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Alina KOWALCZYK-JUŚKO[1]

PROPERTIES OF ASH IN THE COMBUSTION OF SELECTED ENERGY CROPS

WŁAŚCIWOŚCI POPIOŁU ZE SPALANIA WYBRANYCH GATUNKÓW ROŚLIN ENERGETYCZNYCH

Abstract: Chemical composition and fusibility of ash from three species of perennial plants used as energy crops has been analyzed, two of which are grasses: (*Miscanthus sacchariflorus* and *Spartina pectinata*) and a bifoliate plant *Sida hermaphrodita*. Ash parameters have been compared from crops harvested after the first and third year of vegetation. The species selected for analysis are highly productive, however they are not commonly used in cultivation, and the awareness of their possible use as energy crops in this country is fairly limited. The research conducted has indicated that *Sida hermaphrodita* is characterized by the lowest ash content. However, the chemical composition of such ash contains the highest concentration of alkali oxides, responsible for deposit formation in the combustion installations. In the case of *Sida hermaphrodita* harvested in the first year, the c_m coefficient amounted to 20.86, and after three years to 16.60, whereas in the case of miscanthus, the values were 0.24 and 0.19 respectively, and for *Spartina pectinata* 0.69 and 0.39 respectively. This indicates a much higher risk of ash deposits in combustion chambers, and a decreased overall efficiency of boilers fuelled by *Sida hermaphrodita* biomass. The highest content of chlorides was found in the ash of *Spartina pectinata* harvested in the first year, whereas they were not found in the case of *Miscanthus sacchariflorus* harvested after three years of vegetation. Additionally, ash resulting from the *Miscanthus sacchariflorus* biomass was characterized by the highest fusibility temperatures.

Keywords: biomass, energy crops, ash, chemical composition, fusibility

Burning biomass is a way of converting solar radiation energy into a fairly convenient and universal form of heat energy. It is also the oldest and apparently simplest way of generating energy. From a chemical point of view, such combustion is a conversion of organic matter into carbon dioxide and water in the presence of oxygen. Biomass can be burnt as homogeneous fuel in boilers adapted for this purpose, or added in various proportions to coal. The biomass co-burning with coal in high output boilers used for commercial energy generation, is regarded as an opportunity to meet requirements imposed on Poland as part of the EU Accession Treaty. The requirements

[1] Department of Agricultural Production and Agrobusiness, University of Life Sciences in Lublin, ul. Szczebrzeska 102, 22–400 Zamość, Poland, phone: +48 84 677 27 53, fax: +48 84 639 60 39, email: alina.jusko@up.lublin.pl

describe targets that are to be met by the proportion of electrical energy generated from renewable sources in the total consumption of electrical energy. Large generation facilities (such as power plants and heat generation plants) require vast amounts of biomass characterized by constant quality, low price and economically justifiable distance from the source of its production. The product that meets such criteria and that can be used in the co-burning process with coal is wood produced in forests and dedicated cultivation, as well industrial wood waste materials [1].

The constant contraction of biomass supplies originating from forestry and wood manufacturing, coupled with legislation requiring the gradual replacement of wood used in energy generation by biomass coming from other sources have meant an increased interest in the cultivation of crops with a high production potential. In this context, we can mention the highly productive energy crops of perennial grasses, and other perennial species such as bushes and trees with a short production cycle, spanning from a few to several years [2]. The country's legislation governing subsidies to energy crops point to many species that can actually be used in biomass energy generation. At the same time, there is a lack of definite, precise and reliable agro-technical guidelines for many of the crops, as well as specifications of such biomass. The research on the properties of biomass as well as on the standardization of research methods on such fuels is carried out by specialized centers such as the European Committee for Standardization CEN/TC 335 Solid Biofuels [3].

A high diversification of biomass in terms of its chemical composition and physical properties causes certain problems in its combustion and emission of pollutants which are a side effect of the process. Therefore, a thorough knowledge of characteristics of biomass coming from various sources is important form the point of view of energy efficiency. The important parameters are not only the crop volume and energy value, but also ash content, which is left as waste in the combustion of any solid fuel. The ash resulting from burning biomass can actually be used as mineral fertilizer in agriculture [2, 4], but only under the condition that pure biomass has been used in the process. In the case of co-burning with coal or culm, the mineral content of biomass increases the amount of total ash volume, and thus becomes a cumbersome waste product in energy generation industry. The chemical composition of biomass ash is also of importance to the energy generation sector, as the high content of alkali and chemically reactive chloride can cause corrosion to boiler installations and result in deposit formation in convection surfaces [5]. The proportions between the alkaline compounds (Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5) and the acidic ones (SiO_2, Al_2O_3, TiO_2), which can be found in biomass ash, constitute an index of the susceptibility of such ash to form deposits [6, 7]. For biomass ashes, the index is much higher in comparison with the values for coal, which has adverse effects for the convection surfaces in the boiler, as it leads to the decrease in heat transfer efficiency of such surfaces.

