



The Geochemistry of Ash From the Combustion of Energy Grasses

Dalibor MATYSEK¹⁾, Konstantin RACLAVSKY²⁾, Hana SKROBANKOVA³⁾,
Jan FRYDRYCH⁴⁾

¹⁾ Eng., Ph. D.; Institute of Geological Engineering, VSB – Technical University of Ostrava, 17. listopadu 15, 70833 Ostrava – Poruba, Czech Republic; email: dalibor.matysek@vsb.cz, (+420)597324540

²⁾ Prof., Eng., CSc.; ENET, VSB – Technical University of Ostrava, 17. listopadu 15, 70833 Ostrava – Poruba, Czech Republic; email: konstantin.raclavsky@vsb.cz, (+420)597324430

³⁾ Eng., PhD.; Institute of Environmental Engineering, VSB – Technical University of Ostrava, 17. listopadu 15, 70833 Ostrava – Poruba, Czech Republic; email: hana.skrobankova@vsb.cz, (+420)597325325

⁴⁾ Eng.; OSEVA vývoj a výzkum, s.r.o., Hamerská 698, 75654 Zubří, frydrych@oseva.cz, (+420)571658195

Summary

The ash obtained by combustion of energy grasses (five cultivars, three hybrids and clover-grass mixture) was studied by mineralogical and geochemical methods. X-ray diffraction was used for mineralogical phase analysis, electron microprobe for analysis of chemical composition of ash particles. Ash melting temperatures were determined and discussed in relationship to phosphorus concentrations.

Keywords: energy grasses, biomass combustion, ash phase analysis, ash melting point

Introduction

For a long time, using biomass as a fuel has been considered entirely harmless for the environment [1]. Nowadays this opinion is eventually being revised. Biomass combustion brings about a number of advantages, but also some problems that must be either eliminated or minimized [2]. It is mainly necessary to prevent fouling and slagging, which causes defects of the combustion equipment [3]. During thermal processes of energy conversion, physical changes of ashes occur in fire bed, therefore for the operation of various types of solid fuel combustion chambers, it is important to know the ash melting temperature [4]. The ash melting temperature determines how high the temperature of combustion can be so that no problems should occur in connection with the function of the combustion equipment (the ashes melting on the grate, the slots in the grate getting encased by slag, softened particles getting stuck on the walls of the combustion chamber, fouling and slagging, etc.) The melting temperature for ashes is high for most kinds of woody plants and grasses and cereals, it is generally higher than 1,100 – 1,200°C. Cereal ashes have low Ca concentration and high Si and K concentration, therefore ash starts melting at considerably lower temperatures than with wood fuel.

Fouling and slagging formation is influenced by the presence of alkali metals (Li, Na, K, Rb, Cs) and alkaline-earth metals (Ca, Mg, Sr, Ba). Alkali metals lower the melting point of ash, alkaline-earth metals increase the melting point of ashes [4]. Biomass contains both alkali and alkaline-earth elements in ion forms or organically bound; they are not bound

with mineral phases like in fossil fuels [5]. The nature of bond influences their release during the combustion process, they are more volatile and they can easily evaporate in the ion or organic form [6]. Chlorine concentrations often determine the amount of evaporated alkalis during the combustion process more than alkali concentrations themselves do [7]. Potassium contained in wood biomass is released in the form of potassium chloride (KCl), potassium sulphate (K_2SO_4) and potassium hydrate (KOH), while during combustion of grass biomass $K_2Si_4O_9$, KCl and KOH is released [8, 9, 10]. At lower temperatures (< 700°C) KCl may react with sulphur or carbon, which results in the formation of sulphates and carbonates easily resulting in fouling and slagging on the surface of the boiler [7, 11].

The publication aims at identifying the chemical composition of ash from energy grasses and its influence on the melting point of ashes.

Methods and material

The samples of energy grasses - *Bromus marginatus* Nees ex Steud. cultivar Tacit, hybrid Perun (*Lolium multiflorum* Lam. x *Festuca pratensis* Huds.), hybrid Becva (*Lolium multiflorum* Lam. x *Festuca arundinacea* Schreb.), *Arrhenatherum elatius* L. cultivar Roznov, hybrid Lofa (*Lolium multiflorum* Lam. x *Festuca arundinacea* Schreb.), clover-grass mixture, *Festuca arundinacea* Schreb. cultivar Kora, *Agrostis gigantea* Roth. cultivar Roznov, *Phalaroides arundinacea* L. cultivar Lera were taken in the period from May to September 2012 in the research station of the company OSEVA PRO s.r.o. Zubří, the Czech

Republic.

