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Utilization of Renewable Energy Waste (Wood Ash and Straw) in the Production of Mineral Fertilizers

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ABSTRACT

The method of utilization of biomass ash in agriculture as an agrochemical is considered. Studies have shown that biomass ash contains a number of macro- and microelements essential for agriculture, such as phosphorus, potassium, calcium, magnesium and sulphur. Based on the content of the main chemical components and physical and chemical parameters of wood and plant ash, conclusions are drawn regarding its use. Wood ash with a high calcium content is suitable for agromelioration of soils with a low pH value. Ash from agricultural crop straw with a high calcium and potassium content is suitable for the production of potash fertilizers, and with a high potassium and phosphorus content – for the production of phosphorus-potassium fertilizers.

Keywords: biomass, ash materials, straw and wood combustion, physical and chemical properties of ash, nutrients.

INTRODUCTION

The world community has been considering the use of local alternative energy sources as one of the promising ways to solve the growing problems of energy supply for many years in a row. Considerable attention of the world community is paid to the use of biomass both for the purpose of cleaning polluted liquid media (Malovanyy et al., 2021, Tymchuk et al., 2020), and as one of the most powerful and affordable alternative energy sources on Earth (Polyanskyi et al., 2017, Dyakonov et al., 2015). Energy from renewable sources, in particular biomass, is actively used in most developed countries. In some countries, the share of biomass in the total consumption of primary energy carriers significantly exceeds the European average one and, for example, in Finland it is more than 25%, in Sweden – 20% (Dibáczi et al., 2010, Basok et al., 2021). At the same time, biomass is carbon-neutral and usually contains little nitrogen and sulphur (Agbor et al., 2014). Modernization and investment in the construction of elevators were carried out to store and dry large volumes of grain in agricultural and grain processing farms in Ukraine.

Grain dryers in farms were equipped mainly with gas boilers until 2020. As gas prices rise and prices for crop products decrease due to the war in Ukraine, the reconstruction of dryers has begun and continues at an active pace. Solid fuel boilers are installed to generate heat. So, according to data provided by employees of Crop-Inkris LLC (Romny, Sumy region), in 2020, up to 65.4% of the company's customers dried crop products using gas to generate heat, 23.6% of customers combined gas and solid fuel (wood and straw), 5.4% each - only solid and fuel oil. By 2023, the situation has changed dramatically. Today, 34.1% of customers use only gas for grain drying, 30.7%

combine gas with solid fuel, 29.5% – wood and straw, 5.7% – fuel oil. (Table 1). Consequently, the number of farms that use wood and straw to generate heat during grain drying increased from 29.0% to 60.2%. This leads to the formation of significant volumes of ash materials.

The inevitable consequence of biomass combustion is the formation of ash. The properties of ash and slag wastes largely depend on the mineral composition of the fuel and the method of its combustion, and the products formed will differ significantly in content and ratio of the major components (Kashkovskyi et al., 2017, Stankovski et al., 2012). Layer combustion of biomass is mainly used, and only large plants are equipped with cyclones and other flue gas purification systems. Therefore, in 2019, about 131.8 thousand tons, or 80% of the total ash from biomass combustion, including the one that is formed in the individual heating sector, needed to be disposed of or placed in landfills. Currently, Ukrainian legislation does not contain mandatory requirements for the disposal of ash from heat-generating plants, including ash from biomass combustion (Kramar, 2021).

Withal, biomass ash contains several important macro- and microelements that were absorbed by plants from the soil and remained in the ash after combustion. Phosphorus and potassium are some of the major macronutrients necessary for plants and significantly affect the crop yield. Reusing residues after combustion in agriculture can contribute to the implementation of closed nutrient cycles and the need for less use of mineral fertilizers on an industrial scale (Agbor et al., 2014, Stankovski et al., 2012). It will reduce the technogenic load on the soil (Savci, 2012, Vygovska et al., 2008, Slobodianyk et al., 2015) and surface waters (Malovanyy et al., 2020). This strategy of using fertilizers and mineral fertilizer encapsulation is promising for agriculture (Vakal et al., 2020, Bebber et al., 2022, Kukharets et al., 2012). The development of ways to dispose of incineration waste and determine the possibility of using them as fertilizers requires the study of the physicochemical properties of ash, which determines the purpose of the work.