Filipowski [8], although with some degree of simplification, states that a measure for the susceptibility of slagging for a given type of fuel is in fact its fusibility temperature characteristics, defined by four values of temperatures: that of sintering, softening, melting and pouring. Adhesion properties are shown by ashes even in the temperatures between the points of softening and melting. It is also important how the fusibility of ash changes according to the chemical composition of the fuel: iron, calcium, and sodium compounds lower ash fusibility temperature, whereas silicate and aluminium oxides increase it. In such contexts, the determination of both composition, and ash fusibility temperatures is of paramount importance for the assessment of particular biomass products.

Sciazko et al [9] mention that characteristic ash fusibility temperatures of coal and biomass arrived at in laboratory conditions may not provide sufficient information on possible slagging effects of heat transfer surfaces. This seems to be caused by the following phenomena:

– ash fusibility temperatures are assessed on the basis of the ash contained in the fuel, whereas the actual ash content resulting from burning/co-burning may vary, which results from the adhesive properties of ash elements;

– fusibility temperatures are assessed in a relatively short span of time, whereas the deposits in the boiler are formed throughout extended periods of use, and are subject to alternate processes of heating and cooling in the presence of combustion gases;

– ash fusibility temperatures defined in laboratory conditions do not take into account boiler characteristics and conditions in which it is operated, which ultimately influence the processes of deposit formation and slagging;

– the process of fusibility operates in a different way when samples are subjected to a constant temperature for a given period of time; fusibility temperatures thus defined are bound to be lower.

According to Zamorowski [7] the problem of heat transfer surfaces contamination may in fact be far more complicated, but in any case the resulting effect is always an increase in the temperature of exhaust gases, and consequently – the decrease in the overall efficiency of the boiler, especially in the case of biomass co-burning with coal, in comparison with the efficiency of such installation when only coal-fired. The present research enabled us to compare the chemical composition of ash resulting from biomass combustion of several species of energy crops.

Research methodology

Three species of perennial plants were selected for the research, which, according to the Decree of Minister for Agriculture and Rural Development of March 14, 2008 [10] (Journal of Laws No. 44, item 267), are defined as energy crops. The crops comprised two types of grasses:

– *Miscanthus sacchariflorus* Maxim. (Hack),

– *Spartina pectinata* Link., and

– a bifoliate perennial – *Sida hermaphrodita* (Rusby).

The experiment was set up in May 2003 in the Experimental Station of The Faculty of Agricultural Sciences in Zamosc, Poland, on III class soil in a good wheat complex. The soil was characterized by a neutral pH (pH_{KCl} = 6.6), the content of phosphorus, potassium and manganese were the following values: 12.3 g P, 16.8 g K and 11.1 g Mg $\cdot$ kg^{-1}, respectively. The experiment was carried out on the total of 18 plots, 6 for each species of crops. Due to a high content of basic macroelements, no additional mineral or organic fertilizing was applied, and only weeding procedures were carried out. Aboveground parts of the plants were randomly sampled from all plots of particular species. The biomass was harvested twice: after the first and third year of vegetation (2004 and 2006). The samples were analyzed in the Central Laboratory of Power Research and Testing, Company Energopomiar in Gliwice, Poland. Ash content was analyzed in analytic conditions: air dry (A^a) and dry (A^d) using the gravimetric method. Ash, obtained at 600 ^{o}C, was analyzed for chemical element composition with the use of a plasma spectrometer ICP OES and using ASCRM-010 as reference. The loss by roasting was determined according to the research standards outlined in PN-77/G-04528/02. The content of particular elements is given in dry state, with the exception of A^a. Characteristic ash fusibility temperatures were determined in semi-reducing atmosphere: sintering temperature t_S ^{o}C, softening temperature t_A ^{o}C, melting temperature t_B ^{o}C, and pouring temperature t_C ^{o}C.

Based on the analysis results, the c_m coefficient was calculated, which characterizes ash susceptibility to form deposits, according to the following formula [9]:

$$c_m = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2}$$

Result overview and discussion

The crops after the first year of vegetation were characterized by a higher content of ash in comparison with those after three years of vegetation. (Table 1). The least content of ash (in analytic state 2.5 %, in dry state 2.8 %) was shown by aboveground parts of *Sida hermaphrodita* after the third year of vegetation. In the case of grasses, ash content was higher, and was in the range of 5.1–7.1 % for one year vegetation, and 3.5–4.1 % for three-year vegetation.