Determining ash fusibility was carried out in compliance with CSN (Czech Technical Norm) ISO 540 (Coal and Coke – Determining Ash Fusibility). Ash change of state is characterized by four temperatures recorded while measuring the melting temperature: DT (deformation temperature), ST (sphere temperature), HT (hemisphere temperature) – melting temperature and FT (flow temperature).

The phase analysis of ash prepared by combusting a sample of grasses in the muffle furnace LMV2/12 (LAC s.r.o., Brno) at temperature of 815°C was carried out by means of the X-ray diffraction analysis method in order to identify the mineral phases in ash. The method of internal standard for monitoring the content of amorphous matter was not used. The measurement was carried out by means of modernized, fully automated diffractometer URD-6 (Rich. Seifert-FPM, Hamburg) under the following conditions: Radiation CoK α /Ni filter, voltage 40 kV, electric current 35 mA, step-by-step mode with a step of 0.05°2 θ with step time 3 s and with digital processing of the final data. The company programme RayfleX (RayfleX ScanX and RayfleX Analyze, version 2.289) was used both for measurement and for processEng. For qualitative evaluation, the diffraction data database PDF-2, version 2001 (International Centre for Diffraction Data, Pennsylvania, USA) was further used. The chemical phase analysis of ash was also carried out using the electron microanalyzer. Scanning electron microscope FEI FEI Quanta 650 FEG (producer FEI, USA) equipped with analyzers WDX (Wavelength Dispersive X-ray Spectroscopy) and EDX (Energy

Dispersive X-ray Spectroscopy) were used.

Grass ash fusibility

CSN (Czech Technical Norm) ISO 540 (Coal and Coke – Determining Ash Fusibility) provides information on fusibility and behaviour while melting the mixture of inorganic ash components at high temperatures. The results of fusibility of ash of grasses are listed in Table 1. The melting point of energy grasses ranged from 1,045 to 1,295°C. Higher concentration of phosphorus in grasses caused the higher value of the ash melting point (Fig. 1). The stated results show that the temperatures of the ash melting point higher than 1,200°C should not cause problems with ash getting stuck during the combustion process.

Higher values of the ash melting point for grasses were caused by formation of phosphates containing calcium (CaK₂P₂O₇ – the melting point of 1,143 °C) and CaKPO₄ (the melting point of 1,560°C) or the magnesium content MgKPO₄ (the melting point of 1,520°C) [12]. The growing concentration of total phosphorus causes the increase of the ash melting point, which corresponds to the results [13, 14].

Phase analysis of ash

The results of X-ray diffraction analysis of ash show that the samples have high proportion of amorphous matter. The content of non-crystalline, or vitreous component may be estimated at > 50%. Variable amount of arcanite – K₂SO₄ was determined in all samples. A small amount of halite – NaCl was found in the sample from *Bromus marginatus* Tacit, hybrid

Tab. 1 Melting temperatures of grass ash [°C] in oxidation atmosphere

Tab. 1 Temperatura mięknięcia popiołu ze spalania trawy [°C] w atmosferze utleniającej

Sample description	Deformation	Softening	Melting	Flowing
<i>Bromus marginatus</i> Tacit	860	1180	1210	1245
Hybrid Perun	861	1105	1140	1165
Hybrid Bečva	876	1010	1145	1105
<i>Arrhenatherum elatius</i> Roznov	850	1085	1160	1180
Hybrid Lofa	880	1090	1120	1150
Clover-grass mixture	835	910	987	1012
<i>Festuca arundinacea</i> Kora	855	1080	1140	1170
<i>Agrostis gigantea</i> Roznov	877	1095	1040	1210
<i>Phalaroides arundinacea</i> Chrastava	874	1120	1150	1165
Arithmetical mean \pm standard deviation			1121 \pm 66	
Lignite	1260	1280	1360	1500
Spruce wood	1041	1180	1265	1310

