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The evaluation of fertilizer obtained from fly ash derived from biomass

Introduction

Energy forecasts indicate upward trends till 2030. By 2020, the size and structure of domestic demand for primary energy is presented as follows: derived from hard coal – 34.4%, brown coal lignite – 12.5%, renewable energy sources – 30% etc. The data confirms that the domestic base consists of hard coal and brown coal lignite. The share of coals in energy production in EU countries, including Poland, depends both on technical and technological as well as economic and environmental conditions. As a result, it will enable the market to supply various fuels that meet the requirements of customers and the environment (Hycnar and Blaschke 2002).

Forecasts indicate continuous increase in demand for energy e.g. in year 2020 and 2025 – 599 EJ and 657 EJ respectively (Lewandowski 2006). The improvement of the energy balance can be achieved through the use of renewable energy sources. This is due to

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requirements applicable for EU countries as well as the need for the sustainable consumption of raw materials, including energy resources, and meeting the environment protection requirements (Regulation of the Ministry of the Economy 14 August 2008 – Journal of Laws No. 156, item 969). EU directive postulates that the share of renewable energy in the energy balance should reach 20%. Domestic prognostic analyses of the energy demand are based, among others, on assumptions such as: the reduction of greenhouse gas emission in accordance with the climatic policy, an increase in the share of renewable energy in the domestic energy balance sheet, lowering energy consumption of the national economy and so on. Biomass is the third largest natural source of energy in the world, generated mainly from plants for energy purposes (wastes from the wood and agricultural industry and energy crops, etc.).

Research carried out by European Center Energy shows that Poland has a great technical potential enabling it to extensively use renewable energy, in particular energy derived from biomass. Table 1 lists the net calorific values of several fuels.

Table 1. Net calorific values of several biomass and fossil fuels (Wacławowicz 2011)

Tabela 1. Wartości opałowe wybranych paliw kopalnych i biomasy

Kind of fuel	Net calorific value (MJ/kg)
Yellow straw	14.5
Gray straw	15.2
Firewood	13
Pellet	19
Ethanol	25
Hard coal	25
Natural gas	35
Heating oil	42

For comparative purposes, heating values for some conventional fuels are given. From the above data it appears that biomass is an interesting fuel (Tytko 2010; Krawiec 2010).

Obtaining energy from biomass is one of the elements of the Polish Energy program until the year 2050 (Conclusions 2014).

The so-called “Green Unit”, which burns only biomass, was built and launched in 2012 in the Połaniec Power. The biomass consists of woodchips and agricultural by-product such as seeds, straw and sunflower husks. The share of both components amounts to 80% and 20% respectively. The Połaniec Power plant produces 25% of the ecological energy in Poland. It is estimated that in the future, approx. 1.5 million tons of biomass can be burnt in this Unit and the amount of ash will be 50 thousand tons per year. The production of energy by the Green Block causes a significant reduction of annual carbon dioxide emissions compared to the coal-fired unit. The disadvantages of burning biomass include the formation of ashes and NO_X emission. During the combustion of biomass, two types of waste are generated, namely fly ash, marked with code 100101 and bottom ash – 100124. Data in the literature indicates that ashes derived from biomass combustion have slightly different chemical and physical properties than the ashes derived from hard coal or the co-combustion of coal with biomass (Żelazny et al. 2015). The ashes from biomass combustion are richer in potassium and phosphorus and these components hinder their application in the production of cement or building materials. Fly ashes from biomass combustion were analyzed for the application as fertilizers and for the processing by nitric and sulfuric acids to recover potassium and phosphorus. These components are important for the Polish economy. Phosphorous raw materials are classified as critical raw materials and potassium raw materials are key raw materials (Kulczycka 2016).

1. Aim and scope of work

The ashes derived from the "Połaniec Power Plant" have been stored until now and this sole reason substantiates the need for research on their utilization.

The main aim of the work is to develop a procedure for obtaining granular nitric- phosphoric-potassium mineral fertilizer with prolonged action obtained from ashes derived from biomass combustion in the fluidized bed boiler.

The main object of the research was ash from the Połaniec Power Plant, derived from biomass combustion (containing 80% of dendromass and 20% of agromass).

Research encompassed the following stages:

- characteristics of ash derived from the "Połaniec Power plant",
- assessment of the possibility of using fly ash for alkalization (liming) of soils,
- preparation of a recipe for granular fertilizers based on ash and the preliminary applicability assessment of the obtained fertilizer.