Table 1

Determination of ash in plant biomass and coefficient c_m

Species	Crop	Ash [%]		Coefficient c_m
		analytic condition A^a	dry condition A^d	
Miscanthus sacchariflorus	1year	6.5	7.1	0.24
	3 year	3.5	3.7	0.19
Spartina pectinata	1 year	5.1	5.9	0.69
	3 year	3.6	4.1	0.39
Sida hermaphrodita	1 year	4.8	5.2	20.86
	3 year	2.5	2.8	16.60

Ash content in coal, according to research by Sciazko et al [9] amounts to 22.2 %, whereas in pine wood chips 0.3 %, beech wood chips 0.8 %, willow biomass 2.2 %. Grzybek et al [11] report that ash content in coal amounts to 12 %, in cereal straw 3–4 %, and in wood chips is even lower, and ranges between 0.6 % and 1.5 %.

Niedziolka i Zuchniarz [12] report that while burning pure biomass, a small amount of ash is produced, estimated at 0.5–12.5 %, whereas its higher content testifies to the pollution of the product. In turn, Wilk [13] determines ash content in wood biomass at 0.3–7.4 %, and in cereal straw at 4.3–10.4 %. In her opinion, there is a slight negative correlation between ash content and energy value of the material, and she calculated the correlation coefficient to be 0.3093, which means that given the increase of ash content in biomass, there will be a decrease in the value of combustion heat. In the light of the above data, we can concluded that the ash content in energy crops under our analysis was not significantly high and did not exceed average values for other biomass fuels.

We found significant variation in ash content of particular species of plants, where there was a characteristic high content of alkali oxides, responsible for lower ash fusibility temperatures in *Sida hermaphrodita* ash (Table 2). A particularly high content of CaO (44.5 %) was observed in *Sida hermaphrodita* ash after the first year of vegetation, and the highest amounts of K_2O were found in three-year-old *Sida hermaphrodita* (14.3 %). Additionally, in ash from burning three-year-old *Sida hermaphrodita* there was a significant amount of MgO (5.34 %), which is also considered to be an alkali oxide. The total presence of alkali oxides in *Sida hermaphrodita* ash is high and indicates a danger for serious deposit formation in boiler installations while burning the biomass of such species. By contrast, the ash from burning grasses was characterized by a much lower content of alkali compounds, with a high presence of silica at the same time. The SiO_2 content in *Miscanthus sacchariflorus* ash was 76.1 % on average, and in *Spartina pectinata* it amounted to 59.35 %. Thanks to that fact, grass ash shows much weaker tendencies to contaminate heat transfer surfaces. Additionally, a higher content of silica was noted in the ash of three-year-old plants in comparison with one-year-old ones, and this regularity was found across all the species under analysis.

Wasilewski [14] compares the content composition of ashes originating in burning coal and willow and beech chips, respectively. In the case of coal, the content of alkali oxides in ash was relatively low and amounted to 2.66 % CaO, 2.98 % K_2O, 0.89 % P_2O_5, whereas in willow chip ash the values were respectively: 44.5 %, 8.51 % and 5.9 %, and for beech chip ash the respective values were 29.6 %, 10.27 % and 2.68 %. In turn, the percentage content of SiO_2 and Al_2O_3, that is oxides which reduce the adverse effects of ash sediments in boiler installations, was a total of 79.46 % for coal, 22.49 % for willow chips, and 34.1 % for beech chips. Also Sciazko et al [9] point to a significantly higher content of acidic compounds in coal ashes (the total of SiO_2 and Al_2O_3 amounted to 79.7 %) when compared with wood ash (16.9 %), straw ash (50.3 %), sludge (31.4 %) and meat and bone meal (5.96 %). Numerous results of analyses carried out by the Central Laboratory of Energopomiar in Gliwice, represented by Wisz and Matwiejew [5] testify to a vast variance in the presence of various elements in biomass ash. For instance, the content of silica in straw ash ranged from 1.57 to 43.70 %, that of calcium oxide from 7.28 to 34.50 %. Ashes from other biomass fuels were also of significantly variant nature.

