Influence of the Burning Temperature of the Non-Volatile Combustible Content of Wood and Bark of Plantation-Grown, Fast-Growing Tree Species upon Ash Production, and Its Properties in Terms of Fusibility

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The influence of the burning temperature was evaluated for the non-volatile combustible content of wood and bark of plantation-grown trees, at temperature intervals ranging from 500 °C to 1000 °C relative to ash production and the concentration of Ca, Mg, K, Mn, Zn, and Fe in ash, thermal properties, and ash fusibility. Production of ash from combustion of juvenile wood at t = 500 °C was A^d = 0.74% and juvenile bark A^d = 6.88%. Ash production decreased with increasing burning temperature. This was attributed to the chemical diversity of minerals contained in the wood and bark and their slow decomposition. Analyses of the presence of inorganic substances in ash from wood and bark revealed the highest presence of Ca. The concentration of calcium in ash from wood was Ca = 189 ± 46 $g.kg^{-1}$ and in bark Ca = 278 ± 25$g.kg^{-1}$. The ratio of processed calcium, potassium, magnesium, zinc, manganese, and iron in ash from wood at a burning temperature of t = 500 °C was Ca:K:Mg:Zn:Mn:Fe = 1:0.58:0.13:0.04:0.03:0.02 and from bark Ca:K:Mg:Zn:Mn:Fe = 1:0.41:0.07:0.01:0.01:0.003, respectively. The influence of the burning temperature non-volatile combustible was reflected in the concentration of each elements in ash and was contradictory. While concentration of Ca, Mg, Mn, and Fe in ash from wood and bark increased, concentration K and Zn in ash decreased. The decrease in concentration K, had a positive influence upon the thermal characteristics of the ash and the creation of ash in the form of loose matter.

Keywords: Fast growing trees; Non-volatile matter; Burning temperature; Ash, Inorganic elements; Ash fusibility

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INTRODUCTION

In the last 30 years, plantations of fast-growing wood species have been established that have a minimum dendromass production of 10 *t* of dry wood per hectare per year. As noted (Varga and Godó 2002; Weger 2008; Čižkova *et al*. 2010; Liebhard 2010), suitable wood species cultivated on plantations for producing dendromass for energy purposes in Central Europe include black locust (*Robinia pseudoacacia* L.), poplar clones (*Populus* sp.), white willow (*Salix alba* L.), and clones of willow (*Salix viminalis* L.).

Biomass is composed of natural polymers: cellulose, hemicellulose, lignin, and supporting small extent organic and inorganic substances. During their growth, trees obtain inorganic substances from the soil *via* their root system. The concentration of individual elements in the inorganic proportion differs between wood species as well as within individuals of the same species, and it also depends on the place of growth and ecological factors (Blažej *et al*. 1975; Simanov 1995; Zule and Dolenc 2012; Hytönen and Nurmi 2015; Pérez *et al*. 2015; Pňakovič and Dzurenda 2015; Dzurenda and Pňakovič 2016a). Needles, leaves, bark, wood of branches, and roots generally contain a higher concentration of inorganic substances than the wood of the tree stem. There are also differences related to the age of the tree; young individuals contain a higher concentration of mineral substances than older individuals. Deciduous wood species are richer in minerals than coniferous species.

The amount of inorganic substances in dendromass is usually determined indirectly (*i.e.*, ash residue after burning dendromass). During combustion, dendromass produces a low ash content, with A^d values for dry wood of 0.21 to 0.67% and bark of 1.80 to 5.55%. Ash from burning wood is a mixture of oxides including K_2O, Na_2O, CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2, and P_2O_5 (Nikitin 1956; Buchanan 1963; Blažej *et al*. 1975; Misra *et al*. 1994; Zevenhoven 2001). Although the amount and content of ash from dendromass depends on the wood species and the aforementioned factors, the acceptable ranges of individual oxides are as follows: CaO, 40 to 70%, K_2O; 10 to 30%; MgO, 0.5 to 10%; and Fe_2O_3, 0.5 to 2% (Blažej *et al*. 1975). The inorganic proportion of wood matter determined in ash also depends on the combustion conditions and burning temperature of biofuel (Misra *et al*. 1994; Obernberger *et al.* 1997; Malaťak and Vaculík 2008; Zevenhoven *et al*. 2010; Fernandes *et al*. 2013; Dzurenda and Pňakovič 2014, 2016b). The proportion of ash decreases with increased burning temperature. Apart from the oxides of inorganic elements, ash from the combustion process of dendromass below 750 °C also contains thermally undecomposed carbonates, sulphates, and silicates.

The chemical composition of ash has an immediate effect upon its thermal characteristics. The thermal characteristics of ash from biofuel depend significantly upon the content of calcium, magnesium, and potassium in the ash of biofuel (Malaťak and Vaculík 2008; Jandačka *et al*. 2011; Dzurenda and Jandačka 2015). Whereas the calcium and magnesium compounds increase the melting temperature of ash, potassium compounds with a lower ash softening and melting temperature decrease the thermal characteristics of the inorganic residue from burning biofuel.