2. Materials and methods

The subject of the research was fly ash from the combustion of biomass in a fluidized bed boiler. The fuel was composed of 80% dendromass and 20% agromass. Individual samples differed in the type of agromass used (Table 2).

The chemical composition of the tested samples was determined using the Perkin-Elmer emission spectrophotometer ICP – OES Plasma – whereas the mineral composition was determined by means of an X-ray diffractometer (Philips PW 1830). Selected samples were observed under a Scanning Electron Microscope (SEM). A qualitative chemical analysis with an Energy Dispersive Spectrophotometer (EDS) was applied.

Table 2. The chemical composition of used fly ashes

Tabela 2. Skład chemiczny badanych popiołów lotnych

Type of fly ash*	Content (% weight)							
	K_2O	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	SO_3	SiO_2
1	13.2	2.9	17.4	2.0	0.7	0.9	4.6	50.1
2	6.9	4.3	16.2	3.3	2.9	2.1	3.7	58.3
3	4.7	2.3	15.9	2.2	3.4	3.4	2.8	60.5

* Type 1 – obtained from a batch containing 20% agromass, 80% dendromass in the form of straw; Type 2 – 20% in the form of dried fruit, 80% dendromass; Type 3 – 20% in the form of slates of palm nut, 80% dendromass.

Table 3. Content of some elements in fly ashes

Tabela 3. Zawartość niektórych pierwiastków w popiołach lotnych

Type of fly ash	Content (mg/kg)						
	B	Zn	Cu	Pb	Cd	Hg	Mn
1	97	164	32	41.6	5.2	0.0	1 100
2	350	290	88	50.8	7.0	0.0	3 400
3	141	239	61	59.1	6.1	0.0	3 300

Description of samples as in Table 2.

3. Results and discussion

3.1. Characteristics of fly ashes

Knowledge of physical properties is required, among others, in many unit operations, such as transportation, storage of drying and in the case of heterogeneous reactions, etc. For this purpose, some of the properties were determined, for example: density, bulk density, grain composition. The grain composition of tested ash samples is given in Fig. 1 while the sample densities are shown in Table 4.

The above data shows that the ash differs in terms of physical properties and these characteristics depend on the type of agromass load used. These ashes contain mainly fine fractions. After leaching with water the obtained eluate was highly alkaline – pH ≥ 11. Therefore, significant losses of ammonia and phosphorus in the NPK fertilizer should be taken into account (decomposition of ammonia from the nitrate ammonia compound and the for-

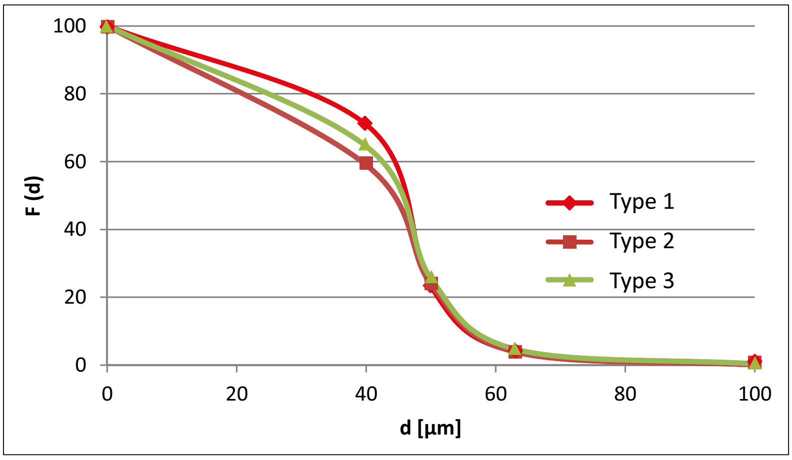

Fig. 1. Grain composition of tested samples of fly ashes
Type 1 – obtained from a batch containing 20% agromass in the form of straw,
Type 2 – 20% in the form of dried fruit, Type 3 – 20% in the form of slates of palm nut

Rys. 1. Skład ziarnowy badanych popiołów lotnych
1 – z próbki zawierającej 20% agromasy w postaci słomy, 2 – 20% w formie suszu owocowego,
3 – 20% w postaci łupków orzecha kokosowego

mation of phosphorus compounds insoluble in water in these conditions). This is confirmed by the leachability results (Table 5).