MATERIALS AND METHODS

The work was carried out at the scientific base of the Research Institute "MINDIP" of Sumy State University. 24 samples of birch wood and 31 samples of oak were used as raw materials for ash. Straw selection of agricultural crops was carried out in the farms of Sumy and Chernihiv regions during the harvest. The 102 winter wheat straw samples, the 25 corn samples, the 33 sunflower samples, the 29 winter rapeseed samples, the 23 soybean samples, and the 18 buckwheat samples were selected in 2021.

The plant material was ground into 1–3 cm pieces. Average samples were created by quartering. The mass of each sample was at least 100 g. Average samples of plant material were dried at a temperature of 60–65 °C to an air-dry state. The sample was ground in a laboratory mill and sieved through a sieve after drying. The ground plant samples were ashed in a muffle furnace at a temperature of 800±25 °C. The specific gravity of ash, pH 1% of aqueous solutions of ash and ash content of wood and straw was determined according to current methods (State Enterprise, 2015). Laboratory tests for the content of macro- and microelements in ash were carried out using the following analysis methods: photometric, gravimetric, complexonometric, atomic absorption (iron, manganese, zinc, copper, cadmium, and lead).

Ash samples were grouped according to the species composition of the plants from which the ash was obtained. The obtained results of physicochemical properties of ash materials for each parameter were subjected to statistical processing.

Table 1. Structure of farms of Sumy and Chernihiv regions using different types of fuel for grain drying

Type of fuel	2020 year		2023 year	
	Number of farms	%	Number of farms	%
Gas	61	65.6	30	34.1
Oil fuel	5	5.4	5	5.7
Gas + solid fuel (wood and straw)	22	23.6	27	30.7
Solid fuel (wood and straw)	5	5.4	26	29.5
In total	93	100	88	100

The average, minimum and maximum values of physico-chemical indicators, the content of chemical elements, and standard deviation were determined. Based on their calculation, the intervals of variation of these indicators in ash from the combustion of plant residues were determined.

RESULTS AND DISCUSSION

During the analysis of ash from burnt wood samples in the laboratory, it was established that the ash content from oak and birch wood ranged from 2.05% to 4.45%, at coefficients of variation of 15.66–16.13. The pH level of aqueous ash solutions was within 10.10–11.55 (Table 2).

Calcium prevailed in the wood in terms of chemical composition. Thus, birch wood contains from 25.70% to 39.10% calcium in terms of CaO, and oak wood - from 37.1% to 48.30%. However, the ranges of variation in calcium content in wood ash from different plant species, statistically calculated on the basis of average values and standard deviations, indicate the absence of significant interspecific differences in the content of this element. Thus, the statistically calculated range for birch ash was 32.9±4.5% (28.9–37.4%), and oak ash – 41.4±4.5% (36.9–45.9%).

Magnesium, biologically significant for plants, was found in much smaller amounts in wood ash. Withal, there were no differences in the amount in ash from different types of wood. So, in birch ash, the magnesium content in terms of MgO ranged from 2.9% to 5.1%, in oak ash – from 2.5% to 4.2%. The study showed that the CaO : MgO ratio in the birch and oak ash was almost close and averaged 1:0.12 and 1:0.09, respectively. Similar ratios of calcium and magnesium were found in the wood and leaves of living perennial plants. Wood ash samples also showed low levels of plant nutrients such as potassium, phosphorus, and sulphur. Thus, potassium in terms of K_2O ranged from 2.1% to 8.5%, phosphorus in terms of P_2O_5 – 1.7–3.8%, sulphur in terms of SO_3 – from 2.1% to 5.3% were determined in birch ash. In oak wood ash, respectively, from 2.5% to 4.2%, from 2.3% to 5.6%, and from 1.6% to 4.3% (Fig. 1). For straw combustion, the lowest ash values were found in cereal straw. Thus, the ash content of winter wheat straw

Table 2. Characteristics of wood ash

Indicator	Average value	Min.	Max.	Standard deviation from the value	Variation coefficient, %
Birch					
Ash content, %	3.15	2.45	3.85	±0.49	15.66
pH	11.05	10.25	11.55	±0.24	2.15
Oak					
Ash content. %	3.05	2.05	4.45	±0.49	16.13
pH	11.01	10.10	11.55	±0.26	2.35