This paper investigated the influence of burning temperature on ash production from non-volatile combustible wood matter from plantation-grown locust, willow, and poplar. The burning temperature ranged from 500 to 1000 °C. The concentration of calcium, magnesium, potassium, manganese, zinc, and iron in ash were quantified, and the thermal properties were examined in terms of ash fusibility.

EXPERIMENTAL

Materials

The fast-growing wood species black locust (*Robinia pseudoacacia* clone Gori), osier (*Salix viminalis* clone Sven), and poplar (*Populus x euroamericana* clone Max 4) were harvested from plantations. Samples of locust wood and bark were taken from the National Forestry Centre at the Fiľakovské Kľačany Research Station (Zvolen, Slovakia). Samples of willow wood and bark were taken from the plantation of the Institute of Christ the High Priest (Ľubica, Slovakia), and poplar dendromass samples were taken from a stand in the Forestry and Game Management Research Institute at Kunovice Research Station (Uherské Hradište, Czech Republic).

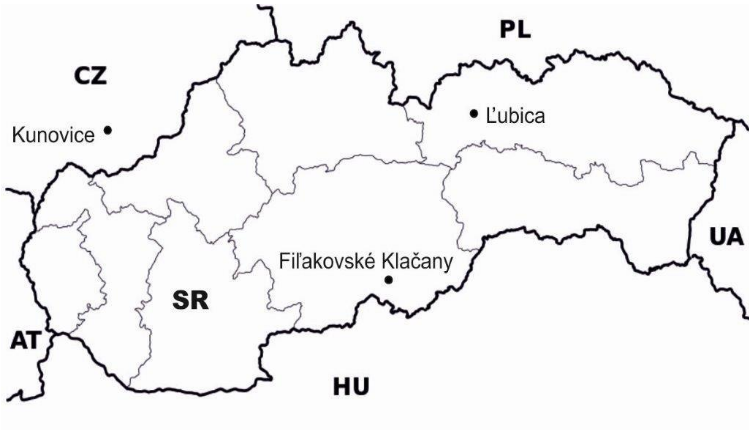

Fig. 1. Plantation locations of locust, willow, and poplar samples

Methods

Quantification of bark

The proportion of bark in chips for energy production from individual wood species was determined in accordance with STN 480058 (2004) and calculated using Eq. 1,

$$X_K = \frac{m_B}{m_{Ch}} * 100 \quad (1)$$

where X_K is the proportion of bark (%), m_B is the weight of bark in the sample of chips (g), and m_{Ch} is the weight of the sample of chips (g).

Quantification of ash

The proportion of ash in non-volatile combustible wood matter was determined by burning samples of dry wood (Wr = 0%), weighing approximately 10 g when placed in a ceramic dish in the muffle furnace (LAC LMH 04/12, LAC Ltd. Rajhrad, Czech Republic). Burning biofuel in the first phase at the temperature t = 500 °C was done by evenly heating the wood sample at a rate of 8 °C/min for 60 min (Fig. 2). This temperature was maintained in the muffle furnace for a further 480 min. A similar method was used for burning temperatures t = 600 °C to 1000 °C.

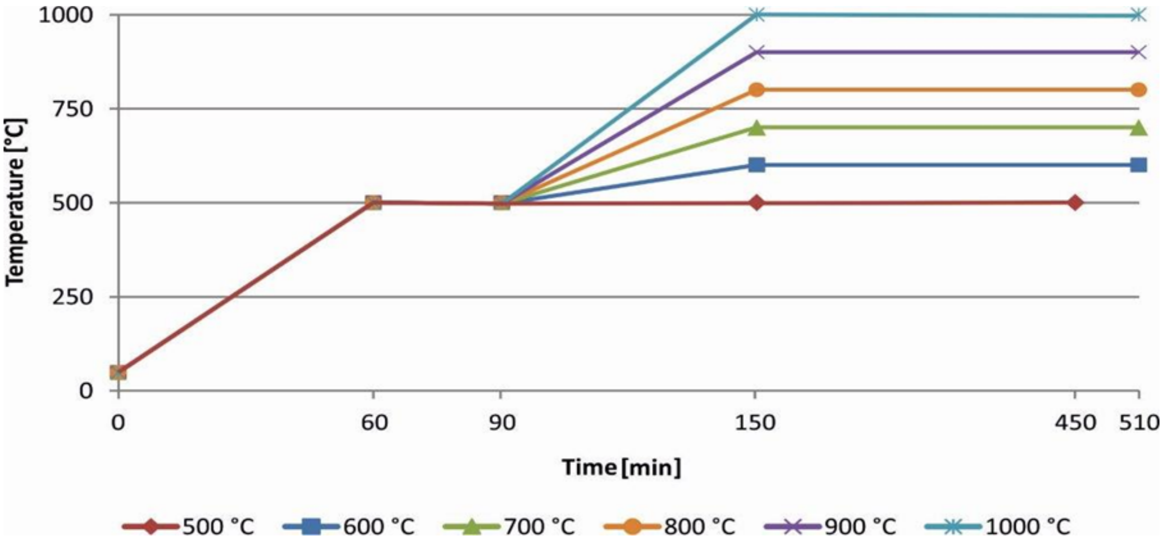

Fig. 2. The development of igniting a sample of biofuel in the muffle furnace

In the first phase of burning, the wood sample was heated to 500 °C at a rate of 8 °C/min and maintained at this temperature for an additional 30 min. In the second phase, the non-volatile combustible matter in the sample was heated for 60 min to the required temperature. This temperature was maintained in the muffle furnace for 360 min (Fig. 2). The content of ash (A^d) was calculated using Eq. 2,

$$A_{fuel}^{d} = \frac{m_3 - m_1}{m_2 - m_1} * 100 \tag{2}$$

where A_{fuel}^{d} 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).

