1 [25]. Three basic wastes were used in the study:

1. Corn cobs (CC)—residues of corn cobs without grains;
2. Corn grains (CG)—residues of grains from corn grain drying and cleaning process;
3. Corn husk (CH)—waste in the form of corn husks.

The study also included the mixtures of these materials at 4:1 (*v/v*) ratios, where the starting material was as follows:

- Corn cobs:
 4. Corn cobs and corn husk (CC-CH);
 5. Corn cobs and corn grains (CC-CG);
- Corn grains:
 6. Corn grains and corn cobs (CG-CC)
 7. Corn grains and corn husk (CG-CH);
- Corn husk:
 8. Corn husk and corn grains (CH-CG);
 9. Corn husk and corn cobs (CH-CC).

2.2. Proximate and Ultimate Analysis

The methodology of determination of the contents of volatile compounds (V), ash (A), and fixed carbon (FC) as well as the contents of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) are presented in the paper [24]. The results were converted for VM, A, and FC into dry form, while C, H, N, and S were converted into ash-free dry form.

2.3. Preparation and Analysis of Ashes

The research material was ground in an analytical mill (IKA A11, IKA-Werke GmbH & Co.KG, Staufen, Germany) to fractions of 0.5 to 1.0 mm grain size. The mixtures were prepared using a universal mixer, mixing the appropriate proportions of starting materials for 2 min. Samples for further tests were prepared in accordance with EN ISO 14780 [26].

The LECO TGA 701 thermogravimeter (LECO Corporation, Saint Joseph, MI, USA) was used to incinerate biomass samples. Approximately 2 g of the biomass studied were weighed into the ceramic crucible and heated from ambient temperature to incineration temperature (550 °C) at a heating rate of 10 °C·min⁻¹ in the air stream. The samples were kept at incineration temperature for 4 h and then cooled to about 100 °C. Then the samples were cooled to ambient temperature in a desiccator.

The elemental content in ash was determined with NEX QC+ QuantEZ (RIGAKU Americas Holding Company, Inc., Austin, TX, USA) elemental analyzer. The apparatus uses the EDXRF (Energy Dispersive X-ray Fluorescence) method. According to the procedure, the ash without prior preparation was dosed into the instrument's measuring cups and analyzed. The content of the following elements

(in order of atomic numbers) P, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, and Pb was determined. Ash components were divided into three categories: macroelements: P, K, Ca, S; microelements: Mn, Fe, Cu, Zn; and toxic elements: Cr, Ni, As, Pb, and their content in ash of particular types of biomass was considered in such categories.

The quality of analytical results regarding their accuracy was verified using standard certified materials. In order to obtain accurate and stable experimental data, each experiment was repeated at least three times.

2.4. Statistical Analysis

The test results were statistically analyzed using Statistica 13 software (Dell Inc. (2016), Dell Statistica (data analysis software system) version 13. Tulsa, OK, USA). A one-factor analysis of variance (ANOVA) was used to assess the effect of the type of material on the amount of obtained elementary components in the ashes of the biomass studied. The Levene test was used to assess the homogeneity of variance. Tukey's honestly significant difference (HSD) test determined significant differences between the analyzed features for the tested materials (small letters in lines indicate significant differences among features in the groups). The tests were performed at the significance level $\alpha = 0.05$.

3. Results

3.1. Characteristics of the Materials Used

The results of proximate and ultimate analysis and energy properties of the studied materials are discussed in detail in the paper [24]. Figure 1 presents basic characteristics of the analyzed biomass materials.

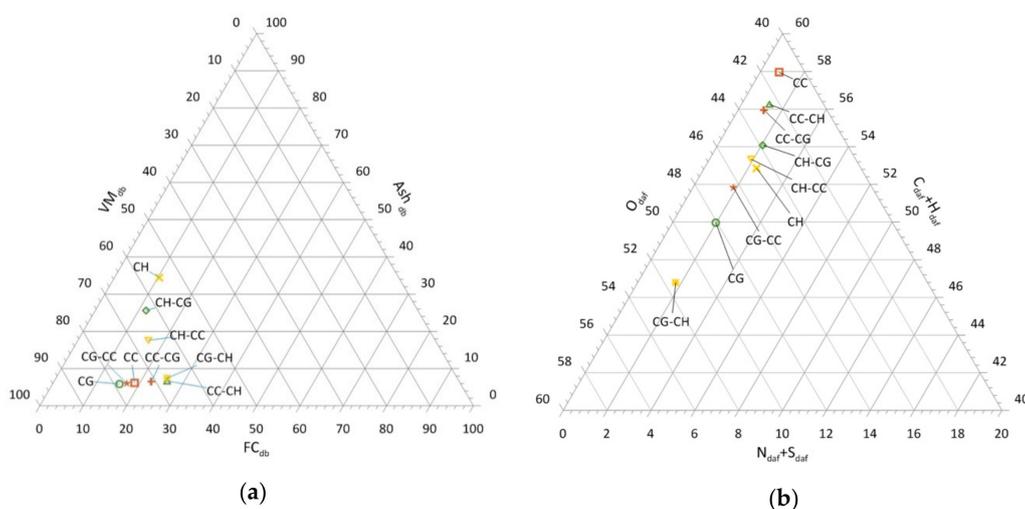


Figure 1. Physicochemical properties of the tested biomass based on (a) proximate and (b) ultimate analysis.