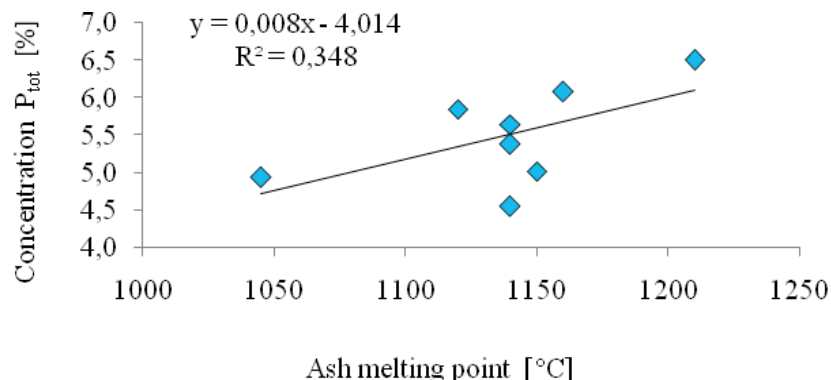


Fig. 1 The dependence of the ash melting point and P concentration in grass ash

Rys. 1 Zależność od temperatury mięknięcia popiołu od stężenia fosforu P w popiele

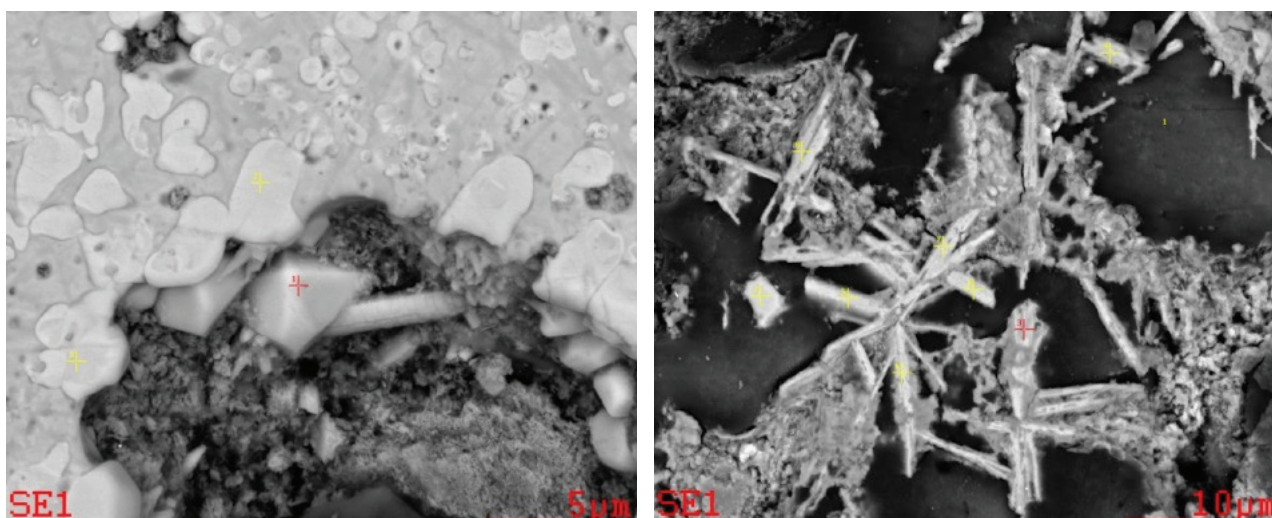


Fig. 2 Ash from combustion of hybrid Perun (pseudocubic crystal on the right, acicular crystal on the left)

Rys. 2 Popiół ze spalania hybrydy Perun (kryształy pseudokubiczne po prawej, iglasty kryształ po lewej)

Perun and *Festuca arundinacea* Kora. Sylvine – KCl was not found in any of the samples. There is a strong possibility that in all samples a variable amount of calcium-potassium phosphate KCaPO_4 was present. This phase has certain shifts in the position of diffraction lines compared to tabulated values. This can be explained by isomorphous substitution $(\text{PO}_4)^{3-}$ in the structure of this phase by the silicate group $(\text{SiO}_4)^{4-}$, which is confirmed by the results from the electron microanalysis. It cannot be excluded as well that $\text{KCa}(\text{PO}_4, \text{SiO}_4)$ may be present in the samples as more polymorphous modifications. The morphology of particles documented in Fig. 2 shows both pseudo-cubic and acicular crystals.