Table 4. Some properties of tested samples

Tabela 4. Niektóre właściwości badanych próbek

No*. sample	Density (kg/m^3)	Bulk density (kg/m^3)	Porosity	pH (10% – aqueous suspension)
1	2 487	450	0.82	11.7
2	2 695	720	0.73	12.3
K	2 543	610	0.76	11.8

* Description of samples as in Table 3, K – sample averaged from fly ash from the batch (20% – straw).

Table 5. Example of the eluate of some components in water from fly ash (agromass – straw)

Tabela 5. Przykłady wymywalności niektórych składników w wodzie z popiołu lotnego (agromasa – słoma)

Fly ash	Content (ppm)				
	K	Ca	S	Mg	B
(20% straw)	4.5	0.7	0.15	1.5	8.7

The data presented in Table 2 and 3 as well as in the literature reports show that in terms of the chemical composition fly ash is a very heterogeneous material.

This data reveals the difference in the content of individual components. In terms of potassium content, the richest material is fly ash from biomass combustion – straw. This material is, however, poorer in phosphorus. Fly ash 1 and 2 are interesting from the standpoint of their use for fertilizing purposes. Fly ash obtained from the combustion of feeds containing agromass in the form of slate is characterized by both a low content of potassium and phosphorus. The chemical analysis of fly ash from biomass combustion confirms the presence of trace elements (micro elements) (Table 3), desirable from the point of view of converting fly ash into mineral fertilizers.

Although silica is neither a macro nor a micronutrient, it plays an important role. Silica improves soil structure and increases plant resistance to fungal diseases.