The A_{db} ash content of corn grains (CG) and corn cobs (CC) and mixtures of these materials was in the range 5.88%–7.44%. These values did not differ significantly from those of typical biomass. Only corn husk (CH) contained quite a significant amount of ash (i.e., 34.73%). The volatile matter content ranged from 55.22% in CH to 78.73% in CC. The average content of volatiles in various types of biomass types is 75.4% [27]. Whereas the fixed carbon content of FC_{db} was in the range of 10.41% in CH to 26.03% in CC-CH.

The content of carbon, hydrogen, nitrogen, sulfur, and oxygen in the tested materials did not differ from the content of these elements in other types of biomass. The carbon content C_{daf} ranged from 41.88% in CH to 51.67% in CC. The obtained level of hydrogen H_{daf} content ranged from 4.93% in CH to 6.79% in CG. The nitrogen N_{daf} content ranged from 0.31% in CC to 1.66% in CG-CC. The sulfur

S_{daf} content in the tested biomass was similar. It ranged from 0.52% in the CG-CC mixture to 0.73% in CH-CC.

3.2. Results of Ashes' Chemical Composition Examination

The assessment of the chemical composition of ash from biofuels (biomass) demonstrates the degree of impact of solid residues from the combustion process on the environment. Moreover, the assessment of ash in terms of macro- and microelements content makes it possible to demonstrate its degree of usefulness (e.g., for fertilizer (agricultural) purposes) [28,29]. On the basis of the analysis of the chemical composition of ash, Table 1 presents the results of macroelements content in ashes from the analyzed biomass.

Table 1. Macroelements content in ash from the examined biomass (ppm).

Component	CC	CG	CH	CC-CG	CC-CH	CG-CC	CG-CH	CH-CC	CH-CG	p-Value
P ± S _x	31,391 ^d ± 264	21,452 ^b ± 165	47,778 ^h ± 346	28,099 ^a ± 57	32,935 ^e ± 150	22,688 ^c ± 94	26,933 ^a ± 184	41,719 ^g ± 301	39,324 ^f ± 63	<0.001
K ± S _x	258,259 ⁱ ± 1036	25,970 ^a ± 357	56,958 ^d ± 219	235,629 ^h ± 519	226,174 ^g ± 90	70,538 ^e ± 148	30,913 ^b ± 144	100,864 ^f ± 300	46,953 ^c ± 63	<0.001
Ca ± S _x	74,537 ^a ± 439	74,201 ^a ± 288	101,954 ^f ± 225	73,280 ^c ± 116	81,521 ^d ± 103	74,268 ^a ± 184	82,742 ^e ± 202	91,647 ^b ± 259	91,583 ^b ± 98	<0.001
S ± S _x	5911 ^{c,d} ± 31	3438 ^e ± 20	6425 ^f ± 37	4942 ^b ± 69	5863 ^c ± 51	3726 ^a ± 57	3852 ^a ± 34	6085 ^d ± 86	4988 ^b ± 53	<0.001

CC: corn cobs; CG: corn grains; CH: corn husk; S_x: standard deviation; mean values with the same letter in a row are not significantly different for $p < 0.05$ by Tukey's honestly significant difference (HSD) test.

The analysis of macroelements content in the group of basic materials CC, CG, CH indicates their great diversity. The lowest content of particular elements was found in CG corn grain ashes. The content of phosphorus in the ashes of the biomass studied was in the range 21,452–47,778 ppm. The highest phosphorus content was recorded in the ash of CH and it was twice as high as in the ash of CG. Potassium content in ashes of basic materials was in a wide range of 25,970–258,259 ppm. It was found that CC ash was characterized by almost ten times higher potassium content than the lowest content obtained in CG ash. Calcium content ranged between 74,201–101,954 ppm and was the highest in CH ash, which was one and a half times higher than the lowest value obtained in CG ash. In addition, sulfur content almost twice as high was found in CH ash, compared to the lowest value (CG), where the results obtained were in the range 3438–6425 ppm.

The analysis of the macroelements content in the ashes of the created mixtures showed the dependence of their content on the content in ashes from the starting materials. Figure 2 shows changes in the content of macroelements in all investigated ashes.

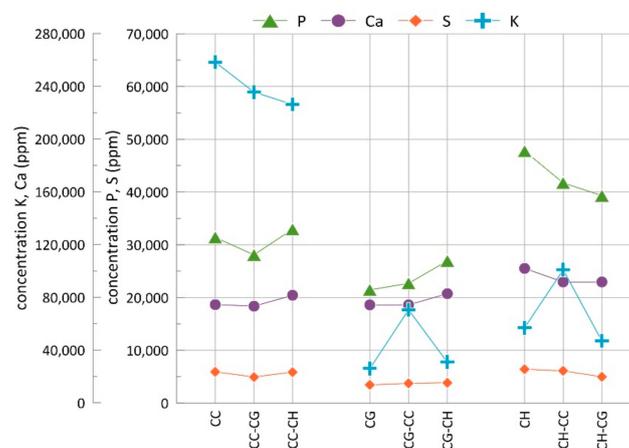


Figure 2. Distribution of macroelements in the ashes of the examined raw materials.

Phosphorus content in ash mixtures ranged from 22,688 to 41,719 ppm. For ash of CC-CH, CG-CH, and CG-CC mixtures, an increase in phosphorus content in relation to starting materials was recorded. In other cases, a decrease in the content of this element was shown. The content in the range 30,913–235,629 ppm was shown for potassium. An increase in potassium content in relation to ash from the starting materials was found in the ashes of CG-CC, CG-CH, and CH-CC mixtures. Calcium in mixtures from residues from corn grain drying was at a high level (i.e., in the range of 73,280–91,647 ppm). In this case, an increase in the ash content of this element can be observed for CC-CH, CG-CC, and CG-CH mixtures. The study carried out on the sulfur content in ash of the mixtures showed a large variation in the content of this element (i.e., 3726–6085 ppm). Only for the ashes of CG-CC and CG-CH mixtures, was an increase in the sulfur content in relation to the ashes from the starting materials recorded.