The identification of further phases by means of the X-ray diffraction method is not definite, but it was confirmed by the electron microanalysis. It is the case of pyrophosphate – $\text{K}_2\text{CaP}_2\text{O}_7$, $\text{Mg}_3\text{Ca}_3(\text{PO}_4)_4$, $\text{Ca}_{15}(\text{PO}_4)_2(\text{SiO}_4)_6$, $\text{K}_5\text{P}_3\text{O}_{10}$, $\text{K}_4\text{P}_2\text{O}_7$, $\text{KNaCa}_2(\text{PO}_4)_2$, K_2CO_3 etc. The chemical composition of acicular crystals of prismatic type is shown in Table 2.

The triangle diagram (Fig.3), constructed from the chemical composition of major elements except oxygen and carbon (normalized at 100 %) shows the common position of the projection points for recrystallized particles with high contents of phosphorus, sodium and calcium for hybrid Perun, *Festuca arundinacea*, *Bromus marginatus* and *Phalaroides arundinacea*. It is also clear from the picture that *Festuca arundinacea* forms two more types of recrystallized particles; one type is formed by *Bromus marginatus*, while the other type relates to clover-grass mixture, *Arrhenatherum elatius* and *Agrostis gigantea*. Low potassium content is typical of clover-grass mixture, the same is true for one type of recrystallized particles of *Arrhenatherum elatius* (with concentrations of $\text{K} < 10\%$). Recrystallized particles of *Agrostis gigantea*, characterized by a high content of potassium (up to 27%) have a specific position.

Chemical composition of crystallized and recrystallized particles without standardized conversion is stated in Table 3. Recrystallized particles form 9 types

Tab. 2 Chemical composition of crystals of prismatic type (wt. %)

Tab. 2 Skład chemiczny kryształów typu pryzmatycznego (% wagowe)

Element	Analysed surfaces								
	1	2	3	4	5	6	7	8	9
C	45.40	15.52	15.57	13.74	29.65	14.04	13.19	12.93	17.38
O	24.06	21.30	27.85	29.98	21.93	27.48	29.15	28.91	24.24
Na	0.40	0.28	0.23	0.37	0.35	0.34	0.20	0.37	0.33
Mg	0.99	1.95	1.05	0.28	0.46	0.78	0.37	0.39	0.30
Al	3.33	1.35	0.52	0.58	0.63	0.71	1.02	1.00	0.45
Si	5.45	18.30	16.40	17.09	12.60	16.52	16.80	16.33	17.40
P	2.62	1.07	2.90	1.24	2.22	2.09	1.83	1.16	1.36
S	1.61		0.44	0.15	0.30	0.08	0.07		0.18
K	10.25	19.23	17.34	18.21	15.98	19.00	18.66	18.63	18.54
Ca	5.89	17.60	16.96	18.06	15.48	18.54	18.31	19.37	19.58
Mn		0.72	0.32	0.13	0.19	0.20	0.16	0.19	0.10
Fe		2.51	0.42	0.17	0.22	0.24	0.23	0.19	0.14