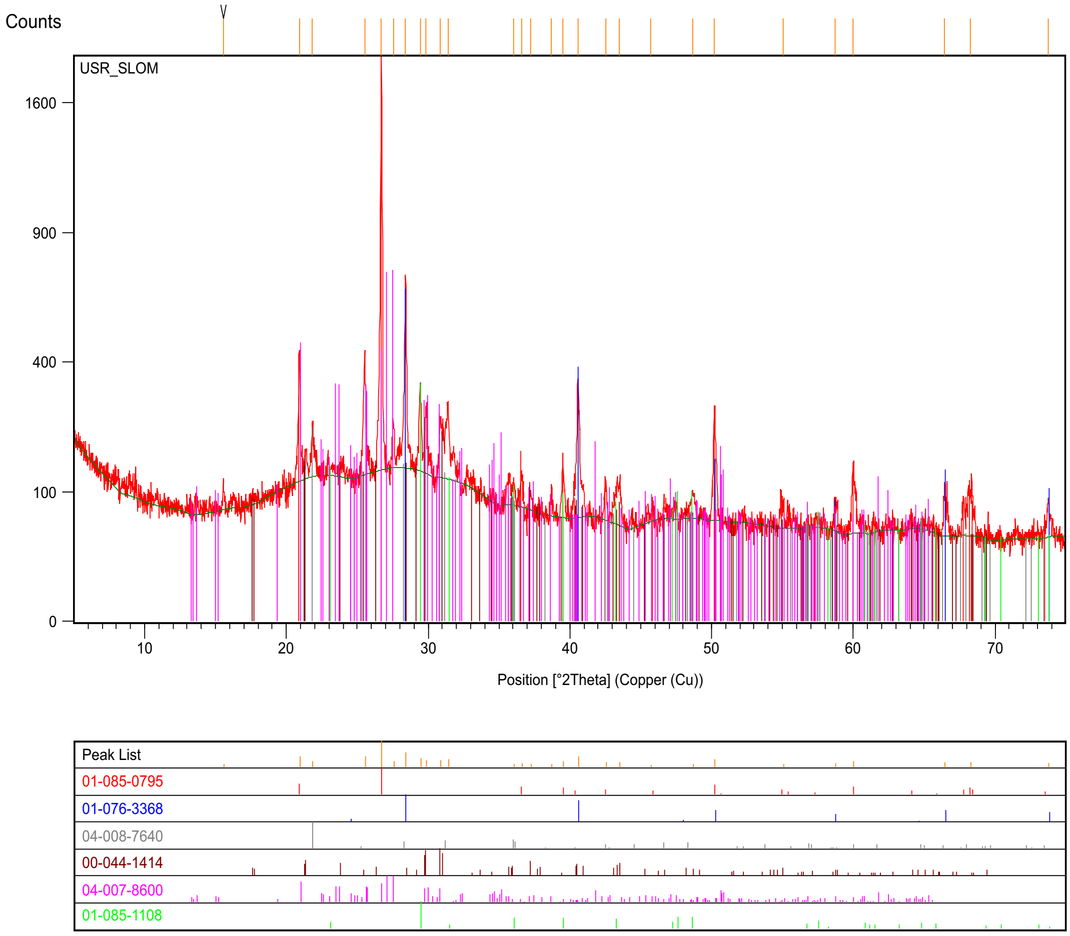

Fig. 2. X-ray diffraction pattern of fly ash from the combustion of biomass (20% agromass – straw)

Rys. 2. Analiza dyfraktometryczna popiołu lotnego pochodząca ze spalania biomasy (20% słomy)

Table 6. Share of individual mineral phases in fly ash (sample 1)

Tabela 6. Udział poszczególnych faz mineralnych w popiele lotnym

Ref. Code	Compound Name	Chemical Formula	Space Group	Semi Quant (%)
01-085-0795	Quartz, syn	SiO_2	P3221	25
01-076-3368	Sylvine	KCl	Fm-3m	5
04-008-7640	Cristobalite low	SiO_2	P41212	1
00-044-1414	Arcanite, syn	K_2SO_4	Pmcn	5
04-007-8600	Potassium tecto-alumotrisilicate	$KAlSi_3O_8$	C-1	60
01-085-1108	Calcite	$CaCO_3$	R-3c	4

X-ray analysis allowed the mineral composition of the tested fly ashes derived from biomass combustion to be determined. For example, the X ray pattern of fly ash derived from a batch combustion with a 20% straw content is shown (Fig. 2). In addition, the presence of a silicate phase in the form of potassium tecto-alumotrisilicate was found. Furthermore, potassium was found in the form of $KAlSi_3O_8$ and KCl and K_2SO_4. Calcium in the form of calcite is present in small amounts. In general, these phases were found in the studied ashes. In summary, it can be stated that in terms of mineral composition, the examined ashes do not differ significantly.

Additionally, the analysis of samples was carried out using a SEM microscope with XRF analysis at selected points. For example, the results of the above analysis for a sample derived

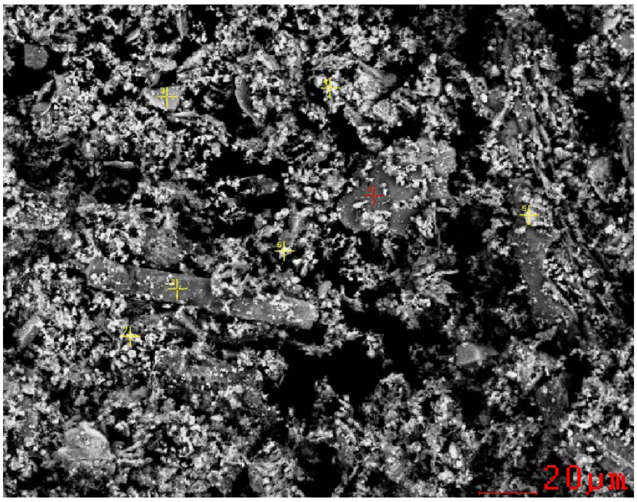

Fig. 3. SEM image of fly ash and point (red +) to XRF analysis

Rys. 3. Zdjęcie SEM popiołu lotnego z zaznaczeniem (punkt czerwony +) miejsca wykonanej analiza XRF from biomass combustion with a 20% agromass (dried material) are shown in Figure 3 and in Table 7. This analysis confirms the presence of silicate phases that form potassium-calcium silicates with potassium. These phases are hardly soluble in water, which is confirmed by the results posted in the work (Żelazny et al. 2014).

Table 7. Composition of fly ash (agromass – dried material) sample in point + red, according to XRF analysis

Tabela 7. Skład próbki popiołu lotnego (agromasa – susz owocowy) według analizy XRF w punkcie „+ czerwony"

Element	C	O	Mg	Al	Si	P	S	Cl	K	Ca
Content (%)	7.10	17.39	0.93	1.29	54.55	0.60	1.36	3.27	7.02	6.21

3.2. Assessment of the usefulness of fly ash for fertilizing purposes

The analysis of characteristics of fly ash from biomass combustion indicates their usability in correcting the pH of soils. According to the fertilization law in Poland, liming materials should meet the requirements for the maximum permissible content of cadmium and lead per kg CaO in the case of products free of magnesium and per kg (CaO + MgO) for liming materials containing magnesium (Table 8).

