

Characterisation of Dendromass Ash Fractions Captured in Power Plant with a View to their Further Utilization

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Abstract

Small and larger dendromass-burning power plants entrust the management of the ash waste to companies which guarantee its ecological disposal. In order to specify the correct disposal or further utilization of the dendromass ash, the various slag and fly ash fractions from a power plant combusting waste wood were analyzed and compared in this work. The plant produces approximately 660 t of ash waste/year. The efficiency of combustion depends on the season, dendromass quality and plant operating conditions. The proportion of carbon residue (incomplete burnt wood-chips) in slag and ash fractions increases in the winter months. Except for the seasonal carbon residue, the crumble slag and fine ashes captured in the flue channel and cyclone are similar in chemical composition and phase (28 – 44 wt. % CaO; 25 – 35 % SiO₂; ~7 % Al₂O₃; ~5 % K₂O; ~4.5 % MgO). The finest ash captured in the fabric filter contains less silicon and alumina compounds (<7 % SiO₂; ~2 % Al₂O₃) and a significantly higher portion of potassium and sulphur, and chlorine compounds (approx. 13 % K₂O; 3.5 % S; <1.5 % Cl) which are well soluble in water. All ash fractions produce strongly alkaline leaches in first contact with water. The differences in the chemical composition of captured ashes provide an impulse for considering the possibility of effective re-utilization of individual fractions.

Keywords

dendromass, waste, crumble slag, fly ash, potassium, alkalinity



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Introduction

Although the calorific value of dendromass is lower compared to coal, the trends in heat and electricity production are increasingly directed towards using fuels from renewable energy sources, so-called 'green energy production'. The determining factors in the partial or complete substitution of fossil fuels with biofuels in existing combustion plants include the calorific value and the lumpiness of the fuel, the dosage method, the potential for achieving perfect combustion, and the composition of flue gases (Michalíková, 2017; Ochodek et al., 2007). The fuel change will also be reflected in the amount of slag/ash and fly ashes (i.e. the incombustible part of fuel). Less crumble slag and ash accrues in biomass/dendromass combustion than in coal combustion.

The quantity and composition of ash from coal and biomass are determined by their genesis (Tab. 1) (Nor et al., 2017; Skála et al., 2007; Tlustoš et al., 2012; Vassilev et al., 2017). Solid fossil fuels are more polluted with clay minerals (alumino-silicates) and sulphur compounds that intrude into coal during carbonizing. Therefore, the flue gases from coal combustion have a higher content of SO₂. Unlike coal, however, biomass is constituted practically only from combustible organic matter. On the other hand, the water content in combusted biomass is higher and, in the case of dendromass, can form up to 25 %. The incombustible remnant of biomass (ash) is very low. The content of aluminium and iron is substantially lower in biomass ashes. The predominant elements are calcium, silicon and potassium. The potassium content is very different in ashes from plants and woods, and more Si is contained in ash from bark and seed husks (Niu et al., 2015; Reinmöller et al., 2017; Vassilev et al., 2017, 2014). The type of biofuel predetermines the ratio and quantity of elements in the ash.

Tab. 1. Informative comparison of the element in a combustible and an incombustible portion of coals and biofuels

Fuels		Brown Coal	Black Coal	Biomass	Dendromass
Heating Capacity [MJ.kg ⁻¹]		11 – 18	20 – 30	9 – 15	9 – 17
		Weight Ratio [wt. %]			
Combustible portion		70 – 85	80 – 90	90 – 99	
Major Components (dry ash-free basis /daf)	C	65 – 75	80 – 92	47 – 50	47 – 50
	H	5 – 8	4 – 6	~ 6	~ 6
	O	25	7 – 15	43 – 44	43 – 44
	N			0.5 – 1.2	~ 0.2
Minor Components	Cl			0.3 – 0.8	< 0.01
	S	0.5 – 5	0.5 – 1.25	0.05 – 0.4	~ 0.02
Incombustible portion		according to pollution		according of plant species	
		15 – 30	10 - 15	0.3 - 5 (bark, seed husks: 8 – 12 %)	
Slag, Ash Fly Ash	SiO ₂		30 – 60	2 – 19 (57)	5 – 60
	Al ₂ O ₃		20 – 30	0.2 – 5	1 – 14
	CaO		2 – 25	4 – 40	10 – 58
	K ₂ O		0 – 2	25 – 35	5 – 15
	MgO		0.5 – 4	3 – 6	2 – 12
	Fe ₂ O ₃		5 – 20	0.2 – 1.5	1 – 10
	P ₂ O ₅		(0.1 – 1)	2 – 6 (10)	3 – 5
	Cl		(~0.01)	0.2 – 3 (10)	1 – 4
	SO ₃		0.1 - 2	1 – 3 (10)	0.2 – 3.5

In addition to the predominant components, heavy metals (e.g. Ag, As, Ba, Co, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn, Sb, Se, Sn, and V) are found in trace amounts in the ash. The presence of these elements in the habitat and the species of plant influences the number of heavy metals in the ash. The content of these elements in the slag and fly ash fractions depends on the evaporation temperature of the elements and their interactions with the flue gas and other solid components of the ash, and last but not least, the method of fuel combustion (Mester et al., 1999; Ochodek et al., 2007; Riding et al. 2015; Vassilev et al., 2014).

