Annals of Warsaw University of Life Sciences - SGGW
Forestry and Wood Technology No 90, 2015: 66-72
(Ann. WULS - SGGW, For. and Wood Technol., 90, 2015)

Influence of the chemical composition of inorganic share plant phytomass and woody biomass on sintering of ash

LADISLAV DZURENDA[1)], JOZEF JANDAČKA[2)]
[1)] Faculty of Wood Sciences and Technology, Technical University in Zvolen, 960 53 Zvolen, Slovakia
[2)] Faculty of Mechanical Engineering, Department of Power Engineering, University of Zilina, 010 26 Zilina, Slovakia

Abstract: *Influence of the chemical composition of inorganic share plant phytomass and woody biomass on sintering of ash*. In the present work there are evaluated the following biofuels: plant phytomass, wood and bark through the proposed criteria (Ca + Mg) / K ≤ 1 from the aspect of ash sintering.The analyses show that the ash content of plant phytomass is 12.5 times higher than the ash content of wood and 2.2 times higher than the ash content of bark. The results of the quantitative representation of calcium Ca, magnesium Mg and potassium K in inorganic matter of plant phytomass, wood and bark indicate, that plant phytomass has more than 7.7 times higher proportion of potassium K than wood and 4.3 times higher than the bark. These facts are reflected in the heat and physical characteristics of the ash. On the basis of the proposed criteria the biofuels can be divided into plant phytomass with the value of ash sintering lower than 1. Inorganic matter of those biofuels on the boiler furnace softens and sinters at temperature range T = 1000 to 1100 °C. On the other hand, woody biomass with significantly higher value of sintering of , more than 1, in the combustion process at temperatures up to 1100 °C is in the form of natural powder.

Keywords: biofuels, ash, calcium, magnesium, potassium, temperature, sintering

INTRODUCTION

Biomass (phytomass and woody biomass) is composed of natural polymers: celllulose, hemicellulose, lignin and in small extent also of accompanying organic and inorganic (mineral) substances. Minerals as in plants also in trees are obtained during the growth from the soil through its root system.

Chemically, the inorganic materials of woody biomass are carbonates: $CaCO_3$, $MgCO_3$, $FeCO_3$, complex silicates of aluminum, magnesium, calcium, iron, sodium and potassium, small amounts of alkali metals and phosphates, halogen minerals: NaCl, KCl, and the trace amounts of heavy metals: Zn, Cu, Co, Ni, Cr, Pb, V, Cd.

Botanists by function and need for the healthy development of plants and trees divided these substances into macro and micro nutrients ***Ditmarova et al.* (*2007*)***, Merilä and Derome (2008)*. Elements such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) in an amount of 1 to 150 $g.kg^{-1}$ of the dry weight of biomass are arranged in the group of macro nutrients. On the contrary, the elements such as iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B) and chlorine (Cl) contained in concentrations of 0.1 to 600 $mg.kg^{-1}$ of dry weight of biomass are classified among the micro nutrients.

Data on the amount of inorganic substances in phytomass and woody biomass in its vast majority are stated based on an indirect determination, i.e. from the ash content after combustion phytomass and woody biomass. According to the works ***Nikitin* (*1956*) *Blažejet al.* (*1975*)*, **Simanov* (*1995*)*, **Dzurenda* (*2005*), ***Jandačka – Malcho –Mikulík* (*2007*)*, ***Otepka – Habán (2011)*, *Dzurenda – Pňakovič* (*2014*), *Dzurenda – Banski – Šustek*** (2015) ash from the

combustion of annual plants, grasses or wood and bark is a mixture of oxides: K_2O, Na_2O, CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2, P_2O_5 and thermally undecomposed carbonates and silicates. While the quantitative share of ash from annual plants in the dry state is A = 4 - 10%, of the dry wood of A = 0,3 - 0,7%, and bark in the dry state A = 1 - 5%

From the aspect of heat-physical characteristics of ash and fouling of furnace boiler by sintering component of the ash in the combustion process of some biofuels authors: ***Malaťák - Vaculik* (*2008*)*, Dzurenda - Jandačka* (*2010*), *Jandačka - Holubčík - Papučík - Nosek* (*2012*)** recommend to burn biofuels with so-called with a low melting ash with the combustion conditions of the temperature under 850-900 °C. Sintering of ash from the biofuel has considerable impact representationcompounds of calcium Ca, magnesium Mg and potassium K in inorganic matter of biomass. While calcium Ca, and magnesium Mg increases the melting temperature of the ash, potassium and chlorides of potassium and sodium melting temperature reduced.