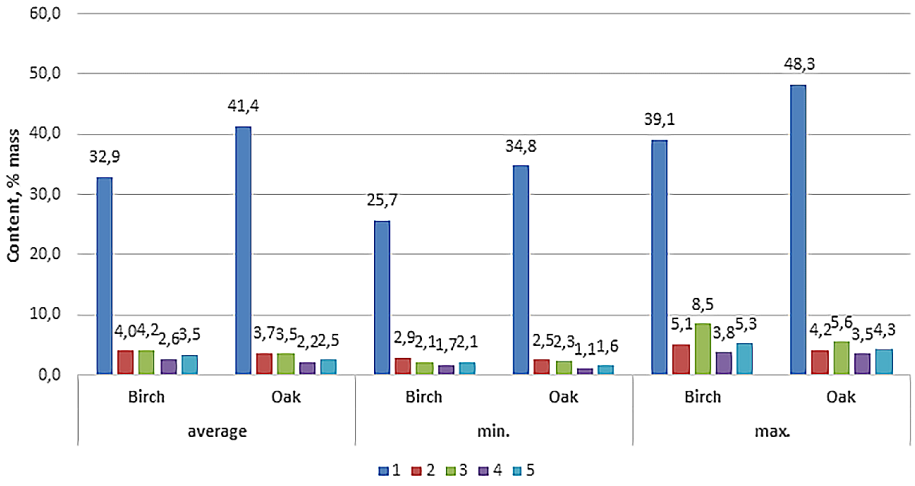

Figure 1. Content of major chemical elements in wood ash: 1- CaO; 2 – MgO; 3 – K_2O; 4 – P_2O_5; 5 – SO_3

averaged 5.55%, and that of maize 6.42%. The ash content of plant residues of dicotyledonous crops ranged from 9.45% to 10.05%.

The ash from field crop straw combustion like wood had alkaline properties. The pH level of aqueous ash solutions was between 10.95 and 11.91 (Table 3). The content of chemical elements in the ash from the combustion of crop residues of the staple annual agricultural crops revealed differences from the ash from perennial wood species.

The lowest calcium content was found in crop residues of winter wheat and corn. The calcium content in terms of CaO in the winter wheat ash averaged 8.04%, in corn one-9.20%. The specific gravity of this element in the ash from dicotyledonous annuals was significantly higher and, depending on the crop, ranged from 21.88% for winter rapeseed to 33.43% for buckwheat (Fig. 2). The standard deviations of calcium in the ash from secondary crop products were calculated to confirm the correctness of the conclusions.

Statistically probable intervals for the content of this element in straw ash from different crops were established. Moreover, they were the smallest for winter wheat and corn. Thus, it ranged from 5.39% to 10.71% for winter wheat, from 5.55% to 12.85% for corn (Fig. 2). Consequently, the research results and statistical analysis indicate with a high probability that the specific gravity of calcium in the stubble ash from grain crops was the lowest.

The magnesium content in stubble ash did not depend on the type of field plants. The magnesium content in terms of MgO ranged from 1.75% to 10.61%. At the same time, the intervals of variation in the values of magnesium content in the ash from crop residues of winter wheat, corn, sunflower, and winter rapeseed had similar characteristics both among themselves (Fig. 3) and with wood ash (Fig. 1).

The high range of variation in the magnesium and calcium content in soybean and buckwheat ash is noteworthy (Fig. 2 and 3). Considering the facts of growing these crops on simplified fertilizer systems, the influence of soil fertility and agricultural cultivation technology on the content of magnesium and other elements in the straw and after combustion in the ash was decisive. But it's a topic of prospective research.

The CaO:MgO ratio in straw ash from annual crops was slightly different from the wood ash. For annual dicotyledonous plants, it ranged from 1:0.13 to 1:0.31. In cereal crops, due to a significant decrease in the specific gravity of calcium, the ratio changed towards an increase in the proportion of magnesium – from 1:0.36 to 1:0.59.

Analysis of ash from burnt straw of annual field crops showed significantly higher potassium content than from woody crops. Depending on the crop, the specific gravity of potassium in terms of K_2O ranged from 19.03% to 42.86%. The most potassium was detected in the corn, sunflower, and winter wheat ash. Thus, the calculated