Bold: Ca=K>Si

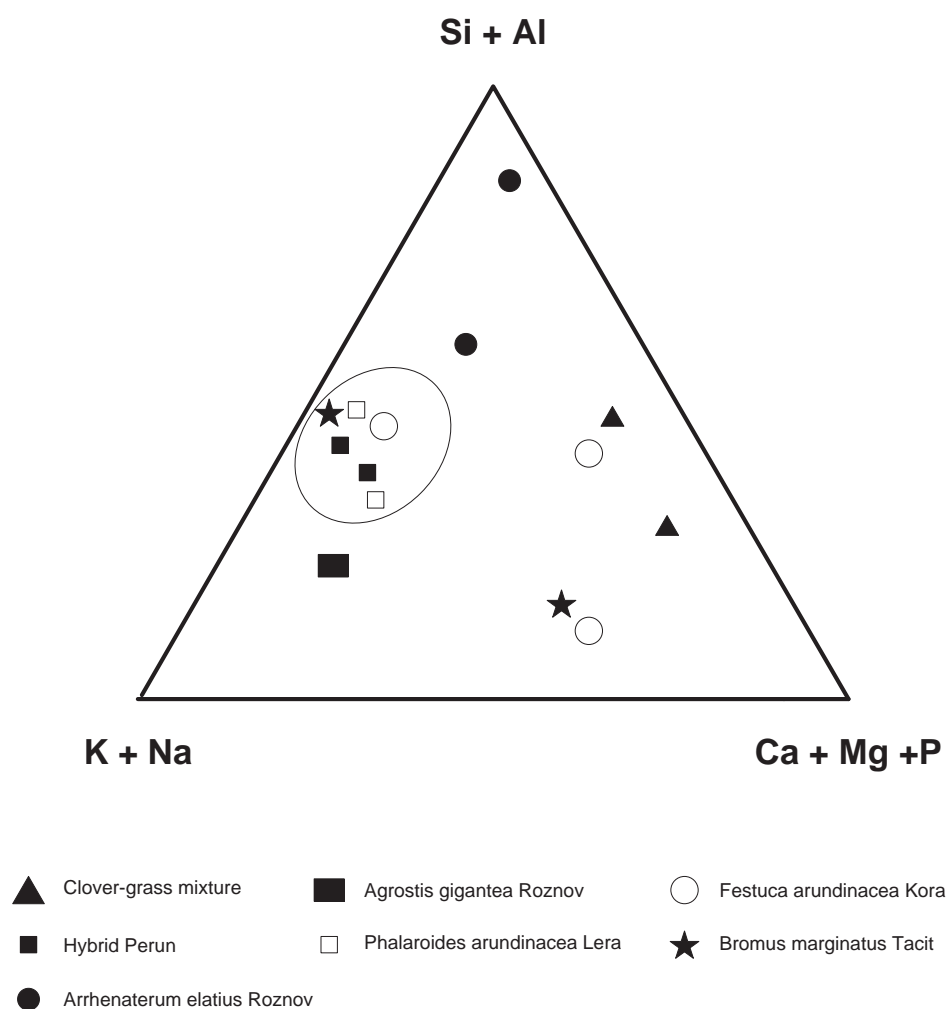


Fig.3 Triangle normalized diagram – chemical composition of recrystallized particles

Rys. 3 Diagram składu chemicznego - skład chemiczny cząstek po rekrystalizacji

differing in mutual concentration of majority elements. From the point of view of element association, the most common type is Si-K-Ca (5 times in various concentrations), K-Ca-P (once), Si-K-Al (once) and Al-Si-K-Ca (once). A considerably smaller variability of chemical composition is shown by the basic matrices of grass ash grains.

In the ash grain matrix, black spots appeared with high carbon content (>50 %). A relatively homogeneous matrix was shown by *Phalaroides arundinacea*, while the matrix of *Bromus marginatus*, *Agrostis gigantea*, *Arrhenatherum elatius* and *Festuca arundinacea* has a very similar character. The highest inhomogeneity was shown by clover-grass mixture and hybrid Lofa. In two cases, clover-grass mixture showed the lowest content of Si in the basic matrix of all the studied ashes. Similar results also applied to the hybrid, where in one case Si was replaced by P and in the second case matrix contained high proportion of carbon. It is clear from the stated results that on the basis of element association, 3 basic kinds of matrix can be distinguished: Si-K-Ca (3 modifications on the basis of concentrations), K-Si, Si-K-Al (Table 4).

Table 1 lists the results of the ash melting point, which shows that the point of melting for the group of grasses: hybrids, *Bromus marginatus*, *Festuca arundinacea* and *Phalaroides arundinacea* is higher than

the average value of the whole set ($1,121 \pm 66^\circ\text{C}$). At the same time, for these grasses, common occurrence of recrystallized particles Ca-K-P is confirmed. If particles of the association Ca-K-P are formed, the ash melting point increases [15]. The melting point for calcium phosphate is $1,391^\circ\text{C}$.

Conclusions

Despite high content of water-leachable potassium of 8.85 – 16 g/kg of dry matter, the values of the grass ash melting point are only slightly lower than the values acquired for spruce wood. The melting point for the group of grasses: hybrids, *Bromus marginatus*, *Festuca arundinacea* and *Phalaroides arundinacea*, containing recrystallized particles with Ca-K-P content, is higher than the average value of the whole set ($1,121 \pm 66^\circ\text{C}$). Clover-grass mixture and *Agrostis gigantea* can be classified as unsuitable for combustion. The reliability of the melting point results should be confirmed by another method, e.g. by calculating alkali index.