The concentration of inorganic elements in ash, *i.e.*, calcium (Ca), magnesium (Mg), potassium (K), zinc (Zn), manganese (Mn), and iron (Fe), was determined from samples of ash obtained from the process of burning locust, willow, and poplar wood or bark at temperatures from 500 °C to 1000 °C in a muffle furnace using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The principle of the ICP-AES method is based on measuring the atomic emissions of individual atoms of elements using optical spectroscopy with an ES 725 atom emission spectrometer (Varian, Palo Alto, CA, USA) and inductively coupled plasma. Samples are then nebulized, which creates an aerosol that is transported to a plasma burner for the excitation of atoms.

Characteristic emission spectra are produced in radio frequency inductively coupled plasma. The spectra are dispersed using Echelle grating, and the intensity of the appropriate lines is monitored using a CCD detector that is based on the wavelength of individually measured elements. Signals from the detector are captured and processed using a computer system.

The quantitative representation of dominant elements (Ca, Mg, and K) in the ash from 1 kg of dry wood or bark burning at temperature t = 500 to 1000 °C, based on the proportion of ash and the concentration of the element in ash, is given in Eq. 3,

$$\mathrm{X_i} = \frac{\mathrm{A_{ti}} \cdot X_{Ati}}{100} \tag{3}$$

where Xi is the amount of elements in ash from 1 kg of dry wood or bark (g.kg^{-1}), A_{ti} is the proportion of ash from the sample of biofuel from the given wood species (%), and X_{Ati} is the concentration of the element in ash from the sample of biofuel from the given wood species (g.kg^{-1}).

RESULTS AND DISCUSSION

The proportions of bark and wood in chips from the dendromass of plantation-cultivated wood species are shown as a mean value and standard deviation (Fig. 3). The proportion of bark in chips did not exceed the permitted value of the proportion of bark in energy chips, which was in compliance with STN 480058 (2004), namely, $X_K \leq 30$ %) (Klašnja *et al.* 2002; Lazdinija *et al.* 2006; Walle *et al.* 2007; Guidy *et al*. 2013; Banski and Dzurenda 2014; Nosek *et al*. 2016).

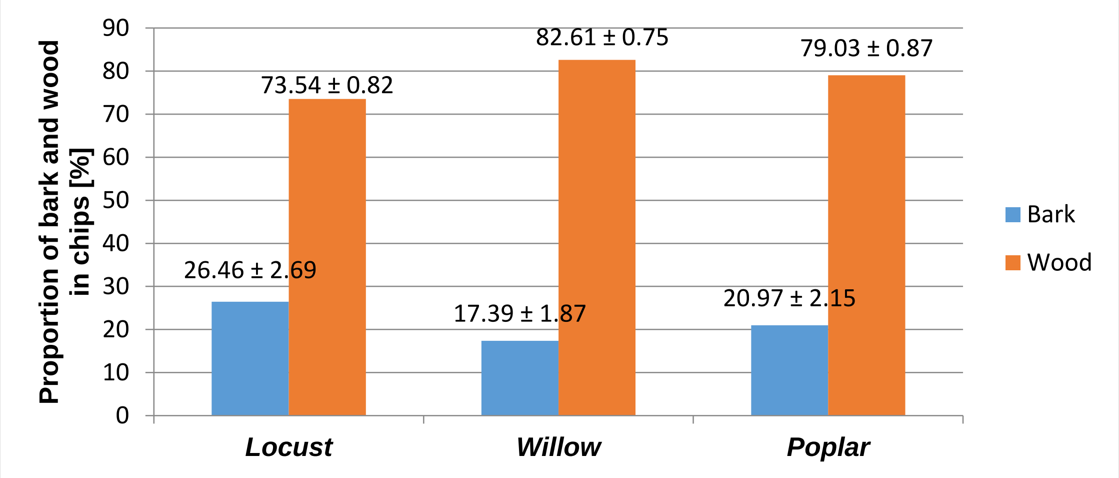

Fig. 3. The proportion of bark and wood in chips from plantation-cultivated dendromass

The proportions of ash from burning non-volatile combustible wood and bark matter at temperatures from 500 °C to 1000 °C are given in Figs. 4 and 5.