Table 3. Characteristics of field crop straw ash

Indicator	Average value	Min.	Max.	Standard deviation from the value	Coefficient of variation, %
Winter wheat					
Ash content, %	5.55	4.85	7.65	0.45	8.11
pH	11.61	11.40	11.91	1.32	2.76
Corn					
Ash content, %	6.42	5.23	7.05	0.65	10.12
pH	11.50	11.31	11.76	0.24	2.09
Sunflower					
Ash content, %	9.60	9.55	10.75	0.75	7.81
pH	11.50	11.40	11.60	0.25	2.17
Winter rapeseed					
Ash content, %	9.45	8.23	10.75	0.89	9.42
pH	11.05	10.95	11.15	0.21	1.90
Soy					
Ash content, %	10.05	8.95	11.05	1.25	12.44
pH	11.50	11.35	11.65	0.24	2.10

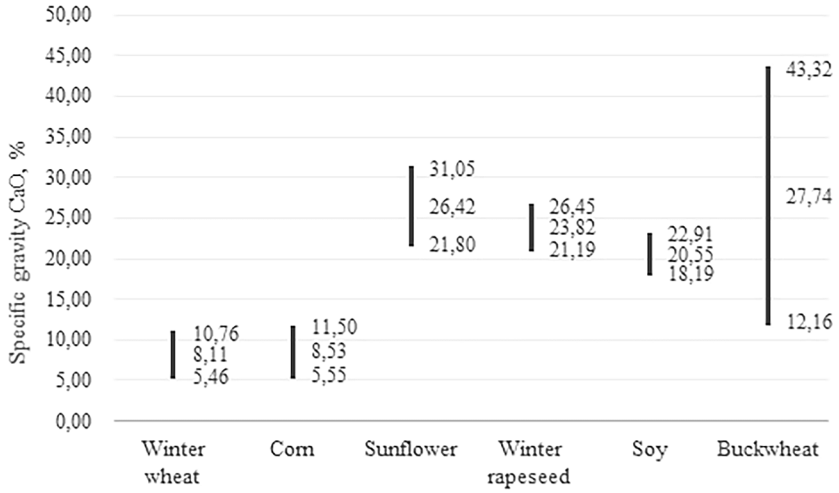

Figure 2. Calcium content in the ash from agricultural crop straw, 2021. The upper values for each crop are the upper range of the values of the elements' contents, the lower values are the lower range of values based on the results of calculating the standard deviation, the middle one is the average value of the content

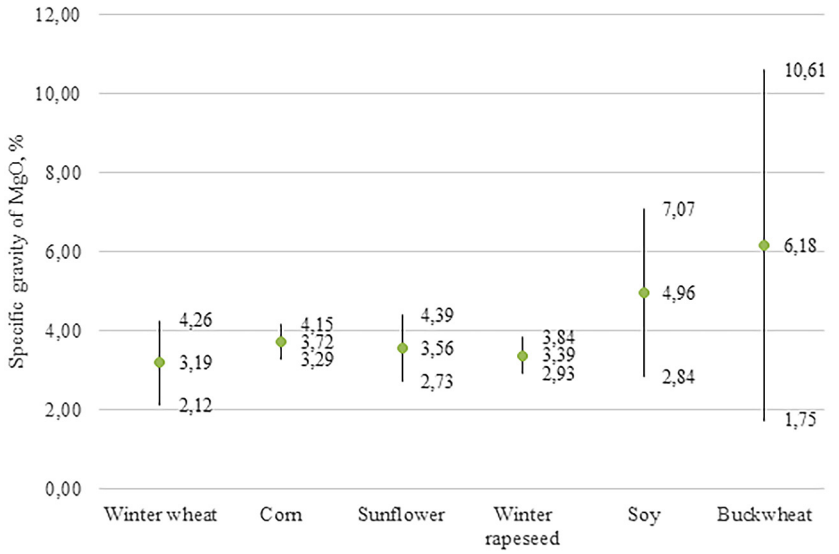

Figure 3. Magnesium content in the ash from agricultural crop straw, 2021. The upper values for each crop are the upper range of the values of the elements' contents, the lower values are the lower range of values based on the results of calculating the standard deviation, the middle one is the average value of the content

intervals of variation of the K_2O content in corn, sunflower, and winter wheat ash were from 27.01% to 42.86%, from 24.33% to 36.72%, and from 25.34% to 35.02%, respectively (Fig. 4).

The potassium content was slightly lower in the winter rapeseed, soybean, and buckwheat ash. However, there were samples of straw ash from these crops with a high potassium content. Therefore, it is impossible to assert the existence of a dependence or connection between the potassium content in plants and their ash, and a certain type of plant. Particularly increased potassium content was found in samples of ash from the burned straw of crops grown on a high agricultural background, in compliance with cultivation and fertilization technology.

