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Chemical composition of agromass ash and its influence on ash melting characteristics

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Abstract. The increasing demand for biofuels leads to a growing need for agromass, such as herbaceous plants and agricultural waste. However, agromass contains high quanitites of alkali metals, mainly potassium and sodium, which limits agromass usage in thermoconversion processes. Alkali metals react with other ash forming elements which leads to ash related problems such as agglomeration, fouling and slagging during agromass burning. In this study, chemical composition and melting behaviour of ashes formed at 550 °C are investigated. Three herbaceous plants (reed canary grass, hemp, orchard grass), four types of agricultural waste (straws of rye, wheat, buckwheat and canola) and two types of woody biomass (birch, spruce) are selected. Ash melting behaviour, composition and bulk structure are determined using a high temperature furnace with a video camera, inductively coupled plasma atomic emission–spectrometry and X–ray diffraction technique, respectively. Ash melting behaviour of selected agromass types shows that the hemp ash has the highest shrinkage starting temperature which reaches 1,079 °C. This is due to the high content of calcium and low content of potassium and sodium in hemp ash. Three main components calcium carbonate, potassium sulfate and potassium chloride have been identified in ashes after agromass and woody biomass are heat–treated at temperature of 550 °C.

Key words: agromass, agrofuels, ash, ash melting, alkali metals.

INTRODUCTION

A growing demand for energy, decreasing resources of fossil fuel and increasing environmental pollution induce search for alternatives of fossil fuel. One of them is biofuel, which until now, was mainly produced from woody biomass. The consumption of such biomass has risen during the past two decades, growing at an annual rate of over 2% (Patel & Gami, 2012). Yet not only woody biomass can be used for biofuel production, but also herbaceous plants of short rotation and agricultural waste such as straw (hereinafter – agro biomass or in abbreviated form – agromass). The fuel produced from agromass is usually called agrofuel. However, agrofuel has several negative properties related to high amounts of alkali and alkaline earth metals as well as chlorine (Cl) and sulphur (S). Therefore, despite the well–known advantages of agromass usage such as carbon dioxide neutrality and high energy generation potentiality, efficient and low–emission burning of such fuels is still limited due to technical problems associated with corrosion of equipment, ash agglomeration, fouling and slagging of partially fused deposits on furnace walls and convection heat surfaces.

The presence of alkali metals, such as potassium (K) and sodium (Na), has the greatest impact on ash melting during combustion. High contents of alkali metals and silicon (Si) results in the formation of sticky molten K silicates that melt under low temperature of approximately 750 °C. Such viscous ash sticks to the unburned fuel particles, which leads to agglomeration (Thy et al., 2006; Magzdiarz et al., 2016). Due to high content of K in the ash, K silicates as well as other compounds of K (chlorides, sulphates, carbonates) are formed. Melting point of these K compounds is low too, i.e. merely 770 °C (Wang et al., 2012). Na, which transformation mechanism in ash is similar to K, also reduces ash melting temperature. However, the content of Na in ash is very low, so for the following reason Na content is not distinguished separately and is attributed to K (Niu et al., 2016).

Woody biomass composition is quite stable, and contains large quantities of calcium (Ca) and Si, yet less phosphorus (P) and K. On the contrary, agromass composition varies greatly. Both grasses and straws contain large quanitites of Si and K. Smaller amounts of Ca and magnesium (Mg) are found in grasses, the same goes for aliuminium (Al) and Na in straw. Aquatic biomass contains large quanitties of K and Mg though less Al and Si (Vassilev et al., 2013). Moreover, the composition of agromass depends on the soil type, harvesting season (Niu et al., 2014), climate, type of fertilizer, its concentration and frequency of fertilization (Schiemenz & Eichler–Lobermann, 2010) and impurities that fall in during preparation and transportation of agromass (Wang et al.,. 2012).

Ash melting temperature depends not only on elemental composition of ash as a mineral matter, but also on the form of mineral compounds. It was determined, that potassium chloride and sulfate (KCl, K_2SO_4) are the dominant alkali–containing compounds that influence ash related issues. K_2SO_4 mainly accumulates on high temperature heating surfaces, while KCl accumulates on low temperature heating surfaces (Niu at al., 2016). However, mineral composition and chemical transformation mechanisms of agromass ash compounds are not fully investigated and further studies are required.

This study mostly focuses on determination of chemical composition and fusion properties of ash of selected types of agromass and woody biomass. The aim is to extend and improve the knowledge on agromass types which are less investigated and analyzed. Ash melting stages related to the shrinkage starting temperature (SST), deformation temperatute (DT), hemisphere temperature (HT) and flow temperature (FT) and their dependance on the ash elmental (Ca, K, Si, P, Mg, Al, Na) and mineral composition of ash are determined. These results can be beneficial with the goal to provide general understanding to industrial users about the agromass diversity and which types of agromass are suitable to use in combustion technologies.