The aim of the present work is the assessment of biofuels - plant phytomass, wood and bark from the aspect of sintering of the inorganic matter on the grate furnace at temperature t = 1000 - 1100 °C based on the criterion (Ca + Mg) / K ≤ 1.

MATERIALS AND METHODS

From samples of phytomass of the annual plants: wheat and barley straw, hay, wood of the species: norway spruce, beech, aspen poplar, black locust and bark of the species: norway spruce, scots pine and white willow there was determined by ICP AES technique the proportion of calcium Ca, magnesium Mg, potassium K, manganese Mn, phosphorus P, sodium Na and iron Fe. The principle of the ICP AES is based on the measurement of various elements of atomic emission using the optical spectroscopy technique via atomic emission spectrometer with inductively coupled plasma ES 725 VARIAN.

Ash content of individual biofuels was determined according to *EN14775: (2010) - Solid biofuels - Determination of ash content*. The samples of the individual biofuels were annealed in a LAC LMH 04/12 muffle furnace at a temperature of 550 ± 10 °C. The share of ash in the biofuel in the analyzed sample was expressed as a percentage by weight and calculated using Eq. 3:

$$A_{Fuel} = \frac{m_3 - m_1}{m_2 - m_1} * 100 \quad [\%] \tag{1}$$

Where A_{Fuel} is the proportion of ash [%], m_3 is the weight of the sample container and the ash [g], m_2 is the weight of the sample container and the sample [g], and m_1 is the weight of the sample container [g].

Sintering of ash was controlled by analyzing the ash from the combustion of individual biofuels with excess combustion air λ = 2.1 in grate boiler furnace in the boiler at a controlled temperature combustion of non-volatile combustibles to grate in the temperature range T = 1000-1100 °C.

The assessment of the biofuel from the aspect of ash sintering in the combustion process in the grate boiler furnace at temperature t = 1000 - 1100 °C is proposed the criterion as a ratio of the sum of calcium and magnesium to potassium contained in inorganic mater of biofuels:

$$\frac{Ca + Mg}{K} \tag{2}$$

RESULTS

The measured values of the share of ash in individual samples of plant phytomass, wood and bark of coniferous and deciduous trees were determined according to EN 14775:(2010) - Solid biofuels and are displayed by histogram in Fig. 1

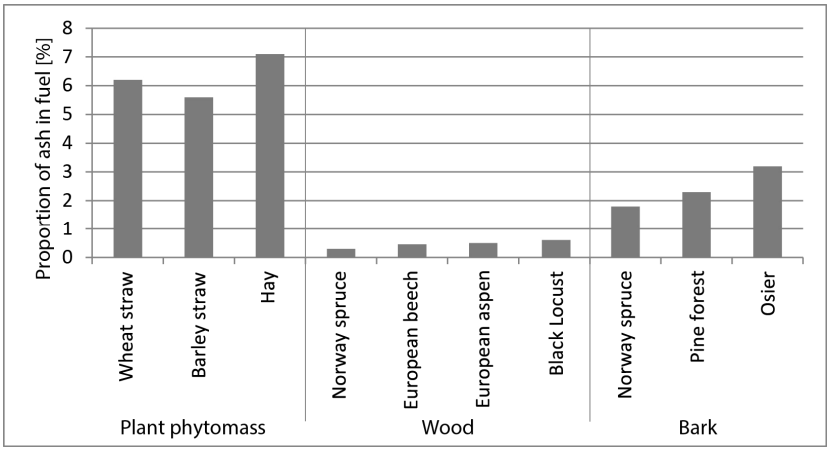

Fig. 1 Ash content of analyzed samples of plant phytomass, wood and bark of coniferous and deciduous trees

Results of laboratory experiments establishing the representation of Ca, magnesium Mg, potassium K, manganese Mn, phosphorus P, sodium Na and iron Fe in plant phytomass, wood and bark of the analyzed coniferous and deciduous trees, which were determined by the ICP AES method, are displayed in the Tables 1-3.