Consequently, ash from corn, winter wheat, and selected batches of other field crops, as well as sunflower, can be considered for producing ash-based fertilizers. It is first necessary to analyse samples for the content of chemical elements in the ash. The primary reason for the low potassium

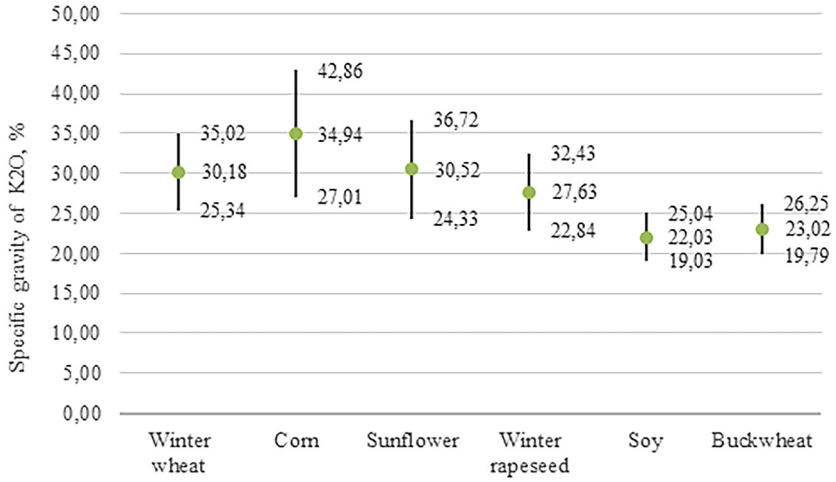

Figure 4. Potassium content in the ash from agricultural crop straw, 2021.
The upper values for each crop are the upper range of the values of the elements' contents, the lower values are the lower range of values based on the results of calculating the standard deviation, the middle one is the average value of the content

content in wood ash, comparing to the ash from annual plants, is the peculiarities of wood formation. The process of wood formation is accompanied by long-term leaching (washing out) of potassium from physiologically "dead" wood due to its mobility (solubility in water) in plants. Potassium, meanwhile, is not integrated into the composition of wood cellulose, unlike calcium, magnesium, phosphorus, sulphur (State Enterprise, 2015).

When burning the straw of annual field crops, it was found that the highest levels of phosphorus content were observed in samples of ash from secondary products of winter wheat, corn, and slightly less-sunflower. Thus, in the winter wheat, corn, and sunflower ash, the specific gravity of phosphorus in terms of P_2O_5 ranged from 6.68% to 11.75%, from 6.92% to 9.87%, and from 3.12% to 7.08% (Fig. 5).

The winter wheat and corn ash had an advantage in terms of average values and in the intervals of fluctuations in phosphorus content in the ash. However, separate samples of sunflower, winter rapeseed, soybean, and buckwheat ash were found with relatively high phosphorus content, which were equivalent to the phosphorus content of winter wheat and corn ash.

The ranges of variation in values calculated on the basis of standard deviations of phosphorus content in straw ash from different crops cannot convincingly indicate significant differences

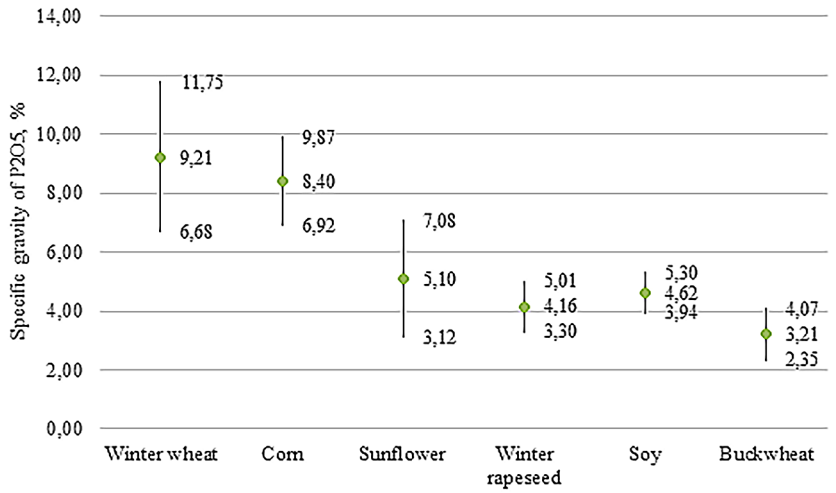

Figure 5. Phosphorus content in the ash from agricultural crop straw, 2021.
The upper values for each crop are the upper range of the values of the elements' contents, the lower values are the lower range of values based on the results of calculating the standard deviation, the middle one is the average value of the content

