

Review

# Utilization of Ashes from Biomass Combustion

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**Abstract:** Biomass is one of the most important sources of renewable energy in the energy industry. It is assumed that by 2050 the global energy deposit could be covered in 33–50% of biomass combustion. As with conventional fuels, the combustion of biomass produces combustion by-products, such as fly ash. Therefore, along with the growing interest in the use of biomass as a source of energy, the production of ash as a combustion by-product increases every year. It is estimated that approximately 476 million tons of ashes per year can be produced from biomass combustion. For example, the calorific value of dry wood mass tends to be between  $18.5 \text{ MJ} \times \text{kg}^{-1}$  and  $19.5 \text{ MJ} \times \text{kg}^{-1}$ , while the ash content resulting from thermal treatment of wood is from 0.4 to 3.9% of dry fuel mass. However, biomass ash is a waste that is particularly difficult to characterize due to the large variability of the chemical composition depending on the biomass and combustion technology. In addition, this waste is, on the one hand, a valuable fertilizer component, as it contains significant amounts of nutrients, e.g., calcium (Ca), potassium (K) and microelements, but on the other hand, it may contain toxic compounds harmful to the environment, including heavy metals and substances formed as a result of combustion, such as polycyclic aromatic hydrocarbons (PAHs) or volatile organic compounds (VOCs). PAHs and VOCs are formed mainly in the processes of incomplete combustion of coal and wood in low-power boilers, with unstable operating conditions. However, it is important to remember that before the fly ash is used in various industries (e.g., zeolite synthesis, recovery of rare earth metals or plastic production) as an additive to building materials or fertilizers for cultivation, a number of analyses are to be conducted so that the by-products of combustion could be used to allow the by-product of combustion to be used. It is important to conduct tests for the content of heavy metals, chlorides, sulphates, microelements and macroelements, grain and phase composition and organic compounds. If such ash is characterized by low pollution levels, it should be used in agriculture and reclamation of degraded land and not directed to landfills where it loses its valuable properties. The purpose of this review is to present the properties of ashes generated as a result of biomass combustion in Poland and the world, to discuss factors influencing changes in its composition and to present the possibilities of their reuse in the environment and in various branches of industry.



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**Keywords:** plant biomass; fly ash; combustion

## 1. Introduction

In the process of electricity and heat production, a significant mass of combustion by-products is generated, which ranks third in the total mass of industrial waste generated in Poland. According to the literature, 900–1000 million tons of energy waste are generated every year in the world. In the European Union (EU), this production reaches 100 million tons per year, and in the United States alone, 130 million tons. Such a large amount of generated energy waste is a serious problem not only for EU countries but also the world [1]. In December 2018, the revised Renewable Energy Directive (Directive (EU) 2018/2001) entered into force as part of the Clean Energy for All Europeans package. The new directive sets a binding target that by 2030, at least 32% of the final energy consumed in the Union should be obtained from renewable sources. It also includes a clause which allows for increasing this target by 2023, setting it for a 14% share of renewable energy in

transport by 2030 [2,3]. The use of biomass as a renewable energy source in the energy sector is an innovative process, not only for economic and technological reasons but especially for sustainable eco-development. In addition, it is rated as a carbon neutral fuel because the CO<sub>2</sub> emitted as a result of its combustion corresponds to the amount previously absorbed by plants from the atmosphere [4].

Among all renewable energy sources, biomass represents the most promising product on the market. In various countries, biomass also refers to municipal waste, which includes waste generated by residential and commercial buildings as well as public services [5]. According to the literature, worldwide annual biomass production ranges from 112 to 220 billion tons: biomass with energy potential from 1.2 to 3.1 billion tons, 1.1 billion tons from municipal solid wastes and approximately 3 billion tons from forest residues [6]. Vassilev et al. [7] stated that with increasing biomass production, it is assumed that by 2050, 33 to 50% of the world's energy deposit could be covered by biomass combustion. However, as biomass combustion increases, more and more waste ash is produced each year. It is estimated that currently approximately 476 million tons of ash is generated from biomass combustion per year [7].

The different chemical composition of the ash from biomass combustion depends on biomass characteristics and incineration conditions [6,7]. Such waste tends to be deposited in landfills or heaps. It can also be stored and, under unsuitable conditions, it can lose its quality. According to Jacobson et al. [8], it is an environmental mistake to divert biomass ash from landfills when valuable components could be returned to the environment and used to fertilise plants and improve soil properties [8]. Therefore, it seems sensible to use ash from biomass combustion in, among others, agriculture, remediation of degraded land, environmental protection, synthesis of zeolites, recovery of rare earth metals or production of plastics (Figure 1). However, its use depends on the physico-chemical characteristics of the ash itself. According to the Regulation of the Minister of Agriculture and Rural Development of 18 June 2008 [9] on implementation of specific provisions of the act on fertilizers and fertilization, the permissible metal content in mineral fertilizers, including ashes from biomass combustion, must not exceed the content of: cadmium (Cd)—50 mg × kg<sup>-1</sup>, arsenic (As)—50 mg × kg<sup>-1</sup>, lead (Pb)—140 mg × kg<sup>-1</sup> and mercury (Hg)—2 mg × kg<sup>-1</sup> [10].