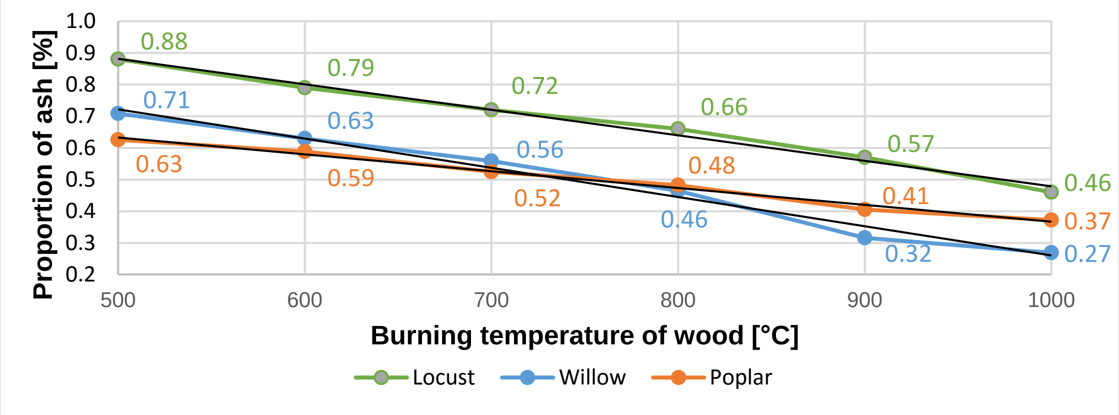

Fig. 4. The proportion of ash from burning wood of at various temperatures

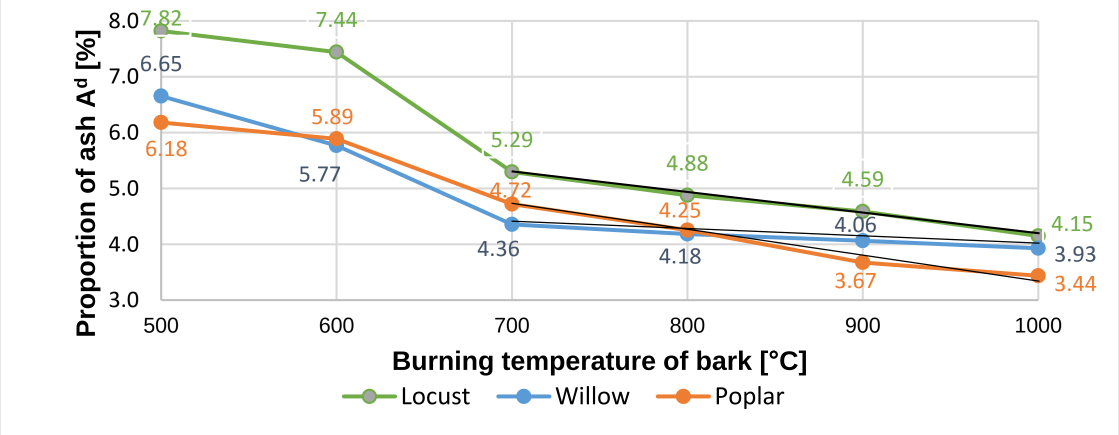

Fig. 5. The proportion of ash from burning bark at various temperatures

Table 1 shows the functional dependencies and determination coefficients for the production of ash from burning non-volatile matter of wood in a muffle furnace with a combustion temperature (*t*) ranging from 500 to 1000 °C. Burning non-volatile bark matter with a combustion temperature ranging from 700 °C to 1000 °C is shown in Table 2.

Table 1. Functional Dependency of Combustion Temperature on Ash Production from Non-volatile Wood Matter

Wood Species Wood	Functional Dependence	Determination Coefficient
Locust	$A^d = -0.0008 \cdot t + 1.2843$	$R^2 = 0.9913$
Willow	$A^d = -0.0009 \cdot t + 1.1832$	$R^2 = 0.9839$
Poplar	$A^d = -0.0005 \cdot t + 0.9910$	$R^2 = 0.9910$

Table 2. Functional Dependency of Combustion Temperature on Ash Production from Non-volatile Bark Matter

Wood Species Bark	Functional Dependence	Determination Coefficient
	700 to 1000 °C	700 to 1000 °C
Locust	$A^d = -0.0037 \cdot t + 7.881$	$R^2 = 0.9944$
Willow	$A^d = -0.0014 \cdot t + 5.331$	$R^2 = 0.9913$
Poplar	$A^d = -0.0041 \cdot t + 7.414$	$R^2 = 0.8977$

The analyses stating the production of ash from burning fuel-wood and bark presented in the works of Simanov (1995), Vesterinen (2003), Jandačka *et al*. (2007), Malatak and Vaculik (2008), and Dzurenda *et al*. (2013) show that ash content of wood is $A^d = 0.5\%$ and bark $A^d = 1.5\%$. The results of analyses ash content juvenile wood and juvenile bark from fast-growing tree species show higher ash content. The ash content of juvenile wood is $A^d = 0.74\%$ and juvenile bark is $A^d = 6.88\%$.