Larger power plants and incinerators use modern boilers with automated dosing and control of the combustion process. The biomass boilers are designed for a defined fuel type (e.g. chips or pellets). During combustion, part of the fuel burns directly on the grate, creating slag, and fine particles of ash are drawn by the current of flue gas into the next spaces of the combustion chamber and heat exchangers. In biomass combustion, the water vapour released together with sublimates of K, Na and trace amounts of S, Cl, P, and N is aggressive towards the linings and metal parts of the heat exchangers. These sublimates interact with fine ashes and form sticky particles which adhere to the hot lining of the combustion chamber and create accretions. In the colder parts of the boiler (the exchanger parts), the fine particles drifted by cooling flue gases gradually lose kinetic energy and fall into the lower parts of the flue channel, and the finer particles are captured in the end in cyclones and on filters. The quantity and composition of the ash residues depend on the fuel type, combustion efficiency and boiler construction (Míka et al., 2011; Niu et al., 2015; Skála et al., 2007; Vassilev et al., 2017).

Most power plants entrust the disposal of ash and dust residues to external firms without investigating ways of further handling this waste. According to Regulation 365/2015 ME SR, the residues from dendromass combustion belong to the group – Wastes from Thermal Processes, subgroup – Wastes from Power Plants and

other Combustion Plants. The ash wastes from peat and untreated wood are classified in category O – other, i.e. not dangerous.

The ash from biomass was a very valuable raw material in the past. It was the key raw material for the production of potash lye, which was used for the staining of substances and in soap and glass production (Pánova et al., 2019; Cílová et al., 2008, 2012). The ash components creating glass (SiO_2 together with alkalis) encourage their testing as fusing agents in the vitrification of inorganic wastes (for example, captured dust). Melting temperatures and chemical stability of the glass/glass-ceramics prepared from ash are increasingly tested (Jordan et al., 2018; Reinmöller et al., 2017).

As in the case of coal-burning power-plant ash, further utilizing options are sought for biomass ash, e.g., reactive additive and filler masses in inorganic building materials, ceramics and other solids (Škvára et al., 2014, 2005). Ash was used in the past and is now being tested again as a component of construction materials based on pozzolan binders activated by alkali addition. Strongly alkaline solution disturbs the structure of the fine particles of silicates, alumino-silicates and glass phases and initiates the formation of silica-gels and geo-polymeric bonds (Khale et al., 2007; Komnitsas et al., 2007).

It is also appropriate to mention the use of ash in homes. In the winter, the ash was used for its soluble alkaline portion and insoluble alumino-silicates as road salt material. It was also used to suppress the growth of moss and was added to manure and compost.

The ash remaining after forest fires enriches the soil with minerals, revitalizes the land and stimulates the growth of plants. In many countries, especially in Scandinavia, where large amounts of dendromass are burned, due attention is given to the issue of using ash as fertilizer and additives for cultivated soil treatment. The effect on forests and lands of ash-waste fertilizer application is monitored in the long term (Ernfors et al., 2010; Mahmoudkhani et al., 2004; Saarsalmi et al., 2004).

This work monitors the composition of ash from burnt wood-chips and pellets under laboratory conditions and characterizes the crumble slag and portions of fly ash arising in the process of burning wood-chips in a steam-producing boiler. The presented results (characterization of slag and ash) provide an impulse for considering the possibilities of efficient use of nature's own waste – biofuel ash. The utilization of ash is determined by its chemical and phase compositions, variability of composition, and, last but not least, by the quantity of ash waste produced.

Material and Methods

Samples of fuel (wood-chips) and ashes (namely crumble slag from the boiler grate (S), ash from the flue channel (T), cyclone (C) and fabric filter (F)) were supplied for analyses in the winter and summer months (January; July) from a power plant combusting dendromass with a power output of 16 MWt (20 t vapour/h).

The wood-chips (sample A) taken from the plant in the winter and summer months were burned in our laboratory at 500 °C. For comparison of the variability of dendromass composition, other wood pellets (sample B) compressed from sawmill waste (a mixture of different types of wood) were also tested. After drying to constant mass at 105 °C, the wood-chips were slowly carbonized and then combusted at 420 °C in air. Part of the resulting ash was annealed at 850 °C/30 min. The loss on ignition was determined by the annealing of samples at 1 050 °C/2 h. The ashes were then analyzed.

Samples of the delivered ash waste were dried at a temperature of 105 °C. The fractions from the winter season were very wet and contained a high proportion of non-perfectly burned chips (carbon residue). For this reason, prior to analysis, the samples were annealed in air at 500 °C to constant mass. Subsequently, the samples were subjected to particle size analysis (mesh 0.04; 0.1; 0.4 mm), and the specific surface area of the samples was determined by measuring the sorption of N_2 gas (NOVA 1000e, Quantachrome Instrument Co.) before and after the annealing.