Analyzing the results presented in Figure 2 for materials based mainly on CC, an increase in P, Ca, and S content for CC-CH mixture was observed compared to CC. In the case of potassium, a decrease in its concentration was noted compared to the initial material for both mixtures created. Comparing the obtained test results for mixtures based on CG, an increase of P, Ca and S content in relation to the CG starting material was noted. On the other hand, an almost three-fold increase in potassium concentration was noted in the ash of CG-CC mixture in relation to the ash from CG. For materials based on CH, a decrease in the concentration of P, Ca, and S was observed for all the mixtures in relation to CH. However, when potassium content was considered, it almost doubled in the mixture formed from CH-CC.

Table 2 shows the material series in descending order of the ash content of the individual macroelements.

Table 2. Series of materials according to decreasing concentration of individual macroelements in ashes.

Component	Material
P	CH > CH-CC > CH-CG > CC-CH > CC > CC-CG > CG-CH > CG-CC > CG
K	CC > CC-CG > CC-CH > CH-CC > CG-CC > CH > CH-CG > CG-CH > CG
Ca	CH > CH-CC > CH-CG > CG-CH > CC-CH > CC > CG-CC > CG > CC-CG
S	CH > CH-CC > CC > CC-CH > CH-CG > CC-CG > CG-CH > CG-CC > CG

As the results of the phosphorus content indicate, the lowest content was obtained in the ash of CG, while the highest concentration was in the ash of CH. The highest concentration of potassium among the materials studied was also found in the ash of CG and the highest in the ash of CC. In the case of calcium, the lowest content was recorded in the ash of CC-CG mixture, while the highest concentration was recorded in the ash of CH. The lowest sulfur content was found in the ash of CG and the highest in the ash of CH.

In relation to the mean potassium content in plant ashes (the world average for all parts of all plants), which is 387,755 ppm [27], the examined ashes were characterized by a moderate and high content of this element. Vassilev et al. [30] considered the aspects of chemical composition of different types of biomass constituting a potential source of energy (beech wood chips, corn cobs, marine macroalgae, plum pits, rice husks, switchgrass, sunflower shells, and walnut shells), found a similar K content in corn cobs ash, which was 277,900 ppm. High K content in corn cobs ash caused the material, together with the ash from marine macroalgae and sunflower shells, to be classified as one of the most problematic biomass resources from the technological and environmental point of view (biomass with similar chemical properties of ash, low acid-“K type”), for which the average K content was 211,600 ppm. However, the average content of this element in all ashes studied by these authors was 151,100 ppm.

Phosphorus was the second dominant element in the examined ashes. The content of this element in corn cobs ash, presented in the literature [30], was 14,880 ppm, with an average content of 13,183 ppm in ash from this type of biomass and an average content of 10,439 ppm in ash from different types

of biomass. The literature data [27] show that the mean K content in plant ashes is much higher and amounts to 40,816 ppm.

Calcium content in corn cobs ash given in another study [30] was lower than that found in this study and amounted to 10,700 ppm, while the mean Ca content in ash from this type of biomass and the mean Ca content in ash from various types of biomass were similar and amounted to 76,200 ppm and 110,800 ppm, respectively. The mean Ca content in plant ashes was 204,082 ppm [27].

Vassilev et al. [30] found a similar sulfur content in corn cobs ash, which amounted to 9700 ppm. The S content in ashes from this type of biomass was much higher and amounted to 47,200 ppm, while the average content in ashes from various types of biomass was also higher at 21,700 ppm. The average S content in plant ashes was also higher and amounted to 61,224 ppm [27].

Table 3 presents the results of the study on the content of microelements in the ashes of the analyzed biomass.

Table 3. Microelements content in ashes from the examined biomass.

Component	CC	CG	CH	CC-CG	CC-CH	CG-CC	CG-CH	CH-CC	CH-CG	p-Value
Cu ± S _x	207 ^{c,d} ± 1	131 ^a ± 2	183 ^d ± 1	158 ^{a,b} ± 11	190 ^{c,d} ± 10	158 ^{a,b} ± 12	145 ^a ± 17	195 ^c ± 12	163 ^b ± 14	<0.001
Fe ± S _x	8387 ^b ± 58	7814 ^a ± 18	15,100 ^g ± 86	7859 ^a ± 51	9730 ^c ± 115	8028 ^a ± 79	9967 ^d ± 56	13,014 ^f ± 41	12,609 ^e ± 65	<0.001
Mn ± S _x	844 ^e ± 16	434 ^a ± 5	710 ^c ± 10	705 ^c ± 46	827 ^e ± 42	497 ^a ± 8	483 ^a ± 32	737 ^{c,d} ± 3	589 ^b ± 18	<0.001
Zn ± S _x	857 ^h ± 6	165 ^a ± 2	430 ^d ± 4	611 ^f ± 36	699 ^g ± 30	292 ^b ± 6	187 ^a ± 13	535 ^e ± 10	358 ^c ± 15	<0.001

S_x: standard deviation; mean values with the same letter in a row are not significantly different for *p* < 0.05 by Tukey's HSD test.

In the case of microelements, also the lowest content was recorded in CG ash. The highest copper content was characteristic for ash obtained from CC and it was one and a half times higher than that obtained in CG ash. Ash with the highest iron content was recorded for CH with a value twice as high as the lowest one. CC ash was the richest in manganese, with the content two times higher in relation to CG. On the other hand, the highest zinc content was also found in CC ash with a value five times higher than the lowest in the group of starting raw materials.