These indicators should not exceed the following values: for cadmium-content:
8 mg Cd kg s.m. or 5 mg/kg (CaO + MgO), while for lead 200 and 600 mg/kg respectively.

Table 8. Cadmium and lead content in fly ashes in relation to CaO or (CaO + MgO)

Tabela 8. Zawartość kadmu i ołowiu w popiołach lotnych w odniesieniu da CaO lub (CaO + MgO)

Type of fly ash	Cadmium content (mg/kg CaO)		Cadmium content (mg/kg CaO + MgO)	
	Cd	Pb	Cd	Pb
1	29.9	239.1	26.8	214.4
2	43.2	313.6	35.9	260.5
3	38.4	371.7	34.3	332.0
4	32.7	98.2	30.0	87.0
5	32.6	34.8	29.1	31.1
6	38.2	303.2	37.9	256.2
7	8	200	5	600

1 – obtained from batch 20% straw; 2 – 20% dried fruits; 3 – 20% shales; 4 – average sample 20% – straw; 5 – according to data (Żelazny 2014); 6 – according to data (Zdunek et al. 2014); 7 – permissible content in calcium fertilizer.

The data given in Table 8 shows that the cadmium content in the examined ashes exceeded the permissible maximum contents several times (at least × 3.7 to × 5.4). Moreover, lead content in samples 1, 2, 3 and 6 exceeded the threshold value. In sample 3, the threshold value was 1.8 times exceeded, while in samples 4 and 5 the lead content was below the limit value. This data confirms that fly ashes from biomass combustion are a material with quite different characteristics resulting from the use of various batches (biomass) with a varying chemical and mineral composition.

It is possible to use fly ash from biomass burning as a liming agent by mixing it with other substances constituting an additional source of calcium. The products obtained must meet the quality requirements and the content of harmful substances. Such a course of action seems appropriate, but economically unjustified.

Data analysis shows that the proper direction of fly ash usage is their use as a source of potassium in complex fertilizers of type NK, PK or NPK. However, the use of fly ash for fertilizer purposes enforces the correction of their chemical composition, granulating them, taking measures to prevent the retrogradation of phosphorus and the loss of ammonia through their stabilization with mineral acids.

Therefore, simple fertilizers such as potassium chloride, salts containing phosphorus, potassium and nitrogen [(diammonium phosphate – DAP – $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, K_2SO_4 and others] are fed into the ashes. Waste products containing nutrients, for example waste solutions originating from the production of polyether polyols (PAG), ashes from the combustion of meat meal, ashes from the combustion of sewage sludge, ammonium sulfate waste (VI) from the production of caprolactam or coke industry, etc., deserve attention.

Requirements for mineral fertilizers of type K, PK and NPK are given in Table 9 while the Table 10 shows the chemical composition of the obtained fly ash based fertilizers.

Table 9. The composition of NPK type fertilizers obtained on the basis of fly ash derived from the combustion of biomass in a fluidized bed boiler

Tabela 9. Skład nawozów typu NPK otrzymanych na bazie popiołu lotnego pochodzącego ze spalania biomasy w złożu fluidalnym

No.	Content of the component (% weight)						pH	Sum ($K_2O_r + P_2O_5 + N$)
	K_2O_c	K_2O_r	P_2O_5	N	CaO	MgO		
1	11.1	7.9	14.3	3.5	7.9	0.9	6.5	25.7
2	13.2	9.1	11.5	3.9	11.4	1.3	6.5	24.5
3	15.0	10.4	5.0	5.0	8.1	–	5.5	20.4

Index: c – total, r – soluble.

1 – fertilizer obtained from fly ash, waste solution derived from PAG production, diammonium phosphate (DAP), potassium sulfate and sulfuric acid solution; 2 – ash, diammonium phosphate (DAP), potassium chloride, sulfuric acid solution; 3 – ashes, waste solution from the production of PAG, potassium chloride, sulfuric acid solution.