Chemical and phase analyses were carried out on the samples of ash fractions, and the temperature of fusibility was also determined. The major elements in the ash (Ca, Si, K, Mg, Al, Na, Fe, Mn) were measured using an atomic adsorption spectrometer (Perkin-Elmer 3100) in leachates prepared by the decomposition melting of samples. The concentrations of sulphur, phosphorus and selected heavy metal elements were measured by means of inductively-coupled plasma atomic emission spectroscopy (ICP–AES/iCAP 6000 Series) in leachates prepared by microwave decomposition in two steps ($\text{HNO}_3 + \text{HF} + \text{H}_2\text{O}_2$ and H_3BO_3) (Mester et al., 1999).

The phase analysis was carried out on a Rigaku MiniFlex600 X-ray diffractometer (Theta–2Theta with $\text{CuK}\alpha$). The diffraction patterns were evaluated using PDXL 2 software with the ICDD database.

The thermal analysis (thermogravimetric TG and differential thermal analysis DTA) was done using NETZSCH STA 449F3 Jupiter/Netzsch Proteus TA version 6.1 software, under the following conditions: dose – 45 mg of sample, Pt-crucible; atmosphere air; heating 10 °C/min, max. temperature 1 400 °C. The fusibility of the ashes was determined according to STN ISO 540 on a high-temperature microscope (Leitz–Wetzlar) with heating up to 1 500 °C. From the measured data, the initial deformation temperature (DT) and the temperature when the test body takes on hemisphere shape (HT) were found, and then the ash fusibility index was calculated according to the equation (Pintana et al., 2016):

$$T_{AF} = (4DT+HT) / 5 \quad (1)$$

Samples of slag and ash were subjected to leaching tests in water and nitric acid solution. The leaching conditions in water were derived from Regulation 310/2013 of the Ministry for Environment of the Slovak Republic (ME SR), which defines the criteria for the disposal of waste in landfills. Even though the slag and ash fractions are much finer in size than commonly-disposed wastes, leaching in water was carried out at the prescribed ratio of liquid to solid waste (L : S = 10) at 25 °C for 24 hours. The same ratio was applied during the acid leaching test (6 h in 2 mol.l⁻¹ HNO₃ (Regulation 521/1994-540)). Concentrations of metal elements (As, Cu, Co, Cd, Cr, Pb, Ni and Zn) in the leachates were measured using an ICP-AES/ iCAP 6000 Series spectroscope.

The cyclic leaching tests in water (with replacement of the leaching medium after 1 h) were carried out at an L : S ratio of 100 (100 ml of water/1 g of sample) at 25 °C. The tests were completed after five cycles. The pH value of the solution was measured after each cycle. Concentrations of some heavy metals and major elements in the leachates were measured using an ICP-AES/iCAP 6000 Series spectroscope.

Results and Discussion

Ashes from dendromass combusted in the laboratory

The predominant elements in the incombustible portion of dendromass, wood-chip (A) and pellets (B), are indicated in Table 2. The composition of ash A taken from the plant in the summer and winter months was similar. Ash, i.e. the non-combustible remnant of wood-chip/pellets, represents less than 1 wt.% of the fuel. The variability of the composition of dendromass ashes is consistent with the results of other works (Ochotek et al., 2007, Plešingerová et al., 2020).

As the results of the phase analyses show (Tab. 3, Fig. 1), the observed composition differences at firing temperatures 420, 850 and 1050 °C related to the decomposition of carbonates and thermally-unstable ash substances at higher temperatures.

Tab. 2. Content of major elements in ash from wood-chip (A) combusted at 500 °C and ash from pellets (B)

Wood combusted at temperature	Content of major elements in ash								L.O.I.	Portion of ash
	Al	Si	Ca	Mg	Fe	Mn	Na	K	1 050 °C	
	[wt. %]									
A-summer – 500 °C	1.7	5.1	32.2	3.1	1.4	2.0	0.2	7.7	24.5	0.60
A-winter – 500 °C	1.9	4.8	31.0	2.5	2.7	1.5	0.1	7.3	25.7	0.75
B – 420 °C	4	11.8	22.2	3.1	2.5	2.7	0.5	3.8	19.1	0.60
B – 850 °C	4.2	14.0	28.9	4.3	2.8	3.3	0.7	5.6	-	0.48
B – 1 050 °C	4.1	11.1	28.3	3.0	1.9	1.7	0.6	2.9	-	0.47

L.O.I. - Loss on Ignition

Tab. 3. Detected phases in ash A and ash B (rtg. analysis)