The analysis of the content of microelements in the ashes of the created mixtures also showed the relationship of their content on the concentration in the ashes from the starting materials. Figure 3 shows the changes of microelements content for all analyzed materials.

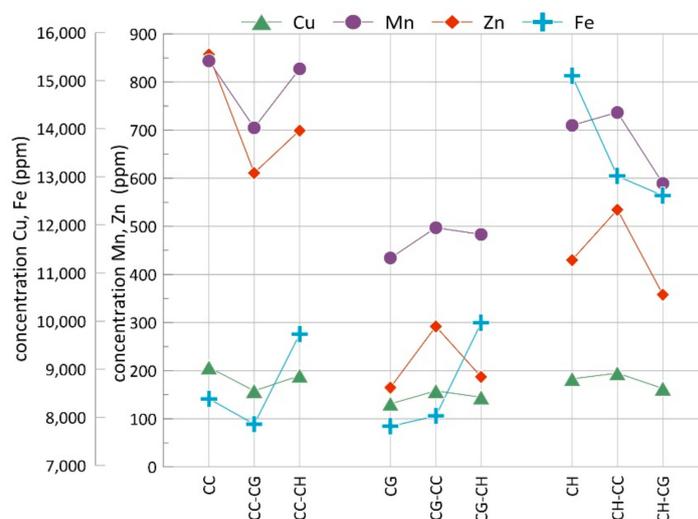


Figure 3. Distribution of microelements in the ashes of the examined raw materials.

Copper content of the ash mixtures ranged from 145 to 195 ppm. An increase in copper content in relation to the ashes of the starting materials was recorded for the mixtures of CC-CH, CG-CH, and CH-CC. In the other cases, a decrease in the content of this element was shown. For iron, the content in the range 7859–13,014 ppm was shown. An increase in iron content in relation to the starting materials was shown in the ash of CC-CH, CG-CC, and CG-CH mixtures. Manganese in the ash of mixtures from the residues of drying corn grain was in the range 483–827 ppm. In this case, an increase in the content of this element in ash can be observed in the formation of CG-CC and CG-CH mixtures. The study carried out on the content of zinc in the ashes of mixtures showed large differences in the concentration of this element in ash (i.e., 187–699 ppm). For the ashes from CG-CC, CG-CH, and CH-CC mixtures, an increase in zinc content was recorded in relation to the ashes of the starting materials.

Analyzing the results of the study presented in Figure 3 showing the content of microelements in ashes in materials based mainly on CC, a decrease in the content of Cu, Mn, and Zn in the ashes of both created mixtures (i.e., CC-CG and CC-CH in relation to CC), while an increase in the concentration of only Fe in the ash of CC-CG mixture can be observed. Comparing the results obtained for the ashes of CG-based mixtures, an increase in Cu, Mn, Zn, and Fe content in the ashes of both CG-CC and CG-CH mixtures was observed in relation to the ashes of the CG starting material. For ashes of CH-based materials, a decrease in Cu and Fe concentrations was noted for ashes of both formed mixtures, CH-CC and CH-CG; Mn and Zn for CH-CG ash as compared to CH ash. However, a higher content of Mn, Zn, and Cu in relation to CH ash was noted for ash of CH-CC mixture.

The analysis of the results allowed the ranking of mixtures in descending order depending on the concentration of particular microelements in ashes (Table 4). For all analyzed microelements, the lowest concentration was found in CG ash. For copper content, the highest concentration was recorded in CC ash and for iron in CH ash. The highest content of manganese and zinc among the materials studied was found in the ash of CC.

Table 4. Series of materials according to decreasing concentration of individual microelements in ashes.

Component	Material
Cu	CC > CH-CC > CC-CH > CH > CH-CG > CC-CG > CG-CC > CG-CH > CG
Fe	CH > CH-CC > CH-CG > CG-CH > CC-CH > CC > CG-CC > CC-CG > CG
Mn	CC > CC-CH > CH-CC > CH > CC-CG > CH-CG > CG-CC > CG-CH > CG
Zn	CC > CC-CH > CC-CG > CH-CC > CH > CH-CG > CG-CC > CG-CH > CG

Similar content of iron in CC ashes to that noted in the study can be found in the literature, and was 7400 ppm [30]; the average content of this element in ashes from this type of biomass was 6100 ppm, and the average content in ashes from various types of biomass was 4000 ppm. On the other hand, the mean Fe content in plant ashes was lower and amounted to 3061 ppm [27].

Manganese content in CC ash was slightly higher than that reported in the literature [30], which was 404 ppm, but at the same time a similar content of this element was found in CG ash. The mean Mn content in ash from this type of biomass was lower and amounted to 312 ppm, while the mean content in ash from different types of biomass was 1862 ppm. The mean Mn content of plant ashes reported in the literature was much higher and amounted to 4082 ppm. [27].

The content of copper in CC ash given in another study [30] was similar to the results obtained in this study and amounted to 139 ppm; this element was found at a similar level of 169 ppm in ashes from biomass of this type. A similar average Cu content was also given for ashes from various types of biomass (232 ppm) and for plant ashes (204 ppm) [27].

Zinc content found in the examined ashes did not differ from that given in the literature. Thus, the Zn content in corn cobs was slightly higher and amounted to 1,232 ppm, but the average content of this element in ashes from this type of biomass was much lower and amounted to 541 ppm. The mean Zn content in various types of biomass was found at 366 ppm [30]. In turn, mean Zn content in plant ashes was 1020 ppm [27].