Table 10. Requirements for mineral fertilizers type K, PK and NPK (Requirements of U(WE) 2003)

Tabela 10. Wymagania dla nawozów typu N, PK i NPK

No.	Type of fertilizer	Production method and basic components	Minimal content of nutrients (m/m)	Other information about the type name	Nutrients declared, their forms and solubility
1	Fertilizer K	The product obtained from unpurified potassium salts	Potassium in K_2O soluble in 10% K_2O water	Add customary trade names	K_2O soluble in water
2	Fertilizers PK	P_2O_5 soluble in mineral acids, including at least 75% of the declared P_2O_5 soluble content it is soluble in 2% citric acid	Total: 18% ($P_2O_5 + K_2O$)	Product obtained as a result of a chemical process or by mixing, without addition of organic nutrients	For each of the nutrients, a minimum of 5% P_2O_5, 5% K_2O
3	Fertilizers NPK	P_2O_5 soluble in mineral acids, including at least 75% of the declared P_2O_5 content it is soluble in 2% citric acid	Total: 20% ($N + P_2O_5 + K_2O$)	Product obtained as a result of a chemical process or by mixing, without addition of organic nutrients	For each nutrient: 3% N, 5% P_2O_5, 5% K_2 O

Table 11. Examples of the content of individual components in fertilizers type K, PK and NPK prepared on the basis of fly ash from biomass combustion

Tabela 11. Przykłady zawartości poszczególnych składników nawozów mineralnych typu N, PK i NPK sporządzonych na bazie popiołów lotnych ze spalania biomasy

Component	Type of fertilizer (K)	Type of fertilizer (PK)	Type of fertilizer (NPK)
K_2O soluble in H_2O (%)	12.8	10.6	8.9
P_2O_5 soluble in 2% citric acid [%] (%)	0.06	9.2	6.8
Nitrogen (N) soluble in H_2O (%)	0	0	5.1
Boron (B) (ppm)	612	597	579
Cobalt (Co) (ppm)	7.4	6.9	6.5
Cupper (Cu) (ppm)	36.8	32.1	28.9
Iron (Fe) (%)	1.32	1.21	1.06
Manganese (Mn) (ppm)	86.7	79.2	75.4
Molybdenum (Mo) (ppm)	7.5	6.9	6.2
Zinc (Zn) (ppm)	249.1	231.2	226.8
Cadmium (Cd) (ppm)	4.6	3.8	3.4
Lead (Pb) (ppm)	4.7	3.6	3.1

[1] Obtained from fly ash with added potassium.
[2] Fly ash with addition of potassium sulfate and phosphoric acid (75%).
[3] Fly ash with addition of potassium sulfate, phosphoric acid (75%) and NH_4NO_3.

Further examples of obtaining fertilizers based on ashes are given in Table 11. Moreover the contents of micronutrients and harmful components in particular types of fertilizers are also presented. Even from the presented examples of obtaining mineral fertilizers based on fly ash, one can conclude about the possibility of obtaining full-value fertilizers. These ashes can be used as components of fertilizers of type K, PK or NPK. According to own research and literature data, ashes from the combustion of biomass in a fluidized bed can be a source not only of macroscopic components but also of microelements.

Remarks and conclusions

Fly ashes from biomass combustion are a material with quite different physical characteristics and in terms of chemical composition. For these reasons, the methods of utilization of fly ash derived from biomass fluidized bed combustion should take the high variability of the properties of this waste into account.

The possibilities of direct use of fly ash from biomass combustion are rather small. From the analysis of such ashes, it appears that ashes are a valuable source of potassium. Moreover, the most important additions that they contain are: phosphorus, calcium and magnesium compounds. The basic component of fly ash is silica (approx. 50% by weight). Although silica is not included in the group of macro and micronutrients, it plays an important role in increasing plant resistance to fungal diseases.

The use of fly ash as a soil liming agent from a technological point of view is possible despite the fact that the indicators of cadmium content in relation to kg CaO or (CaO + MgO) exceed the maximum acceptable values several times. Mixtures made of fly ash and materials rich in ingredients such as calcium and magnesium and low in harmful ingredients, allow for the improvement of the above indicators in order to reach values below the acceptable threshold.

There are possibilities of using fly ashes as components of both multicomponent and simple fertilizers. It was found that without prior processing of fly ash or the application of additional components, it is not possible to use them. Attention is paid to the high content of potassium. However, only part of the potassium is in a water-soluble form, i.e. in the form absorbed by plants. The insoluble part of potassium is essentially in the form of feldspar – $KAlSi_3O_8$.