Ash / Annealing temp.	Detected phases								
	Amorphous phases	CaCO ₃ Calcite	CaO	SiO ₂	Ca ₃ (SiO ₄) ₂ CO ₃ Spurrite	Ca-Si-O Calcium-silicate	Ca-Mg-Si-O Akermanite	(Ca,K)-Si-O	(Ca,K/Na)-Si-Al-O
A – 500 °C		+++		++					+
B – 420 °C		+++		++					+
B – 850 °C	+		++		(+)				+
B – 1 050 °C	+++			(+)		++	(+)	+	

(+) < 2 %; + minor amount; ++ (15 – 35 %); +++ major amount

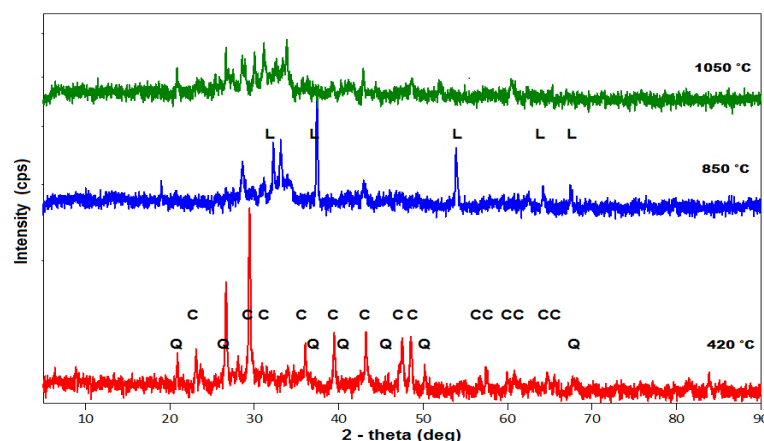


Fig. 1. X-ray diffraction patterns of ash B annealed at 420, 850 and 1 050 °C in air; Q – SiO₂, C – CaCO₃, L – CaO

The thermal analyses (Fig. 2) confirmed the decomposition of carbonates in the temperature range of 600–800 °C. Ash A (500 °C) contains more calcium (Ca) than ash B (420 °C) and so undergoes greater weight loss (19.4 %; TG – curve) in this temperature range. Ash B with higher Si content shows a significant endothermic peak on the DTA curve in the temperature range 1 200 – 1 300 °C, which is most likely related to the more intensive interactions between the alkalis and SiO₂ initiating the creation of melt.

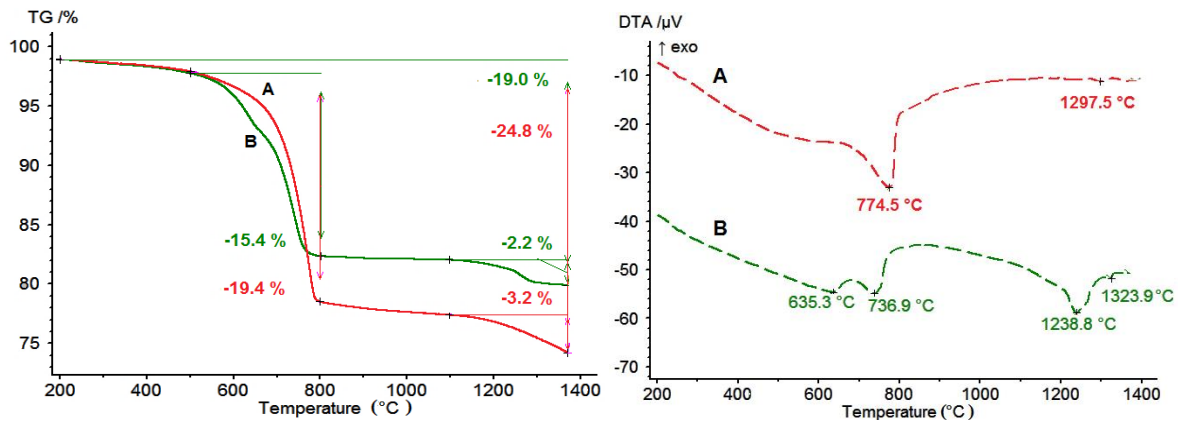


Fig. 2. TG and DTA records of ash A from wood-chips annealed at 500 °C and ash B from pellets annealed at 420 °C

Here it should be noted that the high partial pressure of CO₂ in combustion chambers can inhibit the decomposition, and so calcium and magnesium carbonates are in the fly ash. As the temperature increases, the CaCO₃ and other ash components gradually react with SiO₂ microparticles.

Analyses of crumble slag and fly ash from different parts of a woodchip-burning boiler

During the combustion of dendromass in a grate boiler, most of the ash and slag stays in the grate, but hot flue gases carry away part of the fine ash into the convection flue channel, where the heat transfer happens and transforming water into steam and also preheating the air for combustion. Some of the ash particles are captured here, and the rest are in the cyclone and fabric filter. The hot slag and ash from the first part of the flue channel 2/3 (S) are sprayed with water and deposited in a storage box. Smaller particles fall to the bottom of the next flue channel 4/5 (T). Finer, colder particles are captured in the cyclone (C) and the finest in the fabric filter (F). The fractions are stored in separate boxes in the plant. The total amount of captured crumble slag and ash (660 t per year) represents approximately 1.7 % by weight of combusted dendromass (fuel). The mass ratios of S : T : C : F fractions are 6 : 1 : 2 : 1 respectively.