Acknowledgement

This paper was supported by research projects of the Ministry of Education, Youth and Sport of the Czech Republic: the Centre ENET CZ.1.05/2.1.00/03.0069 and the Ministry of Agriculture: MZ QI101C246.

Tab. 3 Chemical composition of crystallized and recrystallized particles (wt. %)

Tab. 3 Skład chemiczny krystalicznych i rekrystalicznych cząstek (% wagowy)

Area	Hybrid		Phalaroides		Bromus		Arrhenath.		Festuca			Agrostic	Clover	
	1	2	1	2	1	2	1	2	1	2	3	1	1	2
Al	0.77	0.62	0.45	0.38	0.64	0.75	38.8	5.5	0.42	0.51	0.78	0.51	0.55	10.45
Si	21.5	18.1	8.08	18.2	6.45	22.0	5.6	26.3	20.2	8.0	21.0	22.0	15.3	22.41
P	0.72	1.59	12.4	3.42	13.2	1.93	2.3	0.48	1.0	11.8	3.8	5.0	2.2	0.2
K	21.8	16.3	19.8	18.7	22.4	21.8	5.2	18.3	18.4	25.0	12.4	27.9	11.7	11.4
Ca	2.96	9.04	18.5	14.5	18.4	11.1	4.0	1.49	18.9	18.0	10.3	10.1	18.6	1.81
	<i>I.</i>		<i>2.</i>	<i>I.</i>	<i>2.</i>	<i>I.</i>	<i>6.</i>	<i>7.</i>	<i>4.</i>	<i>3.</i>	<i>4.</i>	<i>5.</i>	<i>8.</i>	<i>9.</i>

Explanations: 1. Si=K>Ca; 2. K=Ca>P; 3. K>Ca>P; 4. Si>K=Ca; 5. K>Si>Ca; 6. Al>Si=K=Ca; 7. Si>K>Ca; 8. Ca>Si>K; 9. Si>K>Al

Tab. 4 The matrix chemical composition variability (wt. %)

Tab. 4. Macierz zmienności składu chemicznego (% wagowy)

Area	Hybrid				Phalaroides	Bromus	Arrhenat.		Festuca		Agrostis	Clover		
	1	2	3	4	1	1	1	2	1	2	1	1	2	3
Al	0.9 3	0.8	9.3	3.3	0.77	0.80	8.9	1.2	0.9 1	6.1	0.61	0.5	0.8	3.7
Si	24. 2	3.4	29. 5	5.4 5	25.4	26.1	28. 7	26. 3	24. 4	23. 4	26.6	9.3	13. 4	27. 5
P	1.0	15. 2	0.4 5	2.6	1.3	0.9	0.3 8	0.8 3	1.0	1.2	1.2	6.4	3.7	0.2
K	17. 8	20. 3	11. 9	10. 2	19.0	17.9	11. 2	17. 0	20. 0	18. 0	27.4	10. 2	8.9	7.8
Ca	6.2	20. 3	0.7 1	5.9	6.5	6.6	1.5	4.7	7.2	5.0	6.2	23. 0	14. 6	3.3
	<i>1.</i>	<i>2.</i>	<i>4.</i>	<i>3.</i>	<i>1.</i>	<i>1.</i>	<i>4.</i>	<i>1.</i>	<i>1.</i>	<i>4.</i>	<i>1.</i>	<i>6.</i>	<i>5.</i>	<i>1.</i>

Explanations: 1. Si=K>Ca; 2. K=Ca>P; 3. K>Ca>P; 4. Si>K=Ca; 5. K>Si>Ca; 6. Al>Si=K=Ca; 7. Si>K>Ca; 8. Ca>Si>K; 9. Si>K>Al

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Streszczenie

Popiół uzyskany ze spalania traw energetycznych (pięciu odmian, trzech mieszańców i mieszaniny trawy i koniczyny) badano metodami mineralogicznymi i geochemicznymi. Metoda dyfrakcji rentgenostana fazy mineralogicznej, do analizy składu chemicznego cząstek popiołu wykorzystano mikrosondę elektronową. Określono temperaturę topnienia popiołu i wykazano jej zależność od zawartości fosforu.

Słowa kluczowe: trawy energetyczne, spalanie biomasy, analiza popiołu, temperatura topnienia popiołu