Simultaneously, there was a decrease in ash production with increased temperature when burning non-volatile combustible matter, caused by its thermal decomposition. The inorganic proportion of wood and bark is highly heterogenic, mainly consisting of carbonates and sulphates ($CaCO_3$, $MgCO_3$, $FeCO_3$, $CaSO_4$, $MgSO_4$), which decompose with varying intensity into carbon dioxide (CO_2) and metal oxides. The intensive thermal decomposition and subsequent decrement in the weight of these mineral substances takes place around 600 °C (Misra *et al*. 1994; Olanders and Steenari 1995). This finding was confirmed in the current study using a step change of the decrease in production of ash from bark (Fig. 5). For wood, the change at temperature $t = 600$ °C was not so clear (Fig. 4), which was due to the much lower content of ash matter in wood than in bark. Another process that contributed to the decreased proportion of ash was the evaporation of potassium during the thermal decomposition of the compounds K_2CO_3, KCl, and K_2SO_4, (Olanders and Steenari 1995; Obernberger and Supancic 2009).

Determining the functional dependencies between the decreased production of ash and the combustion temperature of the non-volatile combustible matter of wood and bark of fast-growing wood species will improve the current knowledge of this subject. This information can be used for energy, environmental, and ecological analysis of biofuel that is dependent upon the proportion of ash created in the combustion process. Disregarding the mentioned facts can result in the balances being accompanied by considerable errors. The production of ash from energetic chip burned at $t = 500$ °C compared with $t = 1000$ °C is for locust chip with a proportion of bark at X_B = 26.5 % is higher by 47.1 %, as calculated by following equation:

$$\Delta A^d\ (\%) = ((A^d_{t=500} - A^d_{t=1000})/A^d_{t=500})\ {*}100 \tag{4}$$

The concentration of calcium, magnesium, potassium, iron, zinc, and manganese determined in the ash of the non-volatile wood and bark matter of black locust burnt at temperatures from 500 °C to 1000 °C in a muffle furnace is shown in Figs. 6 and 7. For wood and bark from willow and poplar, the data are shown in Tables 3 and 4.

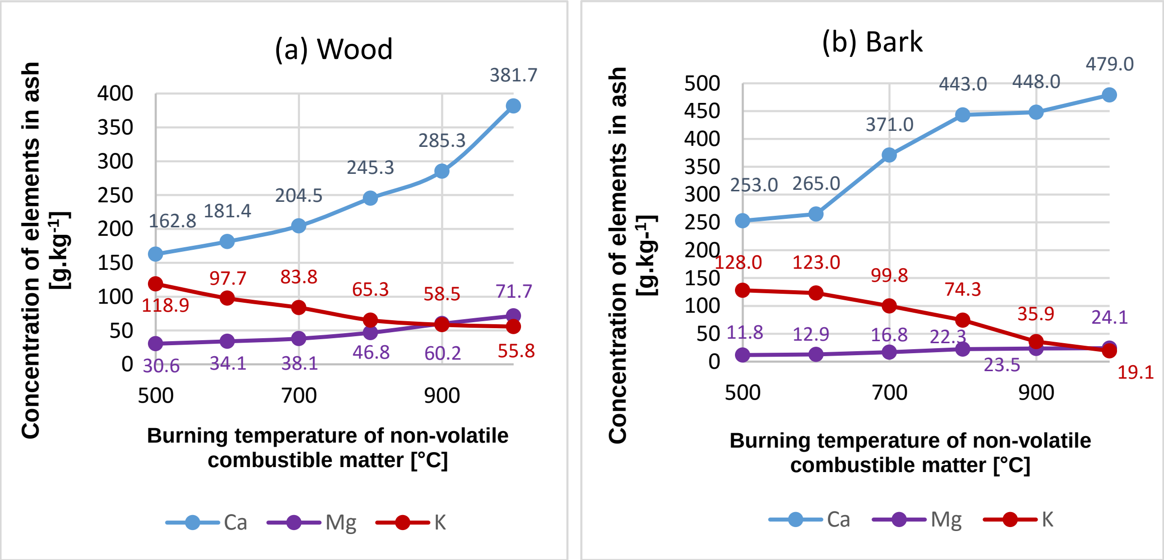

Fig. 6. Calcium, magnesium, and potassium in ash from black locust wood (a) and bark (b) burned at 500 °C to 1000 °C