The humidity of the ash wastes deposited in the storage boxes is variable and depends mainly on the season and the weather. At the higher rate of boiler operation in the winter months, significantly more carbon residue remains in the grate and in the fly ash. The amount of unburned carbon determines the weight loss by annealing at 500 °C presented in Table 4. The carbon residue can form up to 65 wt.% of the ash fraction remaining in the grate in winter. This high content of carbon in the ash corresponds to 2.5 – 3 % of the imperfectly burnt fuel. This confirms that the efficiency of combustion decreases with increasing boiler operation rate. Carbonized pieces of wood-chip (needle-shape, length <20 mm; specific surface area 150 – 200 m².g⁻¹) are nano-porous, and the pores easily adsorb water. The carbon can be totally eliminated by re-burning the ash waste or partially by separating it with sieves. In the case of dry separation with sieves, the process is very dusty. With wet separation, the lighter fractions of carbon go to the top while the alkaline salts are dissolved in water. The need to remove residual carbon from ash depends on the subsequent utilization of this power-plant waste.

Tab. 4. Loss on the weight of ash fractions (s – summer, w – winter) during drying and annealing; granularity and specific surface area

Sample	Loss of weight [wt. %]		Particle size analyses of ash after annealing at 500 °C (without carbon)			Specific surface area of re-annealed ash at 500 °C [m ² .g ⁻¹] (without carbon)
	Annealing at 500 °C of dry-sample	2 nd step Annealing at 1000 °C/ 2h	<0.04 mm	<0.1 mm	<0.4 mm	
S – s	3.9	7.6	20 – 25	35 – 50	60 – 70	~1
S – w	60	10.2	30 – 35	45 – 55	70 – 80	
T – s	0.8	6.6	20 – 25	60 – 70	100	~2
T – w	27	4.8	20 – 25	70 – 75	97 – 100	
C – s	0.8	7.6	30 – 50	90 – 100	100	~2
C – w	10	6.5	45 – 60	80 – 99	100	
F – s	1.7	18.3	adhesion of particles		100	~5
F – w	2	19.6	adhesion of particles		100	

The results of the chemical analyses of re-annealed ashes at 500 °C in Table 5 point to the seasonal variability in dendromass and also confirm the redistribution of components (Si, Al, Ca, K, S, Cl) among fractions (S, T, C) and F.

The S, T, and C fractions of slag and ash have similar chemical and phase compositions (Tables. 5, 6). If these fractions (S, T, C) are mixed at ratios 6 : 1 : 2, approximately 600 t/ year of waste material containing 28 – 44 wt.% CaO; 25 – 35 % SiO₂; ~7 % Al₂O₃; ~5 % (K₂O+Na₂O); 4.5 % MgO; ~3 % FeO, ~1 % MnO is obtained in the monitored power plant.

Tab. 5. Seasonal variability in the composition of ash waste after re-annealing at 500 °C

Sample	The proportion of major elements [wt.%]											
	Al	Si	Ca	Mg	Fe	Mn	Na	K	Cl	S	P	L.O.I.
S – s	4.0	16.3	19.1	2.8	3.0	0.6	0.1	4.0	<0.1	<0.2	1.7	7.6
S – w	3.2	12.1	30.7	3.0	2.6	1.0	0.3	4.6	0.2	<0.5	1.5	10.2
T – s	4.3	18.3	22.7	2.9	2.5	0.9	0.2	4.2	0.2	<0.5	2.0	6.6
T – w	4.0	16.3	31.8	2.4	2.9	1.1	0.3	3.4	0.1	<0.4	2.0	4.8
C – s	4.7	17.1	22.1	1.8	2.4	0.9	0.2	5.1	0.2	0.6	2.0	7.6
C – w	3.6	9.6	37.6	2.9	2.6	1.4	0.2	2.7	0.3	0.5	2.3	6.5
F – s	1.1	3.6	30.6	2.4	1.8	1.0	0.1	9.5	1.1	4.1	2.7	18.3
F – w	0.7	1.7	34.7	2.9	1.4	1.2	0.2	10.5	1.8	3.3	2.2	19.6
Average composition	The proportion of oxides [wt.%]											
	Al ₂ O ₃	SiO ₂	CaO	MgO	FeO	MnO	Na ₂ O	K ₂ O				
S:T:C:F = 6:1:2:1 /s	7.3	33.1	29.0	4.3	3.2	0.8	0.2	5.6				
S:T:C:F = 6:1:2:1 /w	5.9	23.9	44.8	4.8	2.9	1.3	0.4	5.5				

L.O.I. – Loss on Ignition

Tab. 6. Evaluation of phase analysis of ash samples from the summer period (rtg. analysis)