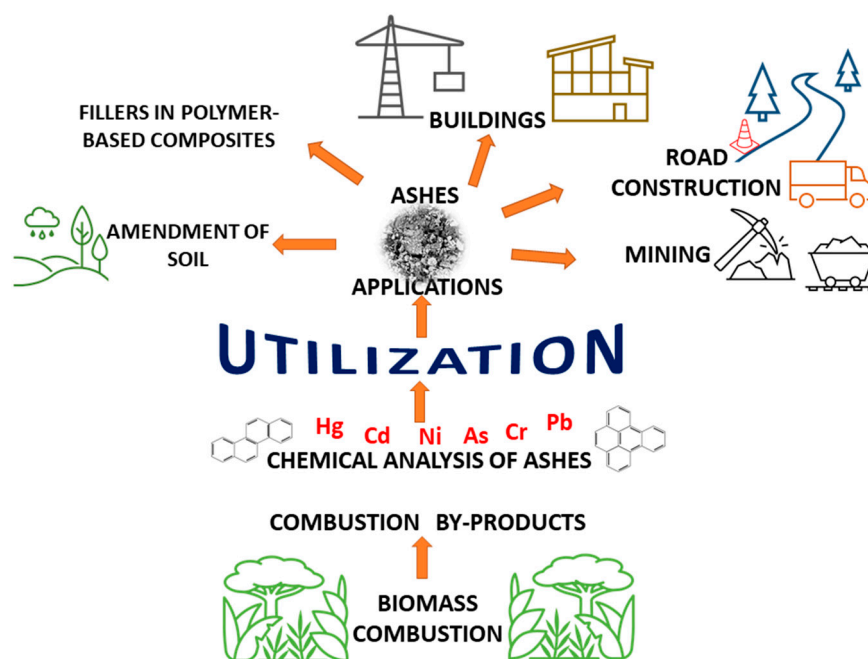


Figure 1. Utilization of biomass combustion ash.

Nowadays, biomass combustion is a common waste disposal and energy technology. The by-product of this process is ashes that require further management. The new approach of this review is to present the various possibilities of using ashes, rather than focus only on one area, which is usually their disposal. This paper presents the possibilities of industrial and construction use, such as being a component for strengthening concrete and hardening surfaces for road construction, or for reclamation and development of areas after coal mining. It also presents the advantages that corroborate their use for natural purposes, including the cultivation of plants not intended for consumption. According to the already mentioned possibilities of bio-waste utilization, it is forecast that in the coming years, the share of new directions in energy waste management may significantly increase due to the entry of new technologies that will allow for better utilization of bio-waste [11,12]. Therefore, the purpose of this literature review was to present the properties of ashes generated as a result of biomass combustion in Poland and the world, factors influencing changes in their composition and the possibilities of their use as fertilizers in agriculture and environmental engineering technologies.

## 2. Methods

On the basis of inclusion and exclusion, all study data were analyzed for possible applications of ashes. Two main databases were used: Web of Science and Scopus. The following key words were used in order to collect the research material: “Sources of fly ash”, “Organic pollutants in ashes”, “Biomass combustion ash”, “Management of ashes from biomass combustion”, “Heavy metals concentration of fly ashes from the combustion”, etc. Moreover, the latest original research articles and review articles were analyzed. The present manuscript used 85 of the publication.

## 3. Results and Discussion

### 3.1. Characteristics of Fly Ash from Biomass Combustion

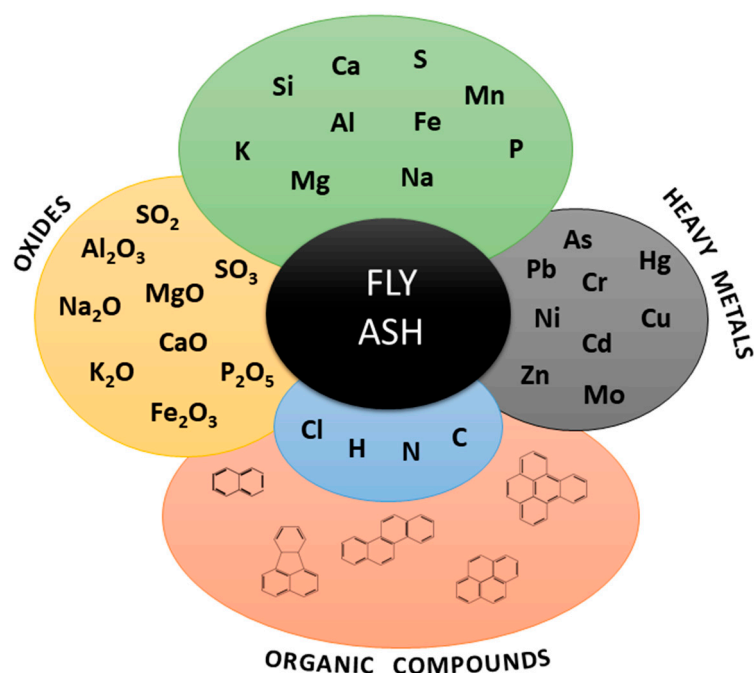
#### 3.1.1. Sources of Fly Ash

The concept of biomass is included in the Regulation of the Minister of the Environment of 20 December 2005 on emission standards for installations (Journal of Laws No. 260 item 2181) [13]. In light of this Regulation, biomass consists of products based in whole or in part on plant substances, which come from agriculture and forestry and are burned in order to recover the energy they contain. Waste from agriculture, forestry and plant waste from the food industry are also biomass. Forest biomass and plant waste from agriculture are most often used in heating plants and combined heat and power plants [14,15]. In Poland, the largest amounts of biomass are ordinary straw (e.g., rapeseed, cereals, sunflowers) [16] and wood chips, sawdust, shavings, bark and waste wood. Pellets, also used for the production of energy and heat are made, e.g., from sunflower hulls or straw and from agricultural processing: oilseed stalks, corn, pomace from the production of cereal coffee, seeds and husks from fruit processing [17]. There are also plantations of energy crops, such as energy willow, poplar, birch and alder, mallow, miscanthus other perennial grasses, reed canary, Pennsylvanian mallow. Fly ashes from biomass combustion are highly diversified, therefore they should be treated with caution, and the decision to use them should be supported by information on their chemical composition and on the kind of material from which they were obtained [11,17,18].

