

The Composition and Use Value of Tree Biomass Ash

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Abstract. Wood-based ash landfilling is increasing issue not only in Latvia but in the whole world as more biomass is used for energy production. Utilization of wood burning waste as fertilizer is already used worldwide, but there is lack of information about chemical composition of wood ash obtained from Latvia plants, so the aim of this study was to determine chemical composition and analyse possible utilization options of wood-based ash from Latvia plants. Therefore wood ash samples from 53 companies were collected, sieved and chemical composition of samples was determined. It was concluded that within higher capacity of furnace more coarse fraction of wood ash was observed which is less valuable as fertilizer. Wood ash is good liming material consisting alkali compounds and other biogenic elements but also heavy metals, which are pollutants and could cause environmental problems.

Key words: wood ash, chemical composition, forest fertilization.

Introduction

A demand of alternative energy is increasing, as fossil fuel resources are decreasing. High forest coverage and soil fertility are factors which make biomass energy profitable for Latvia conditions. In recent years, forest stands are managed more intensively. It has been forecasted that consumption of energy wood in 2015 will increase for about 1.53 milj. m³ comparing to 2011 (Būmanis *et al.*, 2012). To provide energy, either more energy plantations of plants with wood-based biomass should be made or more wood residues should be delivered from forest harvesting (branches, tree tops, stumps). Both actions in long term could lead to soil degradation. Increasing consumption of woody biomass for energy production will lead to waste (wood ash), which usually is landfilled, overproduction. Yet, there are other alternative utilization ways (Pitman, 2006; James *et al.*, 2012; Siddique, 2012). Wood ash use for soil amendment is the way how to return nutrients removed by harvesting and solve ash utilization problem.

Wood-based ash contains almost all biogen elements and minerals. Ash alkalies compounds reduce soil acidity (Saarsalmi, Mälkönen, & Piirainen, 2001; Ozolinčius *et al.*, 2005), which provides favorable conditions for microbial growth that improve decomposition of organic matter and nutrient release (Saarsalmi *et al.*, 2014), yet many studies have shown different results of tree growth in response of wood ash spreading in forest. Wood ash treated forest stand annual increments vary from 1 m³ ha⁻¹ (Saarsalmi *et al.*, 2014) to 4 m³ ha⁻¹ (Emilsson, 2006).

Wood ash chemical properties depend on many factors (subsidiary fuel type, combustion system and season). But even within one tree specie element composition can differ significantly (Reimanna *et al.*, 2008). Qualitative composition of wood ash differs significantly within technology used for biomass combustion (Pitman, 2006). In Latvia, plants are mostly used in relatively small reciprocating grate furnaces with 1 MW capacity. In recent years many plants have been built with high capacity furnaces (20 MW), which produce significantly higher rates of ash.

It is impossible to provide energy plants with large volumes of uniform wood-based fuel so it is pointless to analyse separate tree species ash chemical content. For large scale ash utilization other factors should be analysed, for example, type of furnaces or capacity. The aim of this study is to determine composition and use value of tree biomass ash from Latvia plants.

Materials and Methods

Samples of wood-based ashes from reciprocating grate furnaces with or without ash stabilizing water beds of 53 different companies were received. Ash samples were sieved and divided into three fractions – fine (particle size < 3.15 mm), average (3.15 – 16 mm) and coarse (> 16 mm). For each fraction composition of chemical elements, pH, moisture and density were determined. To determine total carbon (C_{tot}) element analyzer LECO CR-12 was used (LVS ISO 10694). Content of carbonates (C_{carb}) was determined using Eijkelkamp calcimeter adding 20% hydrochloric acid (HCl) (according to LVS ISO 10693: 1995 standard). Organic carbon was calculated as residual between C_{tot} and C_{carb}.