Sample	Detected phases						
	CaCO ₃	(Ca/Mg)CO ₃ K ₂ Ca(CO ₃) ₂	K ₂ SO ₄ Arcanite	SiO ₂	Aluminosilicates CaO·Al ₂ O ₃ ·2SiO ₂	K ₂ O·Al ₂ O ₃ ·6SiO ₂	2CaO·SiO ₂
S	++			++	++		
T	++	+		++			+
C		(+)		++		+	+
F	+++		++	+			

(+) < 2 %; + minor amount; ++ (15 – 35 %); +++ major amount

Approximately 60 t of ash dust (F) is captured in the filter per year. The chemical and phase compositions of the dust are different from the others captured in the warmer parts of the plant. The higher content of potassium salts (K ≈ 10 wt.%) and low content of residual carbon contains. The finest ash, condensates, and products of the interactions of alkalis and flue gas (CO₂, SO₂) accumulate here.

The samples T and F from the summer collection were subjected to thermal analyses (TA; Fig. 3). The TG and DTA records for sample T also represent the behaviour of samples C and S. The weight loss in the temperature range 50 – 150 °C on the TG curve of ash F which accompanies the endothermic effect is caused by the release of hygroscopic water. Next loss is attributed to the decomposition of hydrates and, more significantly, in the range 600 – 750 °C to the decomposition of carbonates (Mg, Ca). In the case of sample T, the small loss (5.3 wt.%) indicates that only part of CaO is bound in CaCO₃ and part reacts to silicates. A slight decrease in weight at about 1 230 °C is accompanied by a significant endothermic effect in the DTA record. This indicates that the components of ash react intensively with SiO₂, and phase changes occur. This temperature correlates with the temperature of ash fusibility (T_{AF}/Eq. 1; Fig. 4). The free SiO₂ in these fractions increases the presumption of vitrification and the formation of silicate phases at higher temperatures.

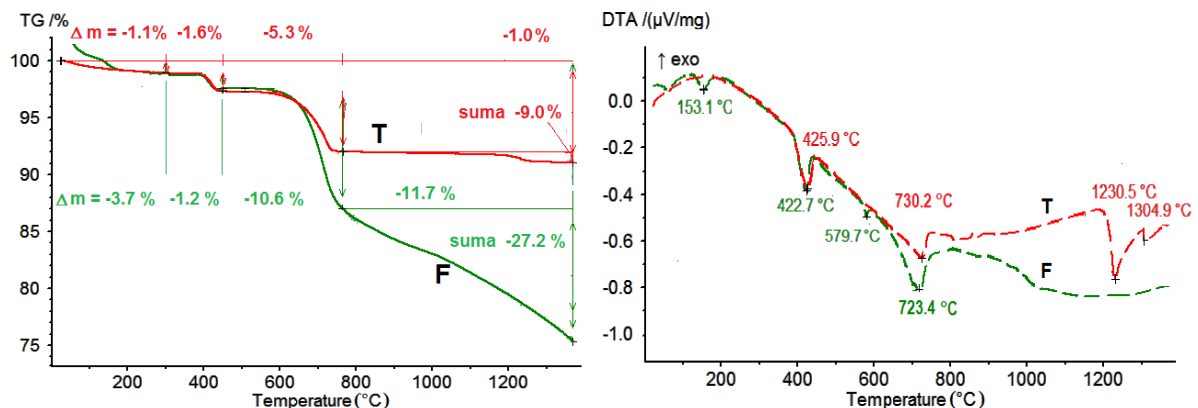


Fig. 3. TG and DTA records of un-annealed ash T and F

In the case of sample F, the more gradual decrease above 750 °C is probably the result of the slower breakdown of alkaline components during interactions and evaporation during heating. Although the ash captured in the fabric filter has the highest K₂O content and is the finest, it shows the highest fusible temperature (Fig. 4) of all fractions. The cause of this is very low Si content in contrast to high Ca content.

In addition to the major elements (Tab. 5), the concentrations of selected trace heavy metal elements were determined in the ash fractions. In Table 7, the results are compared with the limit concentrations for the inclusion of wastes in the relevant category for the disposal of waste in landfills (Regulation 310/2013). As can be seen in the Table, the heavy metals accumulate more in the finest ash captured in the filter. Dendromass ash is not considered hazardous waste.

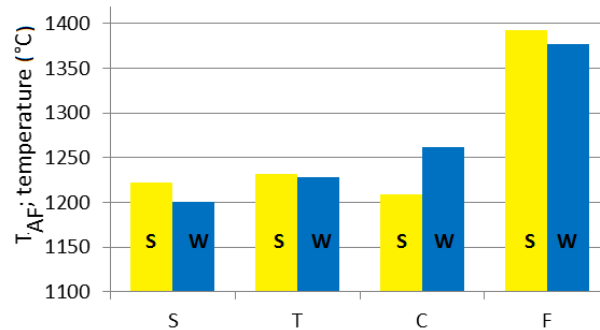


Fig. 4. Comparison of temperature T_{AF} – ash fusibility index of ash (S, T, C, F) from the summer (S) and winter (W) collection