Renewable energy sources, such as biomass are increasingly being used for the production of electricity and heat. In the process of thermal transformation of organic matter of these raw materials, in addition to the generated gases, inorganic oxides are formed, which are anthropogenic minerals, also called as by-products of combustion (UPS) [19]. The furnace waste produced after the combustion of solid biofuels, in accordance with the Regulation of the Minister of the Environment of 9 December 2014 on the waste catalogue (Journal of Laws of 2013, item 21, as amended) is classified as waste group 10 “Waste from thermal processes”, subgroup 01 “Waste from power plants and other combustion plants”, code 10 01 03 “Fly ash from peat and untreated wood” [20].

### 3.1.2. Chemical Composition of Fly Ash

The properties of fly ashes from biofuel combustion depend not only on the type of biomass used to obtain electricity and heat but also on the share of plant organs in the burnt biomass, e.g., the amount of tree bark, branches and the biofuel combustion process, and parameters, grain size, degree of oxidation, or the type of soil on which the energetic plant grew [17]. The chemical composition of wood waste is varied (Figure 2), however, the calorific value of dry wood mass tends to be between  $18.5 \text{ MJ} \times \text{kg}^{-1}$  and  $19.5 \text{ MJ} \times \text{kg}^{-1}$ , while the ash content resulting from the thermal treatment of wood is approximately 0.4–0.8% dry fuel mass. In the case of burning poplars and willows, a high share of ash was observed and it amounted to 1.9% and 2.0%, and for the bark of coniferous trees, it was 3.9% of dry fuel mass [17]. The oxide composition of fly ash is as follows: silicon dioxide ( $\text{SiO}_2$ ) > calcium oxide ( $\text{CaO}$ ) > potassium oxide ( $\text{K}_2\text{O}$ ) > phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) > aluminum oxide ( $\text{Al}_2\text{O}_3$ ) > magnesium oxide ( $\text{MgO}$ ) > ferric oxide ( $\text{Fe}_2\text{O}_3$ ) > sulfur oxide ( $\text{SO}_3$ ) > sodium oxide ( $\text{Na}_2\text{O}$ ) > manganese oxide ( $\text{MnO}$ ) > titanium dioxide ( $\text{TiO}_2$ ). The inorganic components contained in the ash influence their chemical composition. Fly ash contains in the highest content of: calcium (Ca), potassium (K), silicon (Si), magnesium (Mg), aluminum (Al), iron (Fe), phosphorus (P), sodium (Na), sulfur (S), manganese (Mn) and as a trace amounts: chlorine (Cl), coal (C), hydrogen (H) and nitrogen (N) [7,21,22].



**Figure 2.** Chemical components of fly ash.

In addition to the elements available for plants, ashes contain heavy metals, including: Pb, Cd, Cr, Cu, As, Hg, Ni and Zn. Some elements may be present in the water-soluble phase, e.g., Al, Ca, Cl, C, Fe, K, Mg, Mn, N, Na, S, Si, P, As, Cd, Cr, Cu, Hg, Pb, Ni (Figure 2) [23]. Ashes from biomass combustion contain different compounds than ashes originated from burning hard coal. These compounds are: calcium-potassium-manganese silicates, potassium-calcium-magnesium-sodium carbonates and potassium-sodium chlorides and chlorides. The difference in the chemical composition between the above-mentioned ashes results from the lower content of aluminium, silicon, iron and sulphur in fly ash from biomass, and an increased amount of calcium, chlorine, potassium, magnesium, sodium, oxygen and phosphorus [21,24]. Table 1 presents the results of the research on the content of selected oxides included in the fly ash from wood biomass, crops and energy plants [25,26]. The highest amount of CaO is observed in oak ash 50.9%, while

the lowest in spruce ash 14.9%. The ash from the combustion of spruce contains the highest  $K_2O$ , 69.3%. Referring to  $MgO$ ,  $Na_2O$  and  $P_2O_5$ , in all the mentioned ashes, the values oscillated from the lowest value 0.4% to the highest 10.6% [17,21,25].

**Table 1.** Oxide composition of fly ashes from plants and wood biomass as well as energy plants combustion.

Type of Fly	Oxide Composition [%]				
	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
Straw	3.05	1.34	2.3	11.14	10.76
Corn	6.62	2.45	0.05	35.90	9.3
<b>Wood biomass</b>					
Pine	38.9	10.6	1.1	22.0	7.0
Spruce	14.9	3.9	0.6	69.3	3.7
Oak	50.9	5.9	0.5	12.2	3.8
Beech	20.1	14.6	0.4	33.2	4.8
<b>Energy plants</b>					
Willow	46.09	4.03	1.61	23.40	13.01
Poplar	57.33	13.11	0.28	18.73	0.85
Eucalyptus	57.74	10.91	1.86	9.29	2.35
Miscanthus	10.00	-	0.06	11.50	1.61

Various energy crops, can be grown on a larger scale for example: poplar, energy willow, holly willow, basket willow, giant miscanthus, multiflorous rose, sakhalin knotweed, jerusalem artichoke or mallow. The listed plants are characterized by common features; they achieve rapid weight gain in a short time and have a high calorific value from 15 to 19 MJ  $\times$  kg<sup>-1</sup> dry weight of fuel. The content of willow and poplar ashes does not exceed 1% of dry weight. The highest value of ash is obtained after burning miscanthus—approximately 7% and sunflower—5.4%. Table 1 lists four types of ash from the combustion of willow, poplar, eucalyptus and miscanthus and presents their oxide composition [22,27].