Based on the proportion between alkali and acidic compounds, the susceptibility of particular species to form deposits was determined. The highest values of c_m coefficient

Table 2

Content of particular chemical elements (in oxide form) in ash of crops under analysis [%]

Element [%]	Symbol	*Miscanthus sacchariflorus*			*Spartina pectinata*			*Sida hermaphrodita*		
		1-year	3-year	average	1-year	3-year	average	1-year	3-year	average
Silicon dioxide	SiO_2	74.3	77.9	76.10	52.6	66.1	59.35	2.28	3.20	2.74
Iron	Fe_2O_3	0.92	1.33	1.13	0.89	0.98	0.94	0.62	0.76	0.69
Aluminium	Al_2O_3	0.84	2.06	1.45	0.87	0.85	0.86	0.58	0.48	0.53
Manganese	Mn_3O_4	0.07	0.09	0.08	0.05	0.10	0.08	0.06	0.05	0.06
Titanium	TiO_2	0.05	0.06	0.06	0.05	0.04	0.05	0.03	0.04	0.04
Calcium	CaO	9.83	8.35	9.09	12.9	14.3	13.60	44.5	35.7	40.10
Magnesium	MgO	0.84	0.82	0.83	1.76	2.30	2.03	1.91	5.34	3.63
Sulphur	SO_3	4.55	2.21	3.38	5.40	4.63	5.02	2.51	2.42	2.47
Phosphorus	P_2O_5	2.20	1.87	2.04	6.19	2.96	4.58	3.80	4.85	4.33
Sodium	Na_2O	0.42	0.46	0.44	0.95	0.88	0.92	0.61	0.80	0.71
Potassium	K_2O	3.75	2.66	3.21	14.5	4.97	9.74	8.86	14.3	11.58
Barium	BaO	0.02	0.02	0.02	0.05	0.03	0.04	0.04	0.03	0.04
Strontium	SrO	0.03	0.02	0.03	0.03	0.04	0.04	0.15	0.10	0.13
Chlorides	Cl	0.39	n/f	0.20	2.54	0.25	1.40	0.48	0.24	0.36
Loss by roasting	—	0.82	1.26	1.04	0.83	0.70	0.77	32.8	31.0	31.90

were observed in one-year crops of *Sida hermaphrodita* (20.86), whereas they were much lower for grasses, especially after the third year of vegetation: for *Miscanthus sacchariflorus* the value was 0.19 and for *Spartina pectinata* 0.39.

The c_m coefficient for coal ash is 0.241, and in the case of biomass ash its values may be far higher: for wood ash it amounts to 4.886, and for straw ash to 0.980 [15]. It turns out that such values calculated for grasses do not vary from coal values. By contrast, *Sida hermaphrodita* ash shows a high coefficient for deposit formation, exceeding those for straw and wood. That means that the use of biomass originating from this species may be of a limited nature because of sediments formed on convection surfaces of boilers, especially with a high percentage of such biomass being used for co-burning.

A large loss by roasting, resulting from a high content of carbonates, found in *Sida hermaphrodita* ash indicates a significant amount of organic matter, and consequently, not fully combusted carbon in the ash. The results for grass ashes proved that grasses may be far better suited as bio-fuel in this respect.

The highest presence of chlorides, responsible for corrosion to boiler installations, was found in biomass ash of one-year-old *Spartina pectinata* (2.54 %), and in the case of three-year-old *Miscanthus sacchariflorus* no chlorides at all were found. In *Sida hermaphrodita* ash, the chloride content ranged from 0.24 to 0.48 %. In comparison with the data presented by Wisz and Matwiejew [5], the values were not high, as the content of chloride in straw ash was recorded at the values of 9.09–11.20 %. Sciazko et al [9] stress that a high chloride content may lead to increased corrosion and the build-up of aggressive and reactive deposits as a result of direct combustion of biomass.

Table 3

Characteristic fusibility temperature of ash [^oC]

Temperature	Symbol	*Miscanthus sacchariflorus*		*Spartina pectinata*		*Sida hermaphrodita*	
		1-year	3-year	1-year	3-year	1-year	3-year
Sintering	t_S ^oC	760	760	730	730	685	680
Softening	t_A ^oC	1460	> 1500	870	1060	745	740
Melting	t_B ^oC	> 1500	> 1500	1170	1210	1420	> 1500
Pouring	t_C ^oC	> 1500	> 1500	1260	1250	1425	> 1500

Sida hermaphrodita ash was characterized by lowest sintering and softening temperatures (685 and 745 ^oC, respectively for one-year-old crops, and 680 and 740 ^oC for three-year-old crops), and the lowest melting and pouring temperatures were shown by *Spartina pectinata* ash (one-year-old: 1170 and 1260 ^oC, respectively, and three-year-old: 1210 and 1250 ^oC respectively). A low temperature of melting means that sediments may form on the heat transfer surface of boilers, thus deteriorating heat transfer.