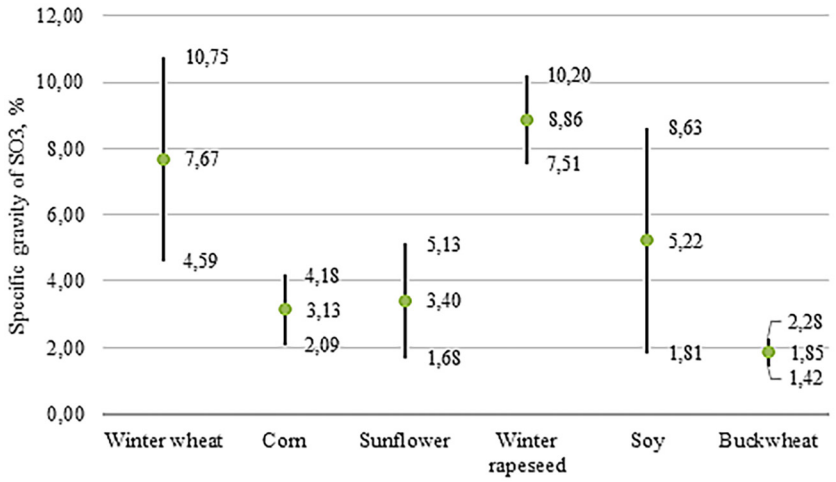

Figure 6. Sulphur content in the ash from agricultural crop straw, 2021.
The upper values for each crop are the upper range of the values of the elements' contents, the lower values are the lower range of values based on the results of calculating the standard deviation, the middle one is the average value of the content

between groups depending on the plant species. Thus, the intervals of variation in the specific gravity of phosphorus in the ash from sunflower, winter rapeseed, soybean, and buckwheat were almost at the same level. Moreover, the variation ranges of the phosphorus content in sunflower ash even reached the values of the variation ranges in the specific gravity of this element in the winter wheat and corn ash.

Establishing the influence of factors affecting the accumulation of phosphorus in the ash from winter wheat, corn, and individual samples from other field crops is possible only with a detailed study of plant growing conditions, agrotechnology, and fertilization systems. The most sulphur was found in the winter rapeseed and winter wheat straw ash. Thus, the average sulphur content in terms of SO_3 in the winter rapeseed and winter wheat ash was 8.86% and 7.67%, respectively. However, ash samples with a high sulphur content were found after soybean and sunflower straw combustion.

The average content and ranges of variation of the specific gravity of sulphur in ash depended more on the amount of sulphur fertilizers applied to annual crops rather than on the type of plants (Fig. 6). Thus, a significant amount of sulphur fertilizers is applied in the technologies of growing winter rapeseed and winter wheat. Less sulphur fertilizers were applied to soybeans and sunflowers. The corn fertilization system places greater emphasis on high doses of nitrogen, phosphorus, and potassium. Buckwheat is grown, as a rule, on agricultural backgrounds with a small amount of fertilizers. The results of studies of physical-chemical properties and the content of chemical elements in ash samples indicate the ways of its disposal. Ash has a high calcium and magnesium content and becomes a valuable material for reclamation of acidic soils.

In conditions of rising prices for phosphate and potash mineral fertilizers, ash with an increased potassium and phosphorus content can be considered a raw material for fertilizer production. Moreover, the technology development for processing ash into fertilizers is a relevant and promising direction for its disposal and reducing the anthropogenic load on the environment.

CONCLUSIONS

Ash can be classified for further use in production and disposal depending on the content of major chemical elements in the ash from the combustion of plant materials:

1. Ash with a high content of calcium and a low content of magnesium, potassium, phosphorus, and sulphur from wood combustion, suitable for use in the agromelioration of soils with a low pH.
2. Ash with a high content of calcium and potassium, with relatively low specific gravity of magnesium, phosphorus, and sulphur from the sunflower straw, winter rapeseed, soybean, and buckwheat ash are suitable for the production

of potash, when enriched with phosphorus-phosphorus-potassium fertilizers.

3. Ash with a high content of potassium and phosphorus, with a low content of calcium and magnesium from the combustion of cereal crops are suitable for the production of phosphorus-potassium fertilizers.

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