In the ashes obtained from biomass, the content of trace elements and most of all the content of heavy metals vary within wide limits. Table 2 presents examples of the amount of heavy metals in ashes from birch and spruce wood given in the literature. In both tested ashes, Zn and Pb had a high value, and Hg content was low [28].

**Table 2.** Heavy metals concentration in fly ash on the example of spruce and birch wood.

Heavy Metals	The Content of Heavy Metals in Ash [Mg $\times$ Kg <sup>-1</sup> ]					
	Birch	Spruce	Poplar	Miscanthus	Eucalyptus	Willow
Cd	26–203	184–4	9	7	-	0.05
Cr	147–508	183–342	101	90	82	0.60
Pb	37–13,700	8–1290	177	57	-	2.84
Ni	18–156	1.4–80	41	45	-	0.21
Hg	0.2–1.7	0.1–1.2	0.2	-	-	-
Cu	138–650	294–860	175	51	158	0.73
Zn	3910–43,500	2630–7910	2274	185	659	1.65

Comparing the content of calcium and sodium oxide in ashes from birch wood chips and spruce and energy plants, the following conclusion can be drawn. In both cases, calcium oxide reaches the highest value, while sodium oxide the lowest. The heavy metal content also follows a similar pattern for the amounts of Pb, Zn and Hg. In poplar ash, zinc and lead are the most abundant: 2274 mg  $\times$  kg<sup>-1</sup> of Zn and 177 mg  $\times$  kg<sup>-1</sup> of Pb, with the lowest value of Hg 0.2 mg  $\times$  kg<sup>-1</sup> (Table 2) [15,22,27].

The final composition of ashes from biomass combustion largely depends on the combustion temperature and the ability of the furnace to create a separate fly ash and bottom ash. Fly ash is the lightest component formed as a result of combustion and deposits on the inside of boiler and ventilation systems. It has a higher content of dioxins and heavy metals as compared to the bottom ash [29].

### 3.1.3. Residual Organic Pollutants in Ashes

After the combustion process, each biofuel leaves a by-product—fly ash, which may contain the so-called persistent organic pollutants (POPs) that include polycyclic aromatic hydrocarbons (PAHs) [30]. As indicated in the literature, PAHs may disturb the proper functioning of organisms due to their toxic, carcinogenic and mutagenic properties [31,32]. Compounds from the PAHs group are classified as non-polar and dissolve in water to a negligible extent. The presence of other organic impurities, e.g., humic compounds, increases the degree of solubility. PAHs adsorb on the surface of solids due to their high affinity to particles, which allows them to travel for long distances. Together with rainwater or meltwater, they can penetrate deep into the soil profile and thus reaching groundwater or surface water reservoirs [30]. PAHs and volatile organic compounds (VOCs), as well as carbon monoxide and nitrogen oxides are formed mainly in the processes of incomplete combustion of coal and wood. The above-mentioned pollutants are emitted during the combustion of biomass in low-power boilers, with unstable operating conditions [33].

Inappropriate conditions during the biomass combustion process lead to the formation of PAHs and their accumulation in fly ash [34]. The content of PAHs in the ash from biomass combustion depends more on the boiler and its operating conditions than on the type of biomass. For example, in the ashes from a wood pellet boiler, mainly high molecular weight compounds were present [35]. On the other hand, the total content of PAHs in straw and wood ash was within a wide range from 15 to 733  $\mu\text{g} \times \text{kg}^{-1}$  [36]. In turn, in fly ash from commercial biomass power plant in the Czech Republic, the content of 16 individual PAHs was 160  $\text{mg} \times \text{kg}^{-1}$  D.M of which the highest content was found in compounds with low molecular weight (75  $\text{mg} \times \text{kg}^{-1}$  D.M) [34]. Masto et al. [37] reported that ashes from biomass burned at a temperature of 850 °C have a relatively high content of PAHs (193  $\text{mg} \text{PAHs} \times \text{kg}^{-1}$  D.M of ash).

Temperature is a factor that leads to the formation of PAHs during the combustion process that takes place at temperatures ranging from 500 °C to 1000 °C or higher [38]. Most of them are formed during combustion at temperatures between 500 °C and 700 °C. Furthermore, at 320–700 °C, their formation is fostered by combusted products containing lignin, cellulose, starch, simple sugars, amino acids, fatty acids,  $\beta$ -carotene, cholesterol glycerides [28,34]. PAHs are determined as the sum of 16 compounds: benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IP), dibenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP), naphthalene (NA), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PH), anthracene (AN), fluoranthene (FLU), pyrene (PY), chrysene (CHR) (Table 3).

To sum up, a larger amount of PAHs volatilizes with other gases and volatile organic compounds, with a smaller one being transferred to the combustion residue. However, before the fly ash is used as an additive to building materials or fertilizers for cultivation, a number of analyses should be conducted to allow the by-product of combustion to be used. It is important to carry out tests for the content of heavy metals, chlorides, sulphates, microelements and macroelements, grain and phase composition and organic compounds, e.g., BaA, BaP, BghiP. The safety of the soil and water depends on the degree of leaching of pollutants contained in materials in contact with the environment [30].