Table 5 shows the results of the concentration of toxic elements in ashes of the biomass tested.

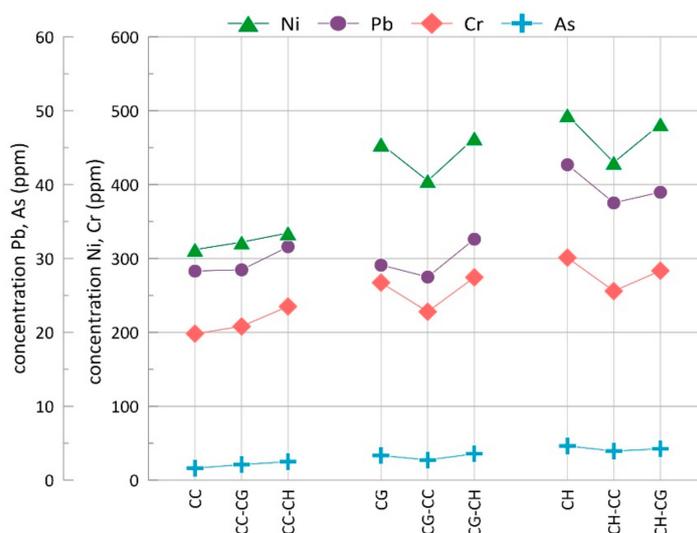
Table 5. Toxic elements content in ashes from the examined biomass (ppm).

Component	CC	CG	CH	CC-CH	CC-CG	CG-CC	CG-CH	CH-CG	CH-CC	p-Value
Ni ± S _x	312 ^a ± 3	455 ^{c,d} ± 2	494 ^e ± 1	322 ^a ± 22	334 ^a ± 10	405 ^b ± 18	463 ^d ± 43	430 ^c ± 13	482 ^e ± 12	<0.001
Cr ± S _x	198 ^a ± 1	267 ^{c,d} ± 9	301 ^e ± 4	208 ^a ± 6	235 ^b ± 13	228 ^b ± 14	274 ^d ± 13	256 ^c ± 20	283 ^d ± 10	<0.001
Pb ± S _x	28.3 ^{a,b} ± 2.02	29.1 ^{a,b} ± 1.15	42.7 ^b ± 2.94	28.46 ^{a,b} ± 9.24	31.57 ^{a,b} ± 8.09	27.49 ^a ± 4.04	32.60 ^{a,b} ± 6.35	37.53 ^{a,b} ± 6.40	38.97 ^{a,b} ± 4.04	<0.01
As ± S _x	1.6 ^a ± 0.58	3.31 ^a ± 1.22	4.62 ^a ± 1.10	2.09 ^a ± 0.28	2.48 ^a ± 0.43	2.72 ^a ± 0.57	3.54 ^a ± 0.74	3.92 ^a ± 0.35	4.22 ^a ± 0.85	<0.03

S_x: standard deviation; mean values with the same letter in a row are not significantly different for $p < 0.05$ by Tukey's HSD test.

CH ash was the richest in nickel, which was one and a half times higher than the lowest obtained in CC ash. The lowest chromium content was recorded in CC ash, while the highest (one and a half times higher) was in CH ash. The ash of CC was also characterized by the lowest content of lead, while the highest content was found in CH ash. The lowest chromium content was found in the ash of CG, while the highest concentration was in the ash of CC (twice as high). In addition, the lowest arsenic content was found in the ash of CC and the highest concentration was in CH ash.

Figure 4 shows the distribution of toxic elements for all analyzed materials.

**Figure 4.** Distribution of toxic elements in the ashes of the examined raw materials.

Analysis of the content of toxic elements in the ashes of the created mixtures again showed the relationship of their content to the content in ashes from the starting materials. Nickel content in the mixtures ranged from 322 to 482 ppm. An increase in nickel content in relation to the starting materials was recorded for the ash of CC-CH, CG-CH, and CG-CH mixtures. In other cases, a decrease in the content of this element was shown. For chromium, content in the range 208–283 ppm was shown. An increase in nickel content in relation to the starting materials was shown for CC-CH, CC-CG, and CG-CH. Lead in ashes of mixtures from residues of corn grain drying was in the range 27.49–38.97 ppm. In this case, an increase in this element in ash can be observed when composing CC-CH, CC-CG, and CG-CH mixtures. The study carried out on the arsenic content in ashes of the mixtures showed a variation in the concentration of this element (i.e., 2.09–4.22 ppm). For ash of CC-CH, CC-CG, CG-CH, and CG-CC mixtures, an increase in arsenic content in relation to ashes of the starting materials was noted.

Analyzing the results of the study presented in Figure 4 showing the concentration of toxic elements in ashes of materials based mainly on CC, an increase in the content of all toxic elements for

both created mixtures (i.e., CC-CG and CC-CH), compared to CC ash can be observed. Comparing the results obtained for the ashes of CG-based mixtures, an increase in the content of Ni, Pb, Cr, and As in the ash of CG-CH mixture was noted in relation to the ash of the CG starting material. On the other hand, a decrease in the concentration of Ni, Pb, Cr, and As in relation to the ash of CG was shown for the CG-CC mixture. For materials based on CH, only an increase in As concentration in the ash of CH-CG mixture in relation to CH ash and a decrease in the content of other toxic elements in ash of both created mixtures can be observed.

Table 6 shows the series of materials in decreasing order of individual toxic elements content in the ashes. The material with the highest concentration of toxic elements is CH ash. The lowest concentration of nickel, chromium, and arsenic was found in the ash of CC, whereas in the case of lead in the ash of CC-CG mixture.