MATERIALS AND METHODS

Nine different samples divided into three main groups, i.e. agricultural waste, herbaceous plants and woody biomass were selected for the analysis. For the group of agricultural waste, rye, wheat, buckwheat and canola straws were selected, because in

Lithuania the annual amount of this harvest waste reaches 3 million tons and only a small part of it is used according to its original purposes, as animal litter or feed. Pellets of orchard grass, reed canary grass and hemp were selected for the group of herbaceous plants. Two wood species spruce and birch (with bark) were selected for comparison.

All samples were dried in low temperature laboratory furnace under the temperature of 105 °C and later grinded with a mill. The ash content of all samples was determined using a muffle furnance (Nabertherm LVT/9/11/P330) at 550 °C according to ISO 18122:2016. Ashing experiment was carried out three times for each sample. Ash melting behaviour was conducted twice in muffle furnaces CARBOLITE with the monochromatic video camera CAF DIGITAL 380–415V with reference to CEN/TS 15370–1. Ashes were grinded with a pestle to obtain particles with a size of less than 0.075 mm. Using a mould with a defined pressure, a moistened (with ethanol) ash powder was used to form cylindrical ash samples with a size of 5 x 5 mm. Samples were heated in ash fusion furnace under reducting atmosphere. A furnace temperature was raised up to 550 °C. Then temperature was gradually raised 5 °C min^{-1} and photos were automatically made every interval of 2 °C till temperature has reached 1,600 °C. The temperature at which the phase of the sample changed was recorded.

Wet–digestion of the ashes and raw materials was applied before elemental composition analysis using a microwave oven Multiwave 3000 according to ISO 16967:2015. Samples were mineralised with solvent of H_2O_2 (30%), HNO_3 (65%) and HF (40%). In order to prevent Si contamination from glass, plastic vessels were used. The concentration of elements K, Ca, Mg, Na, Al, Si, P were measured using inductively coupled plasma atomic emission–spectrometry (ICP–OES) OPTIMA 8000 CROSS FLOW.

Volumetric structure of ash was determined using XRD Bruker AXS D8 diffractometer. Each sample was scanned for 45 minutes using Θ–2Θ modification in the interval from 20° to 70°. A source of X–ray CuKα1. Compounds identification were performed through comparison with standards of EVA Search–Match program from PDF–2 database.

RESULTS AND DISCUSSION

Accomplished analysis revealed that buckwheat (6.4%) and canola (6.5%) straws have the highest ash content (Fig. 1).

Ash content of herbaceous plants, excluding hemp, is also similar to ash content of straw. Ash content of hemp is more than twice lower (2.5%) than the other herbaceous plants. The difference in ash content between various types of agromass can be explained by few factors. Firstly, ash content and its amount depend on the genetic plant properties and its parts used for production of biofuel (Monti et al., 2008). This part of inorganic components source is the agromass itself. Secondly, quite large part of inorganic components, such as potassium, nitrogen, phosphorus and others which are necessary for plant growth, come with fertilizers.

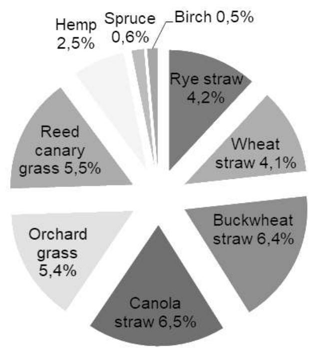

Figure 1. Ash content (% db.) of agromass and woody biomass.

Herbaceous plants, which are specifically cultivated for energy purposes, are fertilized in order to increase the quantity of agromass. The effects of climate, soil composition, harvesting and fuel preparation also can not be underestimated.

The results of ash melting behaviour are presented in Table 1. The obtained data shows that straw ashes have the lowest shrinkage starting temperature (SST), whereas the SST temperatures of herbaceous plants are even higher than the ones of woody biomass. SST temperature is the most important since it is the initial phase of ash melting. Melting formation at low temperatures makes ashes particularly troublesome because it induces stickiness of ashes which causes formation of slag.