**Table 3.** Content of PAHs in fly ash from biomass combustion [29,32].

PAHs	PAHs Content (mg × kg <sup>-1</sup> D.M)		
NA	11.1	1.87	19.1
ACY	0.427	0.018	12.6
ACE	0.030	0.005	3.9
FL	0.022	<0.0007	0.2
PH	0.386	0.551	17.9
AN	0.045	0.067	21.7
FLU	0.198	0.551	16.3
PY	0.119	0.151	6.5
BaA	<0.0004	0.006	7.3
CHR	<0.0003	<0.0003	6.5
BbF	0.003	0.014	13.8
BkF	<0.001	0.022	7.6
BaP	0.003	0.088	15.0
DahA	<0.006	0.117	1.2
IP	<0.006	0.029	3.9
BahIP	<0.006	0.101	6.7
<b>Sum of 16 PAHs</b>	<b>12.3</b>	<b>3.59</b>	<b>160.2</b>

#### 3.1.4. Leachability of Impurities

Ashes resulting from the thermal treatment of biomass may show a high leachability of pollutants into the environment. Ash has a high content of soluble components, such as: chlorides (halite, sylwin), sulphates (syngenite, gypsum), oxides (calcium oxide), hydroxides (portlandite), nitrates, carbonates and bicarbonates. The average content of elements that can penetrate into the environment by their leachability can be ranked as follows: Cl > S > Na > Sr > Ni > Mn > Cd > Cr > Zn > Co > Si > Mo > Li > Mg, Pb > Ca > Cu > Ba > P > Se > Sb > Al > Fe > Br, Hg > As, B, Sn, Ti, V [11,12,16]. The leachability of individual elements depends, among others, on their pH. With the alkaline reaction, the leachability of elements, such as Al, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Zn is lower, while it increases for the following elements: As, B, Cr, Mo [7,39]. Hydration products, including calcium aluminosilicate or portlandite, at a high pH decrease the mobility of pollutants by physical means, reducing the ash porosity or chemically binding toxic elements. The process of natural carbonation lowers the reaction and, as a consequence, releases heavy metals from the ashes into the environment, e.g., Cr [7,21,26]. Table 4 presents the results of the research on leachability of heavy metals from ashes from the combustion of spruce and forest biomass in comparison with the permissible maximum values specified in the Regulation of the Minister of the Environment of 18 November 2014 on the conditions to be met when discharging sewage into or out of water land and on substances particularly harmful to the aquatic environment [12,21].

**Table 4.** Examples of the results of determinations of basic components of ashes from the combustion of energy plants.

Type of Ash	pH	Leachability of Contaminants						
		Cd	Cr	Pb	Ni	Hg	Cu	Zn
Spruce [mg × kg <sup>-1</sup> ]	12.70	<0.01	6.20	0.09	1.10	-	0.07	0.31
Forest biomass [mg × D.M <sup>-3</sup> ]	12.25	0.0003	0.001	0.01	-	0.0001	0.45	-
Permissible max. values <sup>1</sup> [mg × D.M <sup>-3</sup> ]	6.50–12.5	0.40	0.50	0.50	-	0.06	0.50	-

<sup>1</sup> Regulation of the Minister of the Environment of 18 November 2014 on the conditions to be met when discharging sewage into water or soil and on substances particularly harmful to the aquatic environment.

The fly ash from biomass presented in Table 4 is alkaline. According to Vassilev [7], the pH value tends to range from 4.5 to 13.4 and it depends on the high content of components rich in K, Cl, Ca and Mg. The process of biomass combustion creates soluble Ca, Mg, K and

Na compounds (oxides, hydroxides, carbonates, bicarbonates), which in turn results in an increase in the pH. The alkaline character of the ashes decreases with the increase of the combustion temperature and the storage time [21,40].

### 3.1.5. Distribution of Particle Size of Ashes from Biomass Combustion

The grain size composition of biomass ashes depends on the material to be burned as well as the type of boiler in which the biofuel was burned. Cuenca et al. [41] performed a sieve analysis of the residue after burning the biofuel, i.e., olive pomace, obtaining the following results: the fraction sieved through a sieve with a mesh size of 2 mm was 100% of the tested sample and 0.125 mm, approximately 96% and 0.063 mm and approximately 81%, whereas Romero et al. [42] found that the residues after burning wet olive and sugar cane waste in the fluidized bed boiler had 45% of small grains that were below 50  $\mu\text{m}$ , which was the largest share, and only 10% of large particles were above 250  $\mu\text{m}$ . Modrzycka et al. [43] published the results of research on the grain size distribution of ashes resulting from the combustion of a mixture of wood waste and straw and wood and coconut shell. The grain size distribution in ashes from individual types of biomass is as follows Table 5 [43,44].

**Table 5.** Graining of fly ashes from the combustion of selected types of biomass.

Distribution of Particle Size Biomass Fly Ashes	Grain Fractions	Percentage [%]
Wood waste (79%) and straw (21%)	50–56 $\mu\text{m}$	36.3
Wood waste (80%) and coconut shells (20%)	56–63 $\mu\text{m}$	48.6
Eucalyptus bark with forest biomass	<2 $\mu\text{m}$	12
	>2 $\mu\text{m}$ <50 $\mu\text{m}$	76
	>50 $\mu\text{m}$ <2 mm	12

The authors performed a sieve analysis of fly ash using a set of sieves with mesh sizes of 0.2–0.02 mm. The particle size distribution of both samples is in the range of 25–100  $\mu\text{m}$ . The fraction of 50–56  $\mu\text{m}$  (36.3%) for sample 1 is the highest, and the fraction of sample 2 is 56–63  $\mu\text{m}$  (48.6%). Grains between the particle size above 2  $\mu\text{m}$  and below 50  $\mu\text{m}$  constitute as much as 76% [45].