Table 6. Series of materials according to decreasing concentration of individual toxic elements in ashes.

Component	Material
Ni	CH> CH-CG > CG-CH > CG > CH-CC > CG-CC > CC-CH > CC-CG > CC
Cr	CH> CH-CG > CG-CH > CG > CH-CC > CC-CH > CG-CC > CC-CG > CC
Pb	CH> CH-CG > CH-CC > CG-CH > CC-CH > CG > CC-CG > CC > CG-CC
As	CH> CH-CG > CH-CC > CG-CH > CG > CG-CC > CC-CH > CC-CG > CC

The content of nickel in CC ash found in the study was similar to that reported in the literature, which was 286 ppm, while the other examined ashes were characterized by a higher content of this element. The mean Zn content in ashes from this type of biomass was found at the level of 301 ppm and the content in ashes from various types of biomass was 151 ppm [30]. The mean Ni content in plant ashes was much lower and amounted to 31 ppm [27].

Chromium content found in the examined ashes was significantly lower than that reported in the literature [30]. Thus, the content of Cr in the ash from CC was 750 ppm, the average content of this element in ashes from this type of biomass was 733 ppm, and the average content in ashes from various types of biomass was 384 ppm. In turn, the mean Cr content in plant ashes was much lower and amounted to 31 ppm [27].

Vassilev et al. [30] found lead content in CC ashes at a much higher level of 68.3 ppm. In general, the content of this element in ash from biomass was observed within wide limits. The average content of this element in ashes from biomass of this type was 24.2 ppm, while the average content in ashes from various types of biomass was 0.44 ppm. The average content of Pb in plant ashes was 20 ppm [27].

The arsenic content in CC ash found in the study was similar to that reported in the literature for the same biomass, which was 6.4 ppm. The average content of this element in ash from this type of biomass was 5.7 ppm and 6.3 ppm in ashes from different types of biomass [30]. At the same time, the average As content in plant ashes was found at the level of 2 ppm [27].

4. Discussion

In addition to the main elements building the organic compounds such as O, C, H, and N, also P, K, Ca, and S are involved in living organic matter formation. They are very mobile and soluble in various water solutions.

Figure 5 shows the average concentrations of elements in the ashes of the materials tested standardized to the average soil composition. Since they are standardized to the average content of elements in the soil, the element contents, which were close to the average content in the soil in ash, are located in the diagram near 1.0. The elements whose content in ash was lower than the average content in the soil are located below 1.0 and the elements whose content was higher are above 1.0.

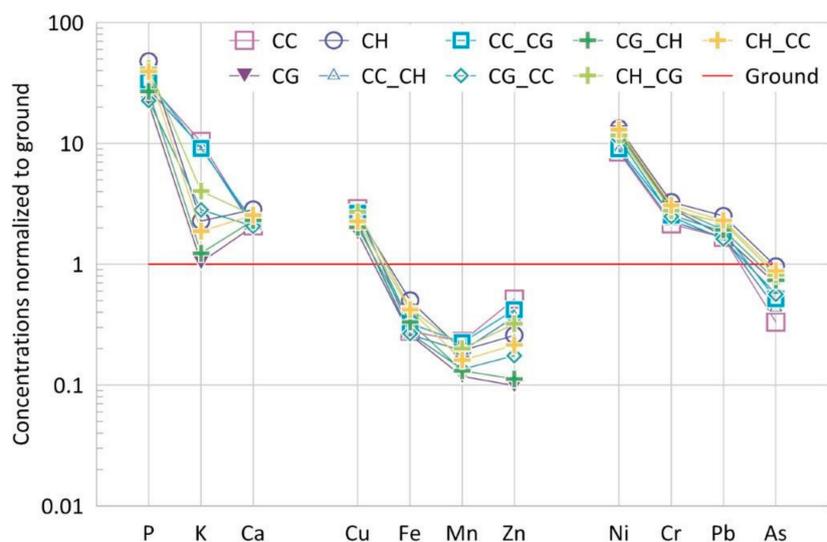


Figure 5. Average elements concentrations in the ashes of the materials tested standardized to their average soil content.

The total phosphorus content in soils ranges from 300 to 1,000 $\text{mg}\cdot\text{kg}^{-1}$ [31]. Ashes from biomass combustion may constitute a valuable, natural source of this element. Another one of the most yield-forming macroelements is potassium. The higher amount of both phosphorus and potassium in ashes obtained as a result of biomass combustion, compared to soil abundance, justifies the use of this material for soil fertilization.

The introduction of calcium into the soil has a direct effect on the change in soil pH. The content of this element in soils ranges from 700 ppm to 36,000 ppm [32].

Analyzing the results of the study presented in Figure 5, it can be concluded that all ashes showed a very strong relative enrichment in P in relation to the soil content. In the case of K, a strong enrichment was observed in the ashes of CC and its mixtures and the ashes of CH were enriched to a lower degree, whereas for the ashes of CG and CG-CH, a low level enrichment was observed. Relatively low enrichment in Ca was observed for all materials.

Copper, as a metal, is a component of many enzymes in plants and is often embedded in the structure of proteins. The copper content in soils is in the range of 5 to 100 ppm [33]. Soils are exposed to Cu pollution from various sources. Apart from industrial emissions, Cu gets into soils together with some organic and mineral fertilizers as well as plant protection products and municipal waste. Some amounts of Cu are added as a fertilizer in soils with deficient content for plants. Cu introduced into soils as a result of agricultural and horticultural activities is subject to constant accumulation in the surface levels of soils and may cause their contamination. Excessive amounts of Cu are often observed in soils of allotment gardens and orchards. Due to the relatively high bioaccumulation rate of Cu and the high degree of anthropogenic activation, it poses a risk of local contamination of the biological environment [33].