Wasilewski [14] quotes melting temperatures for ash of various biomass materials (in semi-reducing atmosphere) with reference to coal. As it is revealed by research from the Institute for Chemical Processing of Coal Zabrze, Poland, characteristic temperatures for energy purpose coal were the following [^oC]: t_S 920, t_A 1230, t_B 1400 and t_C 1420.

For willow chip ashes the respective temperatures were: 830, 1520, 1530 and 1540 ^oC, for pine wood sawdust: 1090, 1190, 1220, 1290 ^oC, for two samples of cereal straw: 800–810, 860–900, 1140–1150, 1220–1280 ^oC. Hamala and Rog [6] distinguish ashes that are easily melted, whose melting temperature t_B measured in reducing atmosphere is lower than 1200 ^oC, medium fusible with melting temperatures t_B between 1200 and 1350 ^oC and ashes that are hard to melt, whose melting temperature exceeds 1350 ^oC. According to Filipowski's evaluation [8], melting temperature lower than 1230–1250 ^oC is characteristic for types of coal that are susceptible to slagging, whereas types of coal with a low susceptibility show $t_A > 1350$ ^oC. Adopting the same criteria for evaluating biomass ashes, we can conclude that among all the species under our investigation only *Miscanthus sacchariflorus* meets the criteria for the prevention of slagging of boiler installations.

Conclusions

1. Biomass of particular energy crops shows significant variance, both in terms of ash content and its chemical composition. This variance should be taken into account when planning the use of biomass in boiler facilities, either as the sole fuel or for co-burning with coal.

2. The least advantageous properties for energy generation purposes were exhibited by *Sida hermaphrodita* ash. A disadvantageous proportion between acidic and alkali oxides was found in its chemical composition, which testifies to its susceptibility to form deposits. Ash composition also influences fusibility temperatures, which are also the least favourable in the case of *Sida hermaphrodita*.

3. Among grasses, the variations were favourable for *Miscanthus sacchariflorus*. A higher content of silica, higher fusibility temperatures, absence of chlorides all predispose *Miscanthus sacchariflorus* biomass to be the best energy crop among the ones under investigation.

4. Ash originating from crops in the first year of vegetation exhibited inferior properties in terms of energy generation purposes in comparison with ash of three-year--old crops. Young plants were characterized by a higher content of alkali oxides in their ash and lower fusibility temperatures. This regularity occurred across the three species under investigation.

5. A high variance in composition and characteristics of ash of energy crops, which seems important for energy generating purposes, indicates a need for further research in this field.

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WŁAŚCIWOŚCI POPIOŁU ZE SPALANIA WYBRANYCH GATUNKÓW ROŚLIN ENERGETYCZNYCH

Katedra Produkcji Roślinnej i Agrobiznesu
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Badano skład chemiczny i topliwość popiołu ze spalania trzech gatunków wieloletnich roślin, stosowanych jako surowiec energetyczny: dwu traw (miskanta cukrowego i spartiny preriowej) i gatunku dwuliściennego, którym był ślazowiec pensylwański. Porównywano parametry popiołu z roślin zebranych po pierwszym i trzecim roku wegetacji. Gatunki wybrane do badań są wydajne, jednak mało rozpowszechnione w uprawie, a znajomość ich właściwości energetycznych jest w kraju niewielka. Przeprowadzone analizy wykazały, że najmniejszą zawartością popiołu charakteryzowała się biomasa ślazowca pensylwańskiego. Jednak w składzie chemicznym popiołu ślazowca stwierdzono największe ilości tlenków alkalicznych, odpowiedzialnych za odkładanie się osadów na urządzeniach grzewczych podczas spalania. Wskaźnik c_m wyniósł w przypadku ślazowca zebranego po pierwszym roku wegetacji 20,86, a dla roślin trzyletnich 16,60, podczas gdy w przypadku miskanta wartości te kształtowały się odpowiednio 0,24 i 0,19, zaś spartiny preriowej 0,69 i 0,39. Świadczy to o znacznie wyższym ryzyku osadzania się popiołu na urządzeniach grzewczych i mniejszej sprawności kotła podczas spalania biomasy ślazowca. Najwięcej chlorków zawierał popiół z biomasy jednorocznej spartiny preriowej, zaś w przypadku trzyletniego miskanta cukrowego nie stwierdzono obecności chlorków. Ponadto popiół z biomasy miskanta cukrowego cechował się najwyższymi temperaturami topliwości.

Słowa kluczowe: biomasa, rośliny energetyczne, popiół, skład chemiczny, topliwość