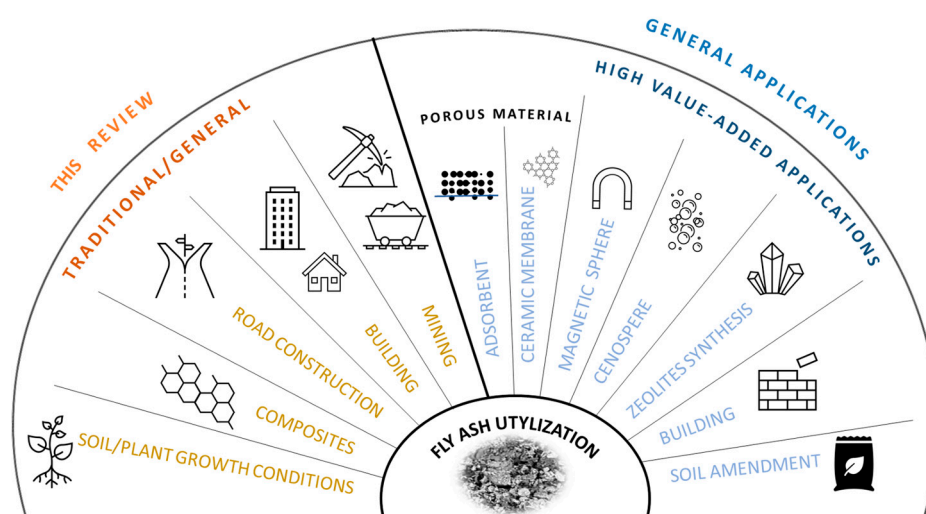
## 3.2. Directions for the Management of Ashes from Biomass Combustion

### 3.2.1. Application of Ashes in Civil Engineering

In the building materials industry, ashes are used on a large scale, mainly for the production of cement (Figure 3). The advantage of ashes is their ability to bind with calcium compounds. These features make them a valuable component of cements, equivalent to mineral aggregates. Ashes are used as active additives that change the functional properties of the binder, leading to the formation of pozzolanic cement; they also increase the mass of cement and improve its frost resistance and are also used as a raw material for the production of Portland cement clinker [46].

Ash is a material used in the production of concrete in the form of mixtures and prefabricated elements. This reduces the water demand and improves the workability of the mixture. In the production of cellular concrete, ashes play the role of the aggregate and partially a binder. Products with good technical properties are obtained with reduced production costs [46,47].

The use of ashes as a raw material allows for reducing the sintering temperature, sometimes even by 200–300  $^{\circ}\text{C}$  and thus decreasing the consumption of process fuel by up to 30%. Depending on the content of individual oxides in the charge, the ashes can be used as a silica, iron-bearing or clay-bearing additive [47].



**Figure 3.** Fly ash utilization.

According to Szcześniak et al. [47], when examining an increase in the strength of mortars with ashes from co-incineration, it was found that replacing 10% of the cement mass with ash does not cause other changes in the mechanical properties of the mortars. The limit of ash content for which the required compressive and tensile strength can be achieved is 20% in relation to the weight of the cement. Moreover, concrete containing ash from co-incineration does not pose a threat to groundwater and soil and thus to humans and animals [48]. The addition of fly ash can also improve the resistance of the concrete to chloride ingress, which results in a reduction in the calorific value of the concrete mixture, thus directly limiting the shrinkage phenomenon of concrete [42]. Rutkowska et al. [49] indicated that the use of fly ash increased the concrete mixture fluidity, reduced water absorption and increased watertightness of concrete compared to ordinary concrete.

The beneficial effect of biomass ashes on cement properties was observed by Rajamma et al. [50]. In these studies, an increase in strength was observed, both early (2 and 7 days) and after a longer curing period (28 and 90 days). Moreover, when analyzing the physical properties, it should be emphasized that there is no drastic increase in the water demand for cement, which is related to the high fineness of biomass ash [51]. As reported in the literature, biomass ash was also considered as an addition in production of ceramic products, such as clay bricks [52] and electrical siliceous porcelain [53].

Due to the high content of lime, they are suitable for the production of road binders, allowing for soil stabilization and lowering the cost of the binder, while achieving the same stabilization parameters as with the use of pure lime or cement [54]. As the research of Skels et al. [55] showed, the addition of wood fly ash (in the amount from 10 to 30%) to dolomite crushed stone and gravel increased the strength and stiffness of the road layer. Moreover, as noted by Cabrera et al. [56], ashes from biomass combustion are used as a cement substitute in the stabilization of the base of roads with low traffic.

In geotechnical application, the biomass derived fly ash might be used as a material applicable for embankments on soft soils, lightweight backfill material behind the retaining wall, to fill underground cavities as cost effective material [57]. Sarkkinen et al. [58] conducted tests on two types of biomass derived ashes as materials to be used as road stabilization binders (Figure 3). The conclusion from the study was that the properties of ashes from biomass are dependent on furnace technology and each use of biomass ash should be preceded with thorough research. In case of highly expansive soils (clayey soils with high swelling potential), the biomass bottom ash added in various portions reduced the expansiveness [59]. An optimum amount of the bottom ash from combusting grapes (16%) was established, and for bottom ash from olive wastes it was 20%.

For many decades, ashes from coal combustion have also been used in underground mining as a component of materials for filling mining workings (Figure 3). Thus, contribut-

ing to the reduction of the amount of quartz sand used for backfilling purposes. The ashes are used for liquidation and filling of old goafs, active goaf walls and redundant corridors, explosion-proof dams and inhibition of explosions, elimination of fire hazards, methane extraction in order to recover methane, counteracting air leakage through goafs [60]. It seems that the ashes resulting from biomass combustion would also be perfect for this purpose and should be used in mining.

### 3.2.2. Application of Ashes in Materials Used in Industry

The new and innovative directions of energy waste management also include the use of ashes as fillers in the processing technologies of polymeric materials, such as polypropylene, poly (vinyl chloride), polyethylene, poly (ethylene terephthalate) [61]. Polymer-based products that use ash fillers are characterized by better mechanical properties, greater abrasion resistance and lower flammability. Kuźnia et al. [61] noted that incorporation of ashes into the polyurethane matrix up to 10% improved the mechanical performance and thermal stability; yet, over 10% caused a deterioration of the mechanical properties of polyurethane composites. Moreover, the use of ashes as fillers reduces the breaking stress and deformation of composites. Furthermore, it increases the modulus of elasticity and hardness so that the composites do not break brittle [62]. As confirmed by the research of Gnatowski et al. [62], the addition of ash from biomass combustion (containing 17% CaO and 57% CaO) to polyamide influenced the thermal and mechanical properties of the material and the compatibility of the polymer matrix and filler. Moreover, it was observed that the addition of 5% ashes as a filler had a greater reinforcing effect than if added in greater amounts.