The total iron content in the soil is about 3% [34]. The metabolic functions of iron in plants are relatively well known and it is the basic metal responsible for energy transformations needed for the synthesis of plant life processes. The iron content not exceeding the total content in cultivated soils does not prevent the use of ashes for fertilizing purposes. Fe and its compounds are not toxic to humans or animals. Fe plays an important physiological role in living organisms and belongs to the group of metals necessary for their normal development, the so-called bio-elements. The deficiency of Fe for plants is not related to its actual lack in soils, but to limited solubility. Fe is one of the most mobile elements in soils, and its degree of mobility varies with periodic changes in conditions. The compounds and minerals of Fe and complex connections with organic matter are of great importance in soil-forming processes and have a significant influence on the behavior of other elements, especially trace elements [33].

Manganese and iron are elements involved in similar processes. Plants have specific requirements for manganese and probably the most important function of manganese is its participation in oxidation-reduction processes. Kabata-Pendias [34] states that the average content of manganese in the soil is $488 \text{ mg}\cdot\text{kg}^{-1}$ and it is about 50% lower than in biomass ashes.

Due to its involvement in redox processes in the soil, Mn influences the behavior of other elements, especially trace metals. Their strong binding by Mn-Fe concretions may cause a secondary deficiency for plants. The correct Mn/Fe ratio is necessary to balance enzymatic processes in plants. With ratio values above 1.5 there are symptoms of Mn toxicity and Fe deficiency, and above 2.5 the excess of Fe is harmful, accompanied by symptoms of Mn deficiency. Soil contamination in Mn is related to its form and not to its quantity. Excessive amounts of easily soluble Mn may occur in soils after the application of municipal waste and after intensive fertilization with slurry [33].

The use of zinc-containing mineral fertilizers, and the penetration of this element from industrial pollution, results in an increase in its quantity in surface soils. Therefore, it is necessary to control the amount of Zn introduced into the soil.

Zn is one of the most mobile metals in soil. Higher plants generally take up Zn in proportion to its concentration in the soil and therefore soil contamination with this metal threatens to increase the amount in the food chain. Lowering the phytoavailability of Zn is achieved by adding Ca, phosphate fertilizers, and sulfur compounds. In addition, the presence of hydrated oxides of Fe and Mn, montmorillonite, and alofans in the soil significantly reduces Zn uptake by plants [33].

Among the microelements Fe, Mn, and Fe, a slight depletion in the ashes of all materials was found in the ashes studied, while a slight enrichment was observed for Cu (Figure 5). The above data justify the use of ash from biomass for soil fertilization.

The total nickel content in soils is $13\text{--}37 \text{ mg}\cdot\text{kg}^{-1}$ [34]. Nickel has both siderophilic and oxyphilic properties and is geochemically similar to iron. Ni is easily absorbed by plants if it occurs in soils in mobile forms. There is no evidence of significant metabolic functions of Ni in plants, although there are reports of beneficial effects of nickel salts on the growth of some plants and on free nitrogen binding processes by microorganisms. Calcification of soils and increased doses of phosphorus fertilizers limit the phytochemical availability of Ni [33].

In almost all soils, the Pb balance is positive and indicates a steady increase in content. Even if these amounts are acceptable from the point of view of ecotoxicity or phytotoxicity, an increased Pb content in soil can pose a risk to humans. Phosphorus introduced into soil contaminated with Pb slightly reduces the amount of easily soluble forms of Pb and those associated with carbonates and oxides. Moreover, the uptake and activity of lead in plants is antagonistically affected by Ca and S. These elements cause the precipitation of Pb in poorly soluble forms both in the root environment and in plant tissues [33].

There is a significant accumulation of arsenic in the soil of gardens and orchards as a result of years of use of arsenic plant protection products that have already been discontinued. Arsenic in soils has properties similar to P and is absorbed by Fe and Al hydroxides, organic matter, and Ca and P compounds. The reduction of the toxic effects of As in soils consists of the periodic reduction of its mobility by changing of reducing conditions to oxidation ones and by binding through the addition of iron sulfate, sulfur, calcium carbonate, or phosphate fertilizers. The biological role of As in plants is unexplained. However, it is collected by all plants in proportion to the As content of the soil, which indicates a passive mechanism. Some plants are characterized by a special As accumulation if the substrate is enriched with this element, such as Douglas fir (*Pseudotsuga*), whose branch ash can contain up to 0.8% As [33].

Of the toxic elements, a lower content compared to soil was found only for As in ashes of all materials, while for the remaining elements a moderate enrichment for Ni, or slight one for Cr and Pb was noted (Figure 5).

Since the beginning of the pellet market, emphasis has been placed on the use of wood pellets, which are an attractive fuel due to their low humidity and low ash content. Currently, the raw materials

used for the production of pellets are sawdust, planed shavings, and dry shavings from sawmills and the wood industry. It is the most popular fuel on the market. Therefore, it was decided to compare the composition of ash from the waste materials tested with the ashes obtained from wood pellet combustion.

The obtained results of the chemical composition of ashes were normalized in relation to the ashes from wood pellets. The chemical composition of wood pellet ash was determined in a group of eight types of wood pellets available on the market using the same methodology as for determining the chemical composition of the materials tested. Standardization results are presented in Figure 6.