Table 1. Ash melting temperatures of investigated types of biomass (°C)

	SST	DT	HT	FT
Herbaceous plants				
Reed canary grass	946	979	1,147	1,164
Hemp	1,079	1,418	1,490	1,496
Orchard grass	1,061	1,167	1,263	1,287
Agricultural waste				
Rye straw	739	875	1,163	1,185
Wheat straw	783	869	1,099	1,175
Buckwheat straw	698	751	1,544	1,549
Canola straw	722	1,061	1,497	1,502
Wood				
Birch	888	1,477	1,514	1,526
Spruce	849	1,497	1,523	1,531

Hemp is considered to be one of the most potent herbaceous plant for production of agrofuel because its ash melts at higher temperatures. Ash melting behaviour and slag formation depends on a component of the lowest melting temperature, chemical composition, combustion duration and conditions, because the longer fuel/ash is kept in high temperature, the more favourable are conditions for slagging (Fang & Jia, 2012).

The results of elemental composition of raw agromass and woody biomass as well as its ash are shown in Fig. 2 and Fig. 3.

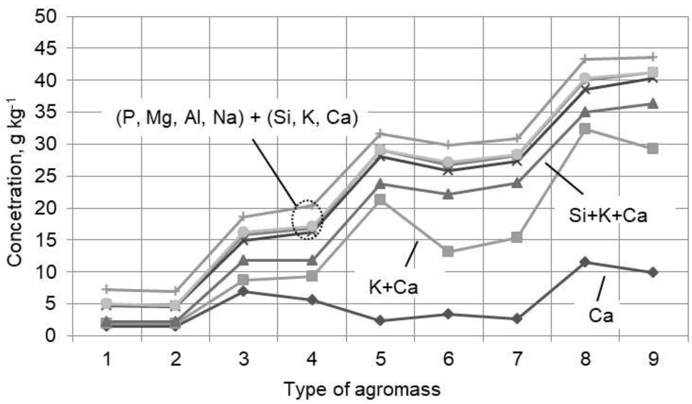

Figure 2. Elemental composition of agromass: 1 – birch; 2 – spurce; 3 – hemp; 4 – orchard grass; 5 – reed canary grass; 6 – rye straw; 7 – wheat straw; 8 – canola straw; 9 – buckwheat straw.

As can be seen from these Figures, the elemental composition of agromass, woody biomass and its ash is well correlated. Three elements Ca, K and Si make up the main part or the total content of all elements which increases consistently from the smallest total concentration value for the woody biomass to the largest value for the straw. For the investigated types of agrobiomass, the ratio of these values approaches 10 (Fig. 2). This trend is mainly due to an increase of K in grasses and especially in straw. The other elements (P, Na, Mg, Al) in the agrobiomass are also clearly visible, but their impact to the total element concentration is almost identical for all agrobiomass and woody biomass types. According to the elemental composition, the herbaceous plants such as hemp and orchard grass are closest to the woody biomass.

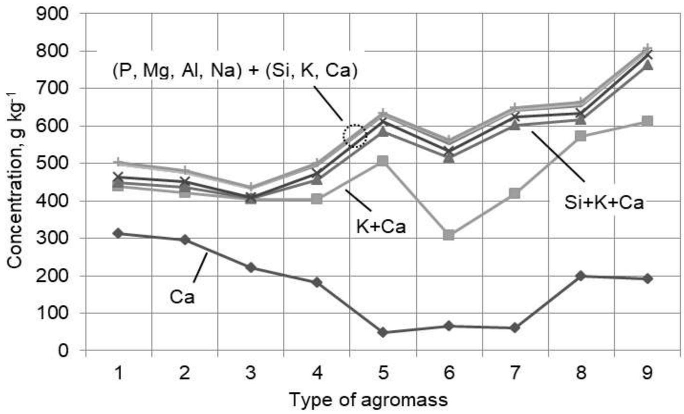

Figure 3. Elemental composition of agromass ashes: 1 – birch; 2 – spurce; 3 – hemp; 4 – orchard grass; 5 – reed canary grass; 6 – rye straw; 7 – wheat straw; 8 – canola straw; 9 – buckwheat straw.

The composition of ash is characterized by a significantly weaker dependence on the type of agromass. The main reason of such trend is the decreasing amount of Ca and K in the grass and straw ashes. Composition of hemp ash is clearly distinguishable. The total concentration of all elements in its ash is lower than a single one for wood ash. Compared to other herbaceous plants and agricultural wastes, hemp has a larger woody part of the stem, which affects the elemental composition of hemp ashes.

As mentioned before, the usage of fertilizers has also a substantial influence on the properties of agrobiomass, its ash, and elemental composition. Higher concentrations of Si in agricultural waste and herbaceous plants ashes may be due to agromass contamination with soil. However, the complex transformation of compounds takes place during combustion which results in reduction of some elements, such as K, in ash.

The results in Table 2 show that only a few cases exibit a sufficient level of correlation which allows to draw conclusions about ash melting behaviour dependence on the content of a single element.