Tab. 7. Content of heavy metals found in ashes compared with limit of hazardous waste and clay soil

Sample / Weight ratio	Seasonal average of heavy metals [$<$ ppm; i.e. $<$ mg.kg ⁻¹]							
	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
S / 6	5	2	5	60	250	80	25	200
T / 1	5	5	7	50	100	50	40	300
C / 2	10	10	7	50	150	90	50	1500
F / 1	40	25	8	50	350	40	100	3000
Limit concentrations in dry residue for Inert waste	200	4	–	–	–	500	500	–
Hazardous waste (Regulation 310/2013)	5000	5000	–	–	–	5000	10 000	–
Limit concentrations of risk elements in dry residue of agricultural soil*								
Clay soil (Regulation 59/2013)	30	1	20	200	70	60	115	200

*decomposition by (HCl : HNO₃) = 3 : 1

These results show that the composition of ash waste from the fabric filter differs significantly from that of the fractions in the grate, flue channel and cyclone.

Leachability of ash components

The ash samples (S, T, C, F) from the summer collection annealed at 500 °C were leached in water and in 2 mol.l⁻¹ HNO₃ solution. The pH values of the leachates after leaching S, T, C and F ash samples in deionized water (L : S = 10, duration 24 h) were 12.5, 13.1, 13.2 and 13.7, respectively. According to Regulation 310/2013 ME SR, any waste which creates strongly alkaline leachate (pH ~ 13) is included in the category of hazardous wastes. Despite the fineness of the ash, the concentrations of heavy metal ions in the water leachates were very low, below the limit for hazardous wastes laid down by Regulation 310/2013 (Tab. 8).

Tab. 8. Content of heavy metal ions in leachates compared with limits for the acceptance of waste for landfill disposal

element	Limit concentration in water leachate for solid wastes (Regulation 310/2013)		Content in water leachate L : S = 10				Content in acid leachate 2 mol.l ⁻¹ HNO ₃ ; L : S = 10			
	Non-hazardous [mg.l ⁻¹]	Hazardous [mg.l ⁻¹]	S	T	C	F	S	T	C	F
As	0.2	2.5	0.015	<0.001	<0.001	*	0.08	0.07	0.10	0.66
Cd	0.1	0.5	*	*	*	*	0.14	0.33	0.67	1.94
Co	1	5	<0.001	*	*	*	0.26	0.25	0.24	0.22
Cr	1	7	0.149	0.045	0.057	1.200	0.71	0.75	0.77	1.11
Cu	5	10	0.132	0.040	0.017	0.166	11.3	5.21	6.01	13.8
Ni	1	4	0.009	0.005	0.003	0.003	5.12	2.25	2.30	1.78
Pb	1	5	0.005	0.004	0.005	0.046	0.67	0.95	1.21	1.89
Zn	–	–	–	–	–	–	15.5	17.5	29	86

– undetermined;

* below the limit of detection;

If metal ions are bound to silica in ash, they are released into the solution poorly. It should be noted here that the pH value of the medium affects the concentration of heavy metal ions in the solution. On the one hand, a strongly alkaline environment creates conditions for the precipitation of heavy metal ions from the solution, while on the other hand, it disturbs the silicate structure (Plešingerová et al., 2015). It goes without saying that the heavy metal content in the leachates produced with nitric acid was significantly higher (Tab. 8). In some cases, almost 50 % of the heavy metal contained in the ash sample was released into the acid solution.

The preferential release of alkalis (Na, K) from the ash samples in water was demonstrated during cyclic leaching (leaching conditions in the cycle: deionized water, L : S = 100, exchange of water after 1 h). The test results are presented in Fig. 5 and Table 9. The easily-soluble salts in water constitute almost 50 wt.% of the F ash fraction but only 18 % of the S, C and T fractions. The binding of K and Na into stable silicates is most evident in fractions T and C. The alkali metals induce an increase in pH value in the first cycle. In the following cycles, the pH decreases moderately, and the solubility of CaCO₃ micro-particles starts to determine the solution's alkalinity (pH). The results are in accordance with the work (Mahmoudkhani et al., 2007), where the pelletizing effect on the leaching rate of K, Na and Ca was studied.

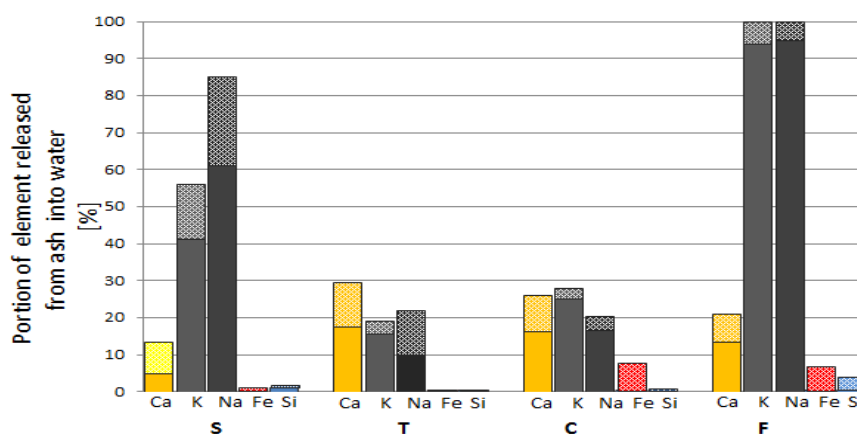


Fig. 5. Leachability by the water of Ca, K, Na, Fe, Si from ash fractions (S, T, C, F) in 1st cycle (below/dark) and 2nd-5th cycles (above/lighter); (relation to the content of the element in the ash fraction)