In another study [62,63], the influence of biomass ash on fracture and thermal behavior on polypropylene composites was tested (Figure 3). Different composites based on polypropylene, olefin block copolymer and biomass ash in various amounts were studied. The ternary composites had higher toughness than polypropylene matrix. The best fracture properties under quasistatic loading conditions were observed for samples with olefin block copolymer to ash ratio was 1:1.

### 3.2.3. Application of Ashes to Improve the Quality of Soils and Plant Growth Conditions

According to Huygens et al. [64] and Zhai et al. [65], in most of the tested ashes from biomass combustion, the content of PAHs is appropriately lower than those proposed by the EU, which makes it possible to use them as a fertilizer (Figure 3). In addition, the low content of heavy metals supports the use of ashes as fertilizers [66].

Although the dominant directions of energy waste recovery are still: building materials industry and construction, road construction and underground mining, attention is increasingly paid to their use in agriculture as fertilizer [6,7]. The introduction of ash into the soil contributes to improving water migration in the soil, reducing fertilizer leaching, increasing the capacity of soil sorbents (solid components of the soil that are involved in the exchangeable ion sorption of the soil solution), reducing soil density and alkalizing acid soils [67].

One cannot ignore the fact that ashes from biomass combustion are the oldest mineral fertilizer. Due to the high concentration of Ca and Mg, the by-products of biomass combustion are a substitute for calcium fertilizers, demonstrating de-acidifying properties [68]. In addition, ashes from biomass combustion are rich in other fertilizing components (K, P, S, Si and micronutrients); therefore, they can be used as a substrate for soil reclamation and/or a fertilizer improving the conditions for plant growth [69,70]. As confirmed by many years of research carried out by Jacobson et al. [8] in which a sustained pH improvement effect was observed, even 5–6 years after the use of ashes. In addition, the application of ash from the combustion of wood chips allows for increasing the yield of plants on certain types of soil by up to 45% as compared to traditional calcium fertilizers [71]. According to Wierzbowska et al. [15], enriching soils with ashes increased the abundance of nutrients, and by increasing the soil pH, inhibited the migration of potentially toxic metals from the soil to the plants.

Moreover, the applied ash did not affect the biodiversity of microorganisms in the soil and did not adversely affect the colonization of mycorrhizal fungi. Moreover, according to Lindvall et al. [72], the alkaline reaction of biomass combustion products is suitable for the care of lawns, which was observed in studies where the application of biomass ash had a positive effect on the yield of some grass species in comparison with the control plots, and the effect of ash on the grass growth rate was comparable to the action of other mineral fertilizers.

One of the basic parameters determining the use of ashes for agrochemical and remediation purposes is the content of both CaO and SiO<sub>2</sub>. Calcium oxide performs two main tasks in soils: regulating the pH of acidic soils and supplying calcium to improve the buffer properties of the sorption complex, while SiO<sub>2</sub> influences water retention and shaping the crystalline structure of soils [73,74]. Ash can also be used to fertilize plantations of organic plants or to enrich forest soils. The return of ash generated from biomass combustion to the soil is the most ecological and sustainable way of their disposal. A significant part of macro- and microelements taken up by plants from the soil returns to the habitat, closing the cycle of minerals. The dose of ash favors the improvement of plant yield [8]. There are many reports in the literature on the impact of the application of ashes from biomass combustion on the improvement of the physicochemical properties of soils. Table 6 summarizes the benefits of soil fertilization with appropriate doses of fly ash from the combustion of individual types of biomass [68,74–76].

**Table 6.** Effect of dose and type of fly ash from biomass combustion on soil properties.

Type of Biomass Burned	The Dose Applied to Soil	Benefits of the Fly Ash Used
Spring barley	32 t × ha <sup>-1</sup>	Change in soil reaction from slightly acidic (pH = 6.5) to alkaline (pH = 8.6). The alkaline reaction lasted approximately 4 months after the application of the powdery material to the soil. Increase in the phosphorus content in the soil from 138 to 274 P mg × kg <sup>-1</sup> . Increase in magnesium content from 22 to 44 Mg mg × kg <sup>-1</sup> .
	30 t × ha <sup>-1</sup>	Increase of available potassium concentration from 160 to 2067 K mg × kg <sup>-1</sup> .
	16 t × ha <sup>-1</sup>	Increasing the amount of magnesium from 22 to 37 Mg mg × kg <sup>-1</sup> .
Rapeseed straw	>8 t × ha <sup>-1</sup>	Change in soil magnesium abundance from low to medium class.
	8 t × ha <sup>-1</sup>	Change in soil pH from 6.5 to 7.5. Increase in the concentration of available phosphorus by 43%. In contrast, potassium by 235% compared to the control sample (160 K mg × kg <sup>-1</sup> ).
	1 t × ha <sup>-1</sup> , 2 t × ha <sup>-1</sup>	Increase in the concentration of available phosphorus by 24% and 27%, respectively.
Wood chips, willow, straw	0.75 t × ha <sup>-1</sup> , 1 t × ha <sup>-1</sup>	Increasing the absorbable potassium in the soil by 22.5% and 40%.
	10.5 t × ha <sup>-1</sup>	Change in pH from 5.20 to 5.74. The decrease in hydrolytic acidity by an average of 0.58 me × 100 g <sup>-1</sup> of soil compared to non-fertilized soil. Increasing the degree of saturation of the complex with alkaline compounds by approximately 12%. Change in potassium from medium to very high in soil.