Si has the greatest influence on the temperatures of DT, HT and FT. High amount of Si cause a decrease of these temperatures. The effect of Ca is more clear in the final ash melting stages. On the contrary, the effect of Na and K is more evident at the initial phases of ash melting, where the higher quantitites of these elements reduces the SST values. Conclusions about the effects of P, Mg and Al can not be made since the determination coefficients are less than 0.25. It can be concluded that a single element does not directly affect the ash melting behaviour. Summarizing the analysis data it can be assumed that higher amounts of Si, Na and K reduces ash melting temperature while Ca raises it. Similar results were obtained by other authors (Niu et al., 2010, Paulrud et al., 2001).

Table 2. Correlation of the ash melting behaviour and individual elements

	SST	DT	HT	FT
Ca	-0.24 (R^2 = 0.06)	0.36 (R^2 = 0.13)	0.65 (R^2 = 0.43)	0.66 (R^2 = 0.44)
K	-0.63 (R^2 = 0.39)	-0.67 (R^2 = 0.45)	-0.44 (R^2 = 0.19)	-0.44 (R^2 = 0.20)
Si	-0.41 (R^2 = 0.17)	-0.86 (R^2 = 0.74)	-0.79 (R^2 = 0.62)	-0.78 (R^2 = 0.60)
P	-0.37 (R^2 = 0.14)	-0.02 (R^2 = 0.00)	-0.25 (R^2 = 0.06)	-0.24 (R^2 = 0.06)
Mg	-0.45 (R^2 = 0.20)	0.21 (R^2 = 0.04)	-0.06 (R^2 = 0.00)	-0.05 (R^2 = 0.00)
Al	-0.50 (R^2 = 0.25)	-0.42 (R^2 = 0.18)	-0.35 (R^2 = 0.12)	-0.36 (R^2 = 0.13)
Na	-0.68 (R^2 = 0.46)	-0.06 (R^2 = 0.00)	-0.01 (R^2 = 0.00)	-0.01 (R^2 = 0.00)

Several chemical changes of ash mineral content take place during combustion in high temperatures. Si melts partially or completely and reacts with other ash forming elements, and mainly silicates of alkali metals (K and Na) are formed. Dissociation of carbonates, chlorides and other salts takes place. Alkali metals and heavy metals become volatile and evaporate. Due to this it is very important to determine the mineral composition of ash.

Analysis of such results, indicating the qualitative presence of crystalline minerals in the ash and melted ash samples are presented in Table 3 and Table 4. It has been found out that ash does not have a clear crystal structure and consists of oxides, silicates, carbonates, sulphates and phosphates, which are the main compounds that are formed during combustion. Ash forming compounds are largely very different depending on the agromass type. However, three main components calcium carbonate ($CaCO_3$), potassium sulfate (K_2SO_4) and potassium chloride (KCl) are the most commonly found in the ashes of agromass and woody biomass that are heat – treated at temperature of 550 °C.

Table 3. Mineral composition of agromass and woody biomass ashes (550 °C)

Herbaceous plants	
Reed canary grass	KCl, K_2SO_4, $Ca_4O(PO_4)_2$, SiO_2, $KCaPO_4$
Hemp	$CaCO_3$, $Ca_4O(PO_4)_2$, SiO_2
Orchard grass	KCl, $Ca_4O(PO_4)_2$, SiO_2, $KCaPO_4$, $Na_2Ca_3Si_2O_8$, $KMg_2Al_{15}O_{25}$
Agricultural waste	
Rye straw	$CaCO_3$, $K_2S_4O_6$, SiO_2, $MgSiO_3$
Wheat straw	KCl, K_2SO_4, $KCaPO_4$, SiO_2
Buckwheat straw	KCl, $CaCO_3$, K_2SO_4, $K_2S_2O_6$, $K_2Ca(CO_3)_2$
Canola straw	KCl, $CaCO_3$, K_2SO_4, $K_2Ca(CO_3)_2$, Ca_2SiO_4
Wood	
Birch	$CaCO_3$, K_2SO_4, $K_2Mg(PO_3)_4$, KMnP, $MnSO_4$
Spruce	$CaCO_3$, K_2SO_4, $K_2Mg(PO_3)_4$, KMnP, $MnSO_4$