Tab. 9 pH value of leachate after successive cycles with the exchange of deionized water (1h; L : S = 100) and solubility of the sample

Sample	Deionized water	pH after the leaching cycle					Soluble proportion in water [wt. %]
		1.	2.	3.	4.	5.	
S	5.75	11.37	10.98	10.63	10.55	10.55	≈ 18
T		12.71	12.10	11.40	10.98	10.92	≈ 15
C		12.75	11.96	11.40	11.00	11.00	≈ 16
F		12.9	12.16	11.50	11.30	11.10	≈ 50

The origin and composition of ash from biofuels directly predetermine the use of this waste in the production of fertilizers and compost additives or for the treatment of acidic soils. The production of fertilizers from bio-ash waste seems to be the simplest; even the differences in composition and residual carbon may not be an obstacle here. The remnant pieces of carbon are inert and porous. Carbon makes the soil lighter and increases its ability to retain moisture and minerals.

The dustiness ash and the instant solubility of alkaline salts in water, with the associated changes in the pH value of soil and water, are problematic. The processing of ash into fertilizer requires the guarantee of dust-free handling, simple dosing and gradual dissolution, with the release of nutritious ingredients into the soil without sudden fluctuations in the soil pH value (Brännvall et al., 2015). For this reason, the heavy metal limits for the use of biomass ash in agriculture and forestry, as well as fertilizer requirements, are set in law in various EU countries.

Conclusions

Around 660 tonnes of ash waste are created per year in the monitored heat/electricity plant using the combustion of wood waste from the forestry and wood-processing industries. This amount of waste is not large, but there are many such power plants producing equally good-quality waste.

The increase in power output during the winter months results in a decrease in the efficiency of dendromass combustion by about 2 – 3 %. This is reflected in the higher volume of imperfectly burnt wood chips in the crumble slag (S), the ashes captured at the base of the flue channel (T) and the cyclone (C). The proportion of carbonized chips in crumble slag can be from 10 to 65 wt.% in the winter months.

After carbon burnout, the chemical composition of ash remaining in the grate (S), under the flue channel (T) and in the cyclone (C) is comparable, and the seasonal differences between the fractions are not significant. The amount of 600 t ash waste/year with composition 28 – 44 wt.% CaO, 25 – 35 % SiO₂; ~7 % Al₂O₃; ~5 % K₂O; 4.5 % MgO, ~3 % FeO, ~1 % MnO and <2 % P is obtained by mixing fractions S, T and C. Calcium occurs in the form of carbonate and silicates. Silicon is present in the amorphous form (glass) as well as silicates and SiO₂ phase. The fusibility temperature of ash is about 1 230 °C. In the first contact with water, about 16 wt.% of the ash mix is easily dissolved, creating an alkaline solution (the pH value of extracts was 12 – 13 for the ratio L : S = 10; and 11.4 – 12.8 for the ratio L : S = 100).

The ultrafine ash waste (F) captured in the fabric filter (60 t/year) is different in chemical and phase composition from the previous fractions. The composition of ash F is 45 – 50 wt.% CaO; ~13 % (K₂O+Na₂O); <7 % SiO₂; 4.5 % MgO; ~2 % Al₂O₃; <2 % FeO, ~3.5 % S; ~2.5 % P; ~1.5 % Cl. This ash contains only small quantities of carbon residue (<2 wt.%), but almost three times more potassium (K), and also more calcium, predominantly in the form of sulphates and carbonates (arcanite, calcite). The easily-soluble fraction in water forms 50 wt.% and a very strong alkaline solution creates at L : S = 10 (pH >13).

The content of the monitored heavy metals (As, Cd, Co, Cr, Cu, Pb, Ni, Zn) in the ash from the fabric filter is a little higher than in the other fractions. The most present are Zn and Cu (average value of Zn ~750 mg.kg⁻¹; Cu ~200 mg.kg⁻¹). The concentrations of heavy metal ions in water found in leaching tests were very low, far below the limit defined for the disposal of hazardous wastes.

Even if the ash from biomass is nature's own, great caution is necessary for the disposal of large volumes of ash waste due to its dustiness and easy solubility of alkalis in water.

Ash has long been highly valued as a raw material in the past, and it would be a pity not to utilize the potential of this commodity nowadays as well.

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