It cannot be ignored that in addition to improving the physicochemical conditions of soils, the application of ashes may affect plants grown on such soil. According to Wierzbowska et al. [15], fly ash from biomass combustion has a positive effect on the yield of the *Festilolium* grass species compared to non-fertilized grass. The rate of grass growth

was comparable to that of other mineral fertilizers. Ashes in their composition contain Fe, which improves the condition and colour of the grass. Fly ash has been shown to increase the yields of Bermuda grass (*Cynodon dactylon*), Sabai grass (*Eulaiopsis binata*), mung (*Vigna unguiculata*), white clover (*Trifolium repens*), wheat (*Triticum aestivum*), alfalfa (*Medicago sativa*), barley (*Hordeum vulgare*), also improving the physical condition and chemical properties of the soil [77–80]. Furthermore, when using biomass fly ash as a fertilizer, other components containing K, Mg, Ca and Fe may not be added. Mixing biomass fly ash with and other mineral fertilizers can cause problems with the uptake of B or Fe, which consequently reduces the growth of the grass [78,81].

Basu et al. [78] investigated that after applying an ash dose of  $125 \text{ MT} \times \text{ha}^{-1}$  on acidic soil with a pH of 6.0, crops such as alfalfa, sorghum (*Sorghum bicolor*), maize (*Zea mays*), millet (*Echinochloa crusgalli*), carrot (*Daucus carota*), onions (*Allium cepa*), beans (*Phaseolus vulgaris*), cabbage (*Brassica oleracea*), potatoes (*Solanum tuberosum*), and tomatoes (*Lycopersicon esculentum*) showed higher levels of As, B, Mg and Se. The use of fly ash also improves the yield of oilseeds, e.g., sesame (*Sesamum indicum*) or sunflower (*Helianthus* sp.). The application of different concentrations of fly ash with the soil resulted in a high yield of aromatic grasses, especially palmarosa (*Cymbopogon martini*) and citronella (*Cymbopogon nardus*) due to the increased availability of the main nutrients necessary for plant growth and development [78,81].

Zapałowska [82] investigated the effect of by-products of combustion of various plant biomass on the yield of cereals. The research used an ash from the combustion of wood chips, wood chips + maize + straw, wood chips + willow, oat grains, winter maize straw and oak wood chips, in doses of 3 and  $6 \text{ t} \times \text{ha}^{-1}$ , respectively. In each case, the application of ash resulted in an increase of the yield by an average of 3–19%, depending on the type of material used. The best results were obtained in the case of fertilization of cereals with ash from the combustion of oats, while the ash from the combustion of a mixture of wood chips and willow was the least effective [82,83].

Combustion by-products are an excellent substitute for highly effective mineral fertilizers. The research of Mohammadi et al. [75] showed that the use of ash at a dose of  $60 \text{ t} \times \text{ha}^{-1}$  allowed for obtaining approximately 10% higher maize yields compared to plants fertilized with commonly available mineral fertilizers. Additionally, the application of ash resulted in an increase in Mg and P content in maize grain, with the best results obtained for the highest tested ash doses, i.e., 60 and  $120 \text{ t} \times \text{ha}^{-1}$ . Mohammadi et al. [64] also noted an increase in the content of K, Ca and Na in maize grain compared to the control sample. However, no clear relationship was found between the content of elements in the cereal grain and the applied ash dose, while the concentration of Mn, Zn and Cu in the green mass of maize was higher for larger amounts of the applied powdery materials.

The literature study shows that the use of fly ash from the thermal treatment of biofuels has a positive effect on the growth and development of plants, such as maize, sunflower, rape, asparagus, barley and couch grass [84]. On the other hand, plants that moderately tolerate salinity caused by fertilization with ash are vetch, alfalfa, flax, potatoes, melon and pumpkin. However, fly ash may adversely affect the development of plants that prefer acidic and slightly acidic soils [85]. Due to the fact that the ash changes the acidic pH soil reaction to alkaline or neutral, the development of certain plants can be reduced, as is the case with the following species: coniferous shrubs, azalea, goi berries, honeysuckle berry, blueberry or rhododendron [83].

#### 4. Conclusions

The possibility of using ashes from biomass combustion is the subject of numerous discussions and comments made by both its opponents and supporters. Regardless of the prevailing trend, it should be remembered that the disposal of ashes from biomass combustion should be in accordance with the best technological practices and legal regulations, while maintaining economic efficiency. In the case of biomass ashes, a large variability of properties and composition is observed, resulting from the differentiation of the raw

materials used and the combustion conditions. Therefore, new directions of development are sought, including the synthesis of zeolites and geopolymers, the recovery of rare earth metals and the production of plastics.

However, in the last years, the ashes from biomass combustion have increasingly been used as material for improving soil quality, in agriculture and in remediation and reclamation techniques. Using ash as a binding additive is also being considered in the production of fertilizers from other wastes, such as sewage sludge. Ashes seem to be a valuable material for improving the yield and growth of plants. However, their safe use for environmental purposes requires extensive knowledge based on research results, taking into account environmental and technical aspects and changes in legal regulations. In addition, as noted by Cruz et al. [44], there is still little information on the potential environmental hazards resulting from the leaching properties of biomass ash after the application to soil and the associated threats to soil biodiversity.

However, the use of fly ash from biomass combustion is a dynamically developing issue that is still insufficiently understood, and the strategy for the management/use of ashes from biomass combustion should be based mainly on the chemical composition of the ashes, in particular their content of heavy metals or PAHs and geotechnical parameters.

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