There is also some difference between mineral composition of ash of the same group. Exclusively in the case of woody biomass ash, the identified compounds were the same: $CaCO_3$, K_2SO_4, potassium magnesium phosphate ($K_2Mg(PO_3)_4$), potassium manganese phosphide (KMnP) and manganese sulphate ($MnSO_4$). The dominant components of agricultural waste are KCl, $CaCO_3$ and K_2SO_4, whereas a vast majority of other K compounds are dominated. Hemp ash is the most distinctive among herbaceous plants. The following three main compounds $CaCO_3$, calcium oxophosphate ($Ca_4O(PO_4)_2$) and silica (SiO_2) have been identified. Ash of other herbaceous plants also contained KCl, but no $CaCO_3$ has been found in them. All other identified compounds are largely the same and K, Ca, P are predominated in composition. It means that alkali metals play a key role in formation of ash. For plants K is one of the most important nutrient that is absorbed from the soil in the form of dissolved salts, especially for one – year rotation fast–growing plants. Therefore, compounds with K, mainly KCl, K_2SO_4, $CaCO_3$, dominate in agromass ash.

Analysis of molten ash, which is obtained at FT (Table 4), reveal that silicates, aluminates and oxides are the main components. Results show that aluminium oxide (Al_2O_3) and spinel ($MgAl_2O_4$) are compounds that have been identified in melted ash of selected woody biomass and agromass samples. In this case, it is also necessary to consider that ash was melted on porcelain plates. Therefore, peaks of aluminium oxide (Al_2O_3) and silica (SiO_2) may be a result of a tray.

Table 4. Mineral composition of molten agromass and woody biomass ashes (at FT)

Herbaceous plants	
Reed canary grass	Al_2O_3, $MgAl_2O_4$, Si
Hemp	$MgAl_2O_4$, $Ca_2Al_2SiO_7$, $CaMg_2Al_6O_{12}$, $CaNa_3Al(P_2O_7)_2$, $CaAl_4O_7$
Orchard grass	Al_2O_3, $KCaPO_4$, SiO_2, $K_2Si_4O_9$, $K_{0,85}Al_{0,85}Si_{0,15}O_2$, KP_6O_{18}
Agricultural waste	
Rye straw	Al_2O_3, Si
Wheat straw	Al_2O_3, $MgAl_2O_4$, $KAlSi_2O_6$, Si
Buckwheat straw	Al_2O_3, $Ca_2Al_2SiO_7$, $CaAl_{12}O_{19}$, $KAl_3Si_3O_{11}$, $MgAl_2O_4$, $KAlP_2O_7$
Canola straw	$MgAl_2O_4$, $Ca_2Al_2SiO_7$, $Ca_3(PO_4)_2$
Wood	
Birch	Al_2O_3, Al, $Ca_3Si_2O_7$, $Al(PO_3)_3$
Spruce	Al_2O_3, $MgAl_2O_4$, $Ca_5(PO_4)_2SiO_4$, SiO_2, $Ca_3Al_2P_2Si_2O_{15}$, $Ca_3Al_2(SiO_4)_3$

Mineral composition of molten herbaceous plant ashes are quite different: orchard grass ash forming compounds mainly contain K, reed canary grass ash – Mg, whereas hemp ash – mostly Ca.

Molten ash mineral composition of agricultural waste is even more diverse. However, two main compounds, i.e. Al_2O_3 and $MgAl_2O_4$ are typical for this entire group of agromass. Al_2O_3 and many other Ca compounds have been identified in molten woody biomass ash.

It should be noted that mineral composition of molten hemp ash is very similar to mineral composition of molten woody biomass ash where Ca and Mg compounds are predominant.

In general, mineral composition of molten ash has less K compounds, so it can be assumed that through thermo–chemical reactions some ash elements become gaseous and are removed with volatile matter. Compounds with higher melting points are found in this type of ash.

The results obtained in this study are in good agreement with the data and conclusions of other authors (Thy et al., 2006, Niu et al., 2016, Fang & Jia, 2012), regarding the influence of temperature on ash forming compounds and their transformation into high melting temperature forms while temperature increasing.

CONCLUSIONS

From all studied agromass species, hemp has been distinguished as the most suitable for agrofuel production due to the lowest ash content (2.5%), highest SST temperature (1,079 °C) and appropriate mineral composition of ash.

Furthermore, it has been determined that higher amounts of Si, K and Na reduce ash melting temperature while Ca raises it. However, the correlation between fusion temperatures and concentration of separate elements is strong only in the case of Si. It means that a single chemical element does not directly affect the temperature of ash melting phase. Summarizing the analysis data of ash mineral composition it has been concluded that ash does not have a clear crystalline structure and oxides, silicates, carbonates, sulphates, and phosphates are the main components of which the most common compounds are $CaCO_3$, K_2SO_4, KCl. The main compounds found in molten ash are silicates, aluminates and oxides, most often in the form of Al_2O_3 and $MgAl_2O_4$.

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