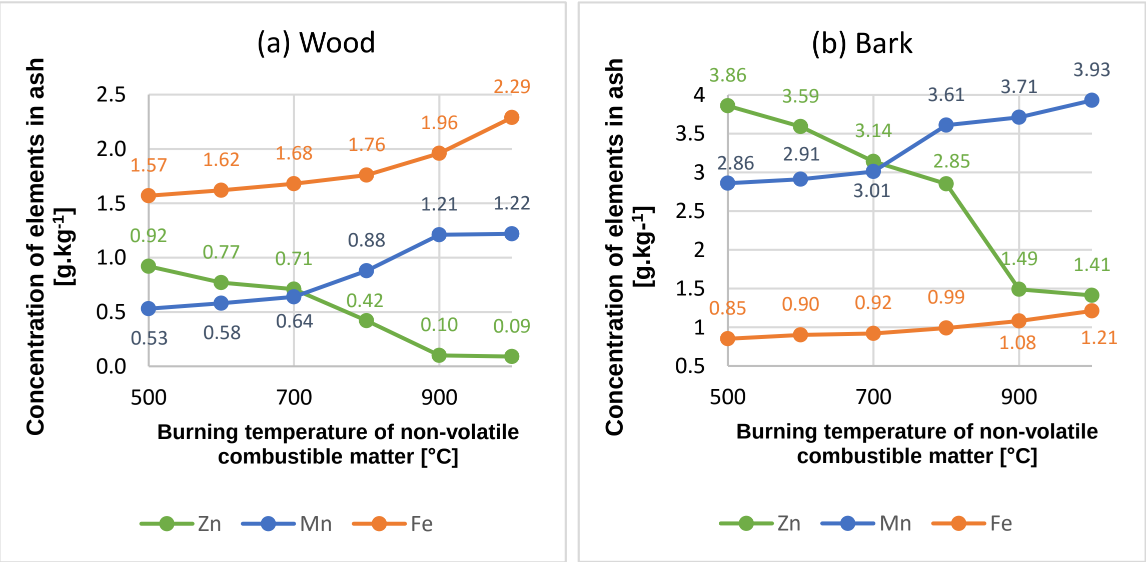

Fig. 7. Zinc, manganese, and iron in ash from black locust wood (a) and bark (b) burned from 500 °C to 1000 °C

Table 3. Concentration of Inorganic Elements in Ash from the Wood and Bark of Willow (g.kg^{-1})

Element	Willow											
	Burning Temperature of Non-volatile Combustible Wood matter (°C)						Burning Temperature of Non-volatile Combustible Bark Matter (°C)					
	500	600	700	800	900	1000	500	600	700	800	900	1000
Ca	181.1	194.2	216.9	249.3	320.3	348.9	280.0	321.0	432.0	453.0	465.0	471.0
Mg	20.1	22.9	25.1	27.1	31.8	39.5	18.3	21.5	27.7	29.3	31.2	32.6
K	130.1	109.9	91.5	78.3	69.2	23.7	116.3	112.0	84.0	63.0	35.0	22.2
Zn	4.92	4.82	4.59	3.96	2.53	1.41	3.86	3.59	3.14	2.85	1.49	1.41
Mn	2.96	3.09	3.79	3.96	4.55	4.86	2.86	2.91	3.01	3.61	3.71	3.93
Fe	1.95	2.09	2.33	2.75	3.06	3.14	0.85	0.90	0.92	0.99	1.08	1.21

Table 4. Concentration of Inorganic Elements in Ash from the Wood and Bark of Poplar (g.kg^{-1})

Element	Poplar											
	Burning Temperature of Non-volatile Combustible Wood Matter (°C)						Burning Temperature of Non-volatile Combustible Bark Matter (°C)					
	500	600	700	800	900	1000	500	600	700	800	900	1000
Ca	250.9	265.1	274.6	341.8	375.5	434.5	302.0	317.0	391.0	482.0	498.0	540.0
Mg	29.5	30.5	32.8	37.6	43.4	50.9	27.3	28.9	35.3	40.4	43.5	47.7
K	100.2	90.8	70.1	55.5	37.9	55.8	96.2	91.3	62.3	35.6	25.5	9.8
Zn	1.89	1.86	1.59	0.63	0.23	0.14	1.99	1.96	1.74	1.37	0.36	0.15
Mn	2.17	2.28	2.65	2.79	3.53	3.98	2.95	3.29	3.36	3.95	4.37	4.41
Fe	1.12	1.32	1.67	1.83	2.08	2.51	0.77	0.88	1.03	1.07	1.21	1.32

Based on the analyzes determining the concentration of calcium, magnesium, potassium, iron, manganese, and zinc in the ash of non-volatile flammable acacia, willow, and poplar bark and burned at a temperature t = 500 ° C, it follows that the highest proportion of ash wood is calcium. The concentration of calcium in ash from wood was Ca = 189 ± 46 g.kg^{-1} and in bark Ca = 278 ± 25 g.kg^{-1}. The ratio of calcium, potassium, magnesium, zinc, manganese, and iron in ash from wood at a burning temperature of t = 500 °C was Ca:K:Mg:Zn:Mn:Fe = 1:0.58:0.13:0.04:0.03:0.02 and from bark Ca:K:Mg:Zn:Mn:Fe = 1:0.41:0.07:0.01:0.01:0.003, respectively. Influence of the burning temperature non-volatile combustible was reflected in the concentration of each element in ash and was contradictory. While the concentration of Ca, Mg, Mn, and Fe in ash from wood and bark increased, concentration of K and Zn in ash decreased. Similar concentrations of calcium, magnesium, and zinc were reported in the ash of pine, larch, oak, and birch woods (Olanders and Steenari 1995; Obernberger and Supancic 2009; Tsuchiya *et al*. 2011).

The mass content of calcium, magnesium, and potassium in ash from 1 kg of dry locust, willow, and poplar wood and bark, burning in temperatures ranging from 500 to 1000 °C is shown in Figs. 8, 9, and 10.