For the tested ashes, using them for obtaining fertilizers of type K, PK and NPK was proposed. In order to correct the chemical composition of fly ash for fertilizers, waste can also be used, for example, ashes from meat meal combustion, waste solutions from PAG production, etc. These additives increase the value and quality of fertilizers enriched with phosphorus and/or potassium from secondary sources.

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THE EVALUATION OF FERTILIZER OBTAINED FROM FLY ASH DERIVED FROM BIOMASS COMBUSTION

Keywords

biomass, fly ash, mineral fertilizers

Abstract

One of the elements of the Polish Energy Policy program is the development of renewable energy, including energy from biomass combustion. In Poland, the Green Block was built at the Połaniec Power Station fired with 100% biomass fuel. This solution is conducive not only to obtaining energy but also to improving environmental protection. During the combustion of biomass in a fluidized bed boiler, about 50 thousand tons of fly ash per year being a source of nutrients for plants, for example potassium salts, phosphorus, calcium, boron compounds, etc. was derived.

The subject of the research were three types of ashes from biomass combustion containing 80% dendromass and 20% agromass. Agromas was made of straw, dried material or sliced palm nuts. The physical characteristics and chemical composition of three basic fly ash samples are presented. Due to the high fineness and thus dusting during spreading, it was found that there is no possibility of the direct use of fly ash from biomass combustion as an alkalizing agent for acidic soils. The lowest bulk density was demonstrated by samples of fly ash originating from the combustion of biomass containing 20% straw as agromass, while the poorest in potassium and phosphorus were ash samples obtained from the combustion of biomass containing 20% agromass in the form of palm kernel slate.

As additional components, mineral acids as well as inorganic compounds, including industrial waste, were used to correct the chemical composition and to mineral fertilizer granulation. The number of introduced components was related to the postulated composition of the produced fertilizer. Examples of mineral fertilizers obtained, both simple and multicomponent fertilizers, are presented.

OCENA PRZYDATNOŚCI WYKORZYSTANIA POPIOŁU LOTNEGO Z BIOMASY DO CELÓW NAWOZOWYCH

Słowa kluczowe

biomasa, popiół lotny, nawozy mineralne

Streszczenie

Jednym z elementów programu Polityka Energetyczna Polski jest rozwój energii odnawialnej, w tym pozyskiwanie z biomasy. W Polsce wybudowano Zielony Blok w Elektrowni Połaniec opalany

w 100% paliwem z biomasy. Rozwiązanie takie sprzyja nie tylko pozyskiwaniu energii, ale także poprawie w zakresie ochrony środowiska. W toku spalania biomasy w kotle fluidalnym powstaje około 50 tys. ton popiołu lotnego w skali roku stanowiące źródło składników pokarmowych dla roślin, na przykład sole potasowe, związki fosforu, wapnia, boru itp.

Przedmiotem badań były trzy rodzaje popiołów pochodzących ze spalania biomasy zawierającej 80% dendromasy i 20% agromasy. Agromasę stanowiły słoma, susz lub łupki orzecha palmowego. Przedstawiono charakterystykę fizyczną i skład chemiczny trzech zasadniczych próbek popiołu lotnego. Ze względu na duże rozdrobnienie, a tym samym pylenie podczas rozsiewu, stwierdzono brak możliwości bezpośredniego wykorzystania popiołów lotnych ze spalania biomasy jako czynnika alkalizującego kwaśne gleby. Najniższą gęstość nasypową wykazały próbki popiołów lotnych pochodzących ze spalania biomasy zawierającej 20% słomy jako agromasę, natomiast najuboższe w potas i fosfor były próbki popiołu uzyskane ze spalania biomasy zawierającej 20% agromasy w postaci łupek orzecha palmowego.

Jako dodatkowych komponentów do korekty składu chemicznego oraz do granulacji nawozów mineralnych stosowano kwasy mineralne, jak również związki nieorganiczne, w tym odpady przemysłowe. Ilość wprowadzanych komponentów związana była z postulowanym składem wytwarzanego nawozu. Przedstawiono przykłady otrzymanych nawozów mineralnych zarówno prostego, jak i nawozów wieloskładnikowych.