Tab.1

Plants	**Inorganic elements in phytomass determined by ICP AES [mg.kg^{-1}]**						
	Ca	**Mg**	**K**	**Mn**	**P**	**Na**	**Fe**
Wheat straw	4 000	700	10 000	40	1 000	500	100
Barley straw	5 400	870	11 100	54	1 350	620	132
Hay (dry grass)	3 500	1 700	15 000	1 000	15 000	3 000	600

Trees species	**Inorganic elements in wood of coniferous and deciduous trees determined by ICP AES [mg.kg^{-1}]**						
	Ca	**Mg**	**K**	**Mn**	**P**	**Na**	**Fe**
Norway spruce	850	180	485	65	64	20	25
European beech	1 230	315	890	83	188	73	76
Aspen poplar	1 320	210	1 035	71	142	88	109
Black Locust	1 463	419	1 298	86	680	95	116

Trees species	Inorganic elements in bark of coniferous and deciduous trees determinedby AES ICP [mg.kg^{-1}]						
	Ca	Mg	K	Mn	P	Na	Fe
Norway spruce	5 880	980	2 109	465	464	420	425
Scots pine	5 230	815	2 098	383	488	473	376
Osier	12 363	619	2 329	138	480	105	135

In Table 2 there are displayed values of the sum of the weights of calcium and magnesium, the weight of the potassium in the individual analyzed samples of biofuels, the value of the criterion (Ca + Mg) / K for the assessment of biofuels from the aspect of ash sintering and the results of the evaluation of ash in terms of its physical state: scab, respectively natural powder.

Tab. 2

Biofuels		Ca + Mg	K	Ration $\frac{Ca+Mg}{K}$	Form
		mg/kg a.s.			
Wheat straw		4 700	10 000	0,47	Scab
Barley straw		6 270	11 100	0,56	Scab
Hay (dry grass)		5 200	15 000	0,67	Scab
Norway spruce	*Wood*	1 030	485	2,12	Natural powder
European beech	*Wood*	1 545	890	1,73	Natural powder
Aspen poplar	*Wood*	1 530	1 035	1,47	Natural powder
Black Locust	*Wood*	1 882	1 298	1,45	Natural powder
Norway spruce	*Bark*	6 860	2 109	3,25	Natural powder
Scots pine	*Bark*	6 045	2 098	2,88	Natural powder
Osier	*Bark*	12 982	2 329	5,57	Natural powder

Evaluation of the analyzed biofuels - plant phytomass, wood and bark of individual coniferous and deciduous trees according to the criterion of ash sintering of biofuels is in the form of the histogram shown in Fig. 2.

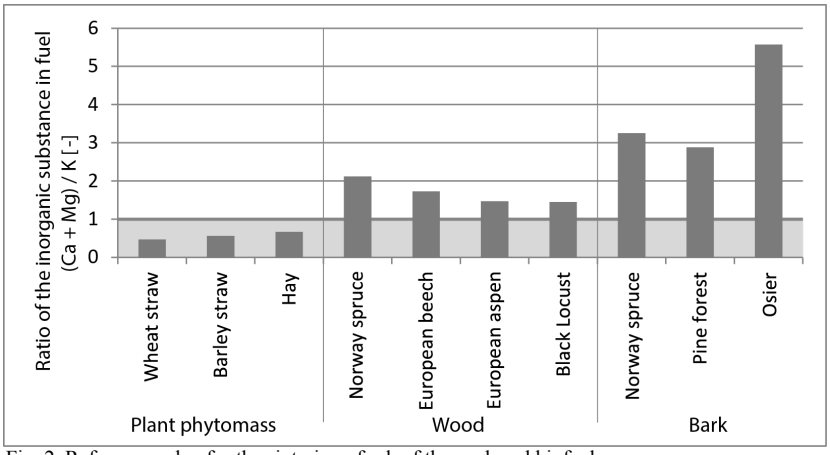

Fig. 2 Reference value for the sintering of ash of the analyzed biofuels

Based on the results presented in Table 2 and Figure 2 it can be concluded that biofuels which are burned in the boiler furnace at temperature T = 1000 to 1100 °C, can be evaluated from aspect of ash sintering according to the criterion in the form of the following inequality:

$$\frac{Ca + Mg}{K} \leq 1$$

Biofuels with the value of ash sintering equal to 1 or with the value less than 1 generate by combustion processes ash in the form of scab and biofuels with the value of sintering of inorganic matter greater than 1, produce ash in the form of natural powder.

DISCUSSION

The results of the analysis of inorganic elements in plant phytomass, wood and bark of coniferous and deciduous trees show that the analyzed biofuels vary considerably, both in quantitative terms, as well as in the representation of individual inorganic elements in biofuels. Ash content of plant phytomass is 12.5 times higher than ash content of wood and 2.2 times higher than ash content of the bark.

The results of the quantitative representation of calcium Ca, magnesium Mg and potassium K in inorganic mater of plant phytomass, wood and bark indicate that plant phytomass has more than 7.7 times higher representation of potassium than wood and 4.3 times higher representation than bark. The differences are also represented in calcium, while the plant phytomass has 3.3 times more calcium than wood, the representation of calcium in the plant phytomass is comparable to the bark, except for the species Osier. These facts are reflected in the heat and physical characteristics of the ash.

Significantly higher proportion of calcium and magnesium i.e. elements with higher melting temperature of calcium and magnesium in inorganic mater than potassium in inorganic mater of biofuel is projected in the physical state of ash in the process of combustion. Ash from wood and bark is in the form of natural powder, while ash from the plant phytomass with significantly higher representation of potassium in inorganic matter of biofuels than calcium and magnesium is sintered in the form of scab. The mentioned finding is also documented in the reports of physical analysis of ash from combustion processes of particular biofuels on grate of the boiler furnace.

The criterion of sintering of ash from biofuels generated by inequality $(Ca + Mg) / K \leq 1$ allows to divide the biofuels according to the proportion of calcium, magnesium and potassium in inorganic mater of biofuel into the biofuels producing from a combustion process at temperature t = 1000 to 1100 °C inorganic matter - scab and respectively ash in the form of natural powder. This criterion can become a simple tool for assessing biofuels from aspect of sintering ashes and operating conditions, and the impact of ash on its transport from furnace of heat generators.

CONCLUSION

The results of the analysis of inorganic elements in plant phytomass, wood and bark of coniferous and deciduous trees show that the analyzed biofuels vary considerably, both in quantitative terms, as well as in the representation of individual inorganic elements in biofuels. These facts are reflected in the heat and physical characteristics of the ash.

On the basis of the proposed criteria (Ca + Mg) / K ≤ 1 the biofuels can be divided into plant phytomass with the value of ash sintering lower than 1. Inorganic matter of those biofuels on the boiler furnace softens and sinters at temperature range T = 1000 to 1100 °C. On the other hand, woody biomass with significantly higher value of sintering of , more than 1, in the combustion process at temperatures up to 1100 °C is in the form of natural powder.

REFERENCES:

1. BLAŽEJ, A. et al 1975: *Chemistry of wood*. ALFA, Bratislava. (in Slovak).
2. DITMAROVA L., KMET J., JEŽIK M., VALKA J. 2007: *Mineral nutrition in relation to the Norway spruce forest decline in the region Horny Spiš (Northern Slovakia),* Journal of Forest Science 53 (3):93-100.
3. DOMAŃSKI M., DZURENDA L., JABŁOŃSKI M., OSIPIUK J. 2007: *Wood as a material energetic.* SGGW, Warszawa. (in Polisch).
4. DZURENDA L. 2005: *Wood combustion and bark*. TUZVO, Zvolen. (in Slovak).
5. DZURENDA L., JANDAČKA J. 2010: *Energetic utilization of dendromass*. TUZVO, Zvolen. (in Slovak).
6. DZURENDA L., PŇAKOVIČ Ľ. 2014: *Quantification of the ash content from biofuel - wood according to ISO 1171 (2003) and EN 14775 (2010).* Annals of Warsaw University of Life Sciences, No. 86 (2014) ISSN 1898-5912.
7. DZURENDA L., BANSKI A., ŠUSTEK J. 2015: *Dendromasa - biofuel for production of heat and electricity* TUZVO, Zvolen. (in Slovak).
8. JANDACKA J., MALCHO M., MIKULÍK M. 2007: *Biomass as a source of energy*. GEORG Zilina. (in Slovak).
9. JANDACKA J., HOLUBČÍK M., PAPUČÍK Š., NOSEK R. 2012: *Combustion of pellets from wheat straw*. In: Acta Montanistica Slovaca 17(4):283-289.
10. MERILÄ P., DEROME J. 2008: *Relationships between nedele nutrient composition in Scots pine and Norway spruce stands and the respective concentrations in the organic layer and in percolation water,* Boreal Environment Research 13 (suppl. B):35-47.
11. MALATAK J., VACULÍK P. 2008: *Biomass for production of energy*. CZU, Praha. (in Czech).
12. NIKITIN I.N. 1956: *Wood chemistry*. SNTL. Praha., 552 p. (in Czech).
13. OTEPKA P., HABAN M. 2011: *Osier willow Salix viminalis L. grown as a renewable source of energy in warm agro-climatic microreegion of Slovak Republic*. SPU, Nitra. (in Slovak).
14. OTEPKA P., TÓTHOVA S. 2011: *Properties of wood ash and the possibility of its use for growing energy plants.* Bratislava, (in Slovak).
15. SIMANOV V. 1995: *Energetic use of wood*. Terapolis, Olomouc. (in Czech).

Streszczenie: *Wpływ składu chemicznego części nieorganicznej fitomasy roślinnej i biomasy drzewnej na spiekanie popiołu*. W niniejszej pracy poddano ocenie następujące biopaliwa: fitomasę roślinną, drewno i korę, według zaproponowanego kryterium (Ca + Mg) / K ≤ 1, w aspekcie spiekania popiołu. Analizy pokazują, że zawartość popiołu z fitomasy roślinnej jest 12,5 razy wyższa od zawartości popiołu z drewna i 2,2 razy wyższa od zawartości popiołu z kory. Wyniki reprezentacji ilościowej wapnia (Ca), magnezu (Mg) i potasu (K) w części nieorganicznej fitomasy roślinnej, drewna i kory wskazują, że fitomasa roślinna ma ponad 7,7 razy wyższy odsetek potasu niż drewno i 4,3 razy wyższy niż kora. Fakty te znajdują odzwierciedlenie w cechach fizycznych i właściwościach cieplnych popiołu. Na podstawie proponowanych

kryteriów z biopaliw można wydzielić te z fitomasy roślinnej ze spiekaniem popiołu o wartości mniejsza niż 1. Materia nieorganiczna z tych biopaliw spieka się w zakresie temperatur od 1000°C do 1100°C w formie żużlu blokującego ruszt paleniska. Z drugiej strony, biomasa o znacznie wyższej wartości spiekania - powyżej 1, spala się w temperaturze ponad 1100°C w formie sypkiego proszku.

Ackonwledgement: *This experimental research was undertaken with the financial support based on the grant agreement KEGA–SR No: 006TU Z-4/2014, of the agency KEGA–SR.*

Author's addresses:

Ladislav Dzurenda,
Faculty of Wood Technology,
Technical University of Zvolen,
T.G.Masaryka 24, 96053 Zvolen,
SLOVAKIA,
e-mail: dzurenda@vsld.tuzvo.sk

Jozef Jandačka
Faculty of Mechanical Engineering,
University of Zilina,
Univezitna 8215/1, 010 26 Zilina,
SLOVAKIA
e-mail: jozef.jandacka@fstroj.uniza.sk