From the balance of amount of each element in ash from 1 kg burning wood or bark in Figs. 8 to 10, it follows that the production of calcium Ca and magnesium Mg due to temperature does not change. Production of potassium (K) exhibited a declining trend, which can be attributed to its evaporation in the processes of thermal decomposition of K_2CO_3, KCl, K_2SO_4, and their emission to the atmosphere with the combustion gases (Tissari 2008; Sippula *et al*. 2007).

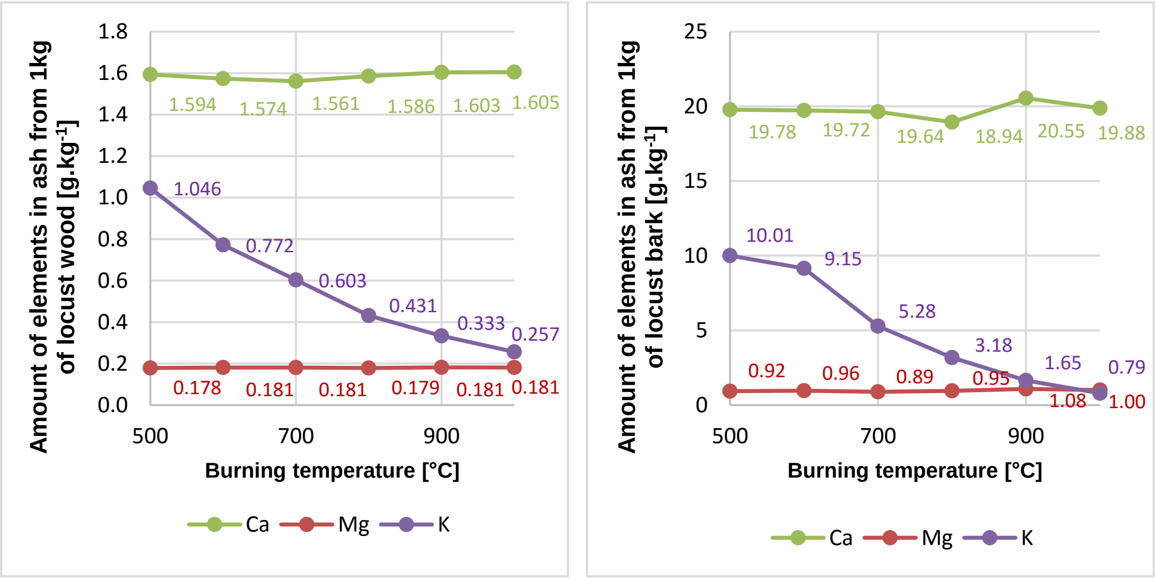
(a) (b)

Fig. 8. The amount of Ca, Mg, and K in ash from 1 kg of locust wood (a) and bark (b)

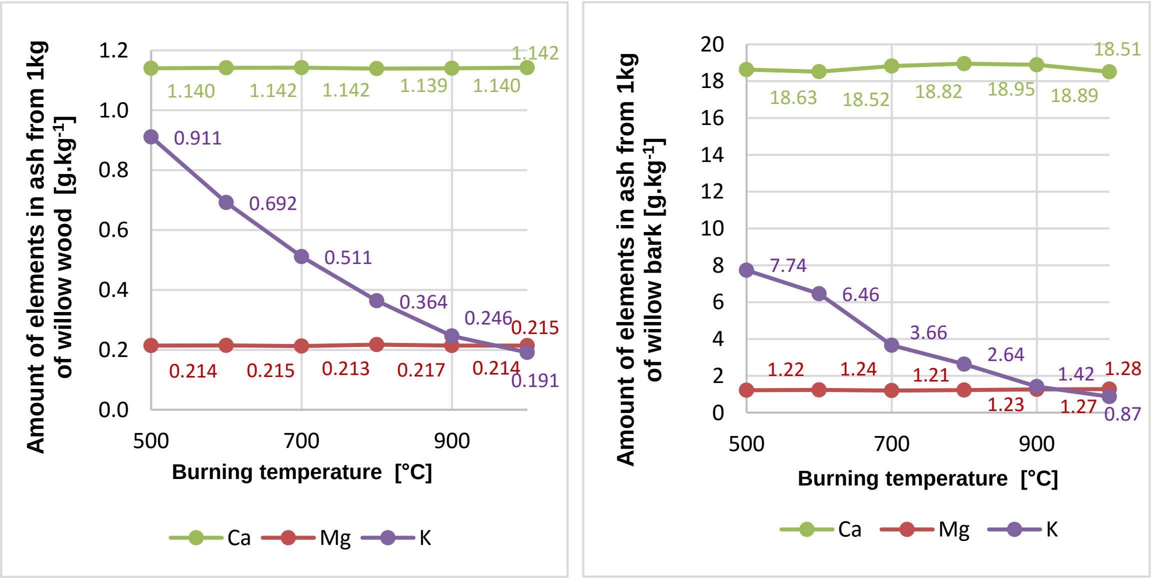
(a) (b)

Fig. 9. The amount of Ca, Mg, and K in ash from 1 kg of willow wood (a) and bark (b)