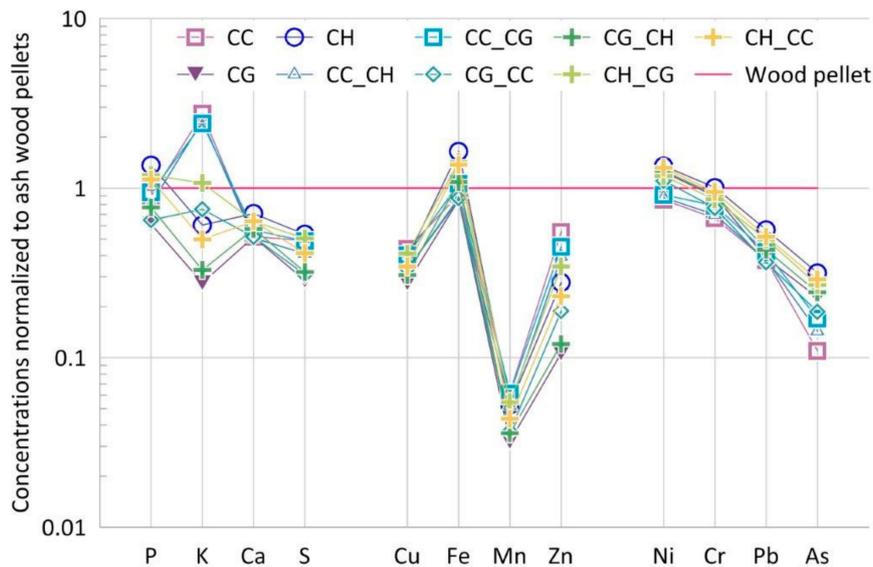


Figure 6. Average elements concentrations in the ashes of the materials tested standardized to their average content in ashes of wood pellets.

Analyzing the results of the study presented in Figure 6, it can be seen that only ashes from CH and ashes from CH-CC and CH-CG mixtures had a higher P content than ash from wood pellets. In addition, ashes from four materials had a higher K content: CC, CC-CG, CC-CH, and CH-CG. Ca and S were determined below the content in ashes from wood pellets. Further, the content of Cu and Zn was below the content in ashes from wood pellets. The Mn content, which was significantly lower in all the examined ashes than in the ashes of wood pellets, was noteworthy. In the case of Fe, only ash from CH and mixtures (CH-CC, CH-CG) had a higher content of this element than wood pellets. Moreover, it should be emphasized that the content of Pb and As in the studied materials was lower than that of ash from wood pellets. Taking into account that Pb and As contained in the ashes of the materials studied would enrich the soil with them, it should be concluded that ash from corn grain drying waste is a safer fertilizer in comparison with ashes from wood pellets and does not pose a risk of introducing these toxic elements into the environment.

5. Conclusions

Sustainable use of biomass for energy purposes on both a small and industrial scale requires recognition of the fact that biomass ash can be used to a large extent by applying it to the soil, thus by introducing extracted nutrients, especially P and K. The literature reports on the influence of ashes from biomass on the physicochemical properties of soils and the content of assimilable macro- and microelements proves that as the doses of ashes increase, their content in soil, especially the assimilable forms of K, P, and Mg, increased significantly. The soil content of assimilable K increased from medium to very high [35,36].

The analysis of the results of the study on the chemical composition of ashes from the combustion of waste biomass from the drying of corn grains showed that this byproduct of combustion is a good source of valuable nutrients for plants such as potassium, phosphorus, calcium, and magnesium. At the same time, the factors determining the possibility of using the ash for fertilization purposes are the content of heavy elements such as nickel, arsenic, and lead.

The study proved that, regarding macroelements, the material with high fertilizing potential is CG ash. At the same time, this ash is characterized by the lowest content of microelements, and the ash from CC proved the most enriched in these components. In the case of toxic elements, CH had the highest concentration of these components and therefore the introduction of ash from this material into the soil as a fertilizer should be avoided.

The analysis of the results showed that regardless of the ash of the type of biomass studied, all materials were strongly enriched with phosphorus in relation to the soil content. CC and its mixtures are materials with strong enrichment in potassium and CH in calcium. In the case of microelements, a slight depletion in Fe and a slight enrichment in Cu were found for all analyzed ashes. For toxic elements, only a lower level was found in relation to the soil, while a slight enrichment was found for Pb and Cr, and a moderate one for Ni in all materials. Comparing the results obtained in relation to wood pellet ashes, it was shown that only ashes from CH and CH-CC and CH-CG mixtures were characterized by a higher content of P, while CC, CC-CG, and CC-CH were characterized by a higher content of K. Therefore, the materials studied were characterized by high fertilizer usefulness.

Author Contributions: Conceptualization, G.Z., J.S.-B., G.M., and T.S.; methodology, G.Z., G.M., and J.S.-B.; validation, G.Z., G.M., and J.S.-B.; formal analysis, G.M.; investigation, G.Z. and W.G.; resources, G.M. and P.K.; writing—original draft preparation, G.Z., J.S.-B., and G.M.; writing—review and editing, G.M., G.Z., J.S.-B., T.S., and M.D.; supervision, G.Z. and G.M.; project administration, G.M.; funding acquisition and project conceptualization, G.M., P.K., and M.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Center for Research and Development (NCBiR) grant number BIOSTRATEG3/344490/13/NCBR/2018.

Acknowledgments: Research was performed within the project “Developing of innovative air purification methods for grain and seed drying, along with pollutant emissions reduction—ECO-Dryer” co-funded by the National Center for Research and Development (NCBiR) within the framework of the Strategic Research and Development Program “Environment, Agriculture and Forestry”—BIOSTRATEG3/344490/13/NCBR/2018.

Conflicts of Interest: The authors declare no conflicts of interest.

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