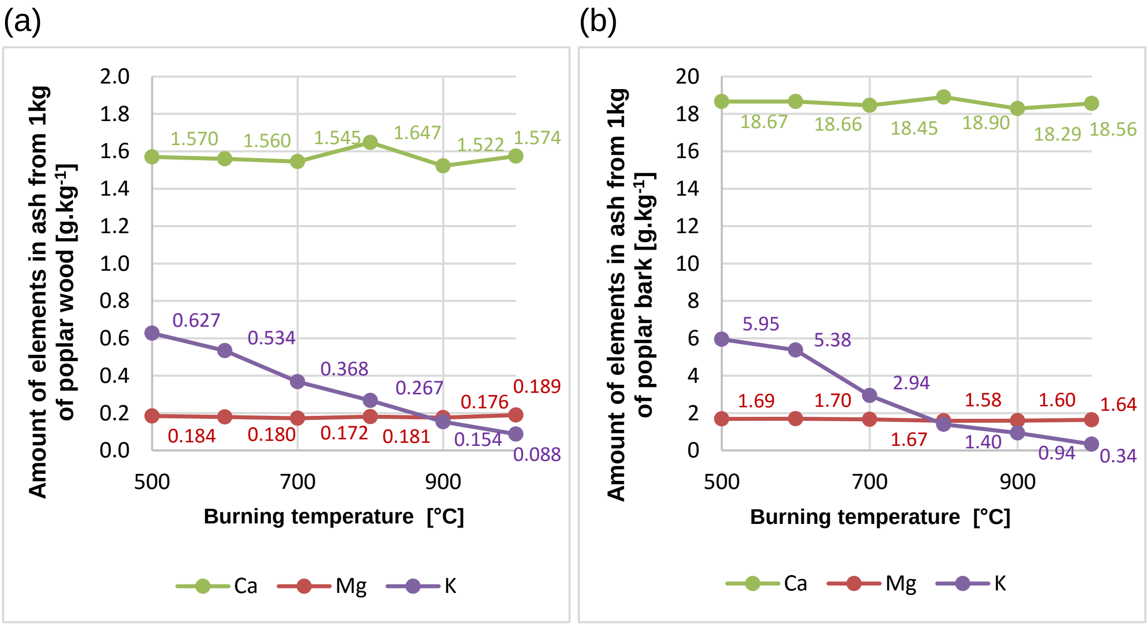

Fig. 10. The amounts of Ca, Mg, and K in ash from 1 kg of poplar wood (a) and bark (b)

A decrease in the concentration of potassium in ash from wood and bark proportionate to the burning temperature of non-volatile matter had a positive impact upon the stability of the creation of ash in the form of loose matter. In terms of slagging, the ash from biofuel (Ca+Mg)/K ≥ 1, at an oxidation temperature ≤ 1100 °C, does not sinter and also is in the form of loose matter without conglomerates created by sintering ash on the boiler grid (Dzurenda and Jandačka 2015). The value of the stated criterion for ash from locust, willow, and poplar wood at a combustion temperature of 500 °C was (Ca+Mg)/K = 1.5 to 2.8. At the combustion temperature of 1000 °C, the given ratio increased to (Ca+Mg)/K = 7.0 to 20.0. For bark of the analysed wood species, the values of this criterion were even higher. At a burning temperature of 500 °C it was 2.1 to 3.4, and at 1000 °C, the ratio was 22.7 to 59.9. Thus, bark in the energy chips from stands of plantation-cultivated, fast-growing wood species contributed to the stability of the loose ash that is created. Non-slagging of ash from the wood and bark of the analyzed wood species was also confirmed by experiments on burning non-volatile combustible matter in a muffle furnace, from which the ash was always in the form of dust.

CONCLUSIONS

1. This influence of the burning temperatures, ranging from 500 °C to 1000 °C, on ash production from non-volatile combustible wood matter or bark of plantation-cultivated, fast-growing wood species was analysed. The concentration of calcium, magnesium, potassium, manganese, zinc, and iron in the ash were examined, and the thermal properties were determined in terms of ash fusibility.
2. Linear equations quantified the rate of decrease in the production of ash from locust, willow, and poplar wood at temperatures ranging from 500 °C to 1000 °C, as well as ash and bark from these wood species at 700 to 1000 °C. These dependencies quantify

the creation and production of ash for energy, environmental, and ecological analyses of biofuels, depending on the burning temperature of wood and bark.

3. Qualitative and quantitative analysis of the concentration of calcium, magnesium, potassium, manganese, zinc, and iron in ash produced from burning non-volatile combustible wood and bark matter at 500 °C showed that calcium was in the highest proportion in ash from wood and bark. Depending on the burning temperature of the non-volatile combustible matter, concentrations of Ca, Mg, Mn, and Fe increased proportionally to the decrease in ash production. The concentrations of K and Zn decreased, which was attributed to the partial evaporation of these elements during the thermal decomposition of mineral substances present in the biofuel.
4. The decrease in the concentration of potassium in ash from wood and bark proportionate to the burning temperature of non-volatile matter had a positive influence upon the thermal characteristics of the ash and the creation of ash in the form of loose matter.

ACKNOWLEDGMENTS

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