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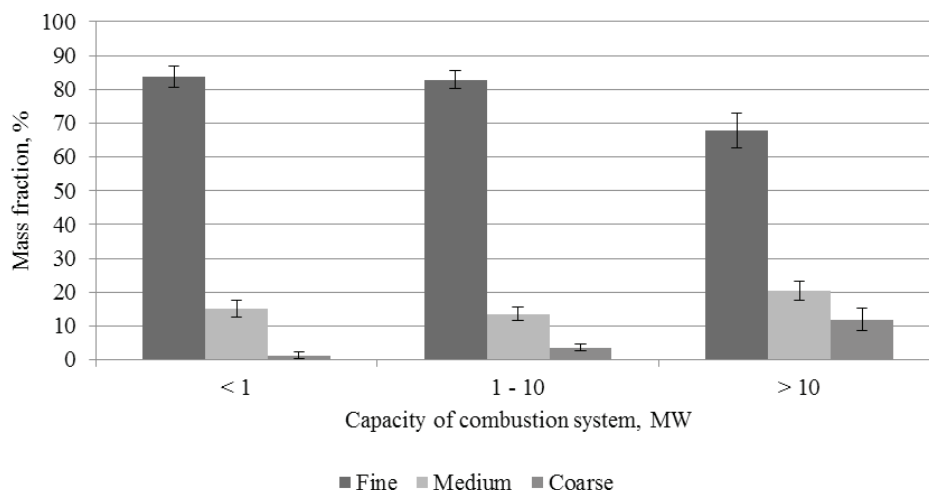


Figure 1. Mechanical composition of wood ash depending on combustion system capacity.

Total sulfur (S) was determined using ELTRA CS-530 method, oxidizing S to SO₂ at 1340 °C (ELTRA CS 530 methodology). To determine nitrogen (N), the modified Kjeldal method was used (LVS ISO 11261). Phosphates were determined calorimetric in aqua regia (LVS 298 (2002), LVS ISO 11466: 1995, LVS EN 14672 (2006)). Total potassium (K), calcium (Ca), magnesium (Mg) and manganese (Mn) were determined using an atom absorption spektrofotometer (ISO 11466:1005). Heavy metals cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) were determined according to LVS ISO 11047 standard using flame emission method. Furnaces were divided into three groups according to their capacity – furnaces with up to one MW, 1 to 10 MW and 10 to 20 MW. Statistical analysis was made of received results within capacity

groups. Considering that Ca and Mg could be found as carbonates or hydroxides and oxides proportion of these elements attached to carbonates was calculated. T-test ($\alpha=0.05$) was used for significance analysis and correlation analysis was used for data evaluation.

Results and Discussion

Combustion system capacity was used to compare wood ash properties from different furnaces, assuming that temperature is higher and temperature regime is more stable in high capacity combustion systems. Results showed that by increasing boiler capacity, proportion of coarse ash fraction (Figure 1), which is explained by fusion of small particles at higher temperature, increases. Fusion of particles starts at 700 °C and fusion intensity increases within temperature (Vassilev, Baxter, & Vassileva, 2013).

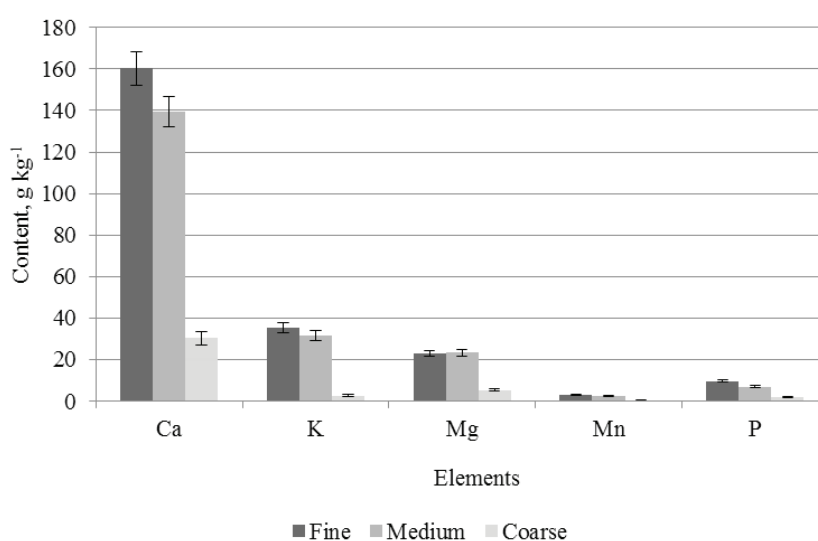


Figure 2. Mineral content in different ash fractions.

However, fine ash dominates in every furnace and form more than 69% of total ash.

Coarse ash fraction significantly ($\alpha=0.05$) differs from fine and average fractions containing less biogenic elements (Figure 2). Due to low element content, coarse ash fraction should be sieved off before application in forest. According to preliminary results of ash utilization in Finland, it could be used for road construction (Vanhanen, Dahl, & Joensuu, 2014). However, chemical composition between fine and medium fractions does not differ significantly.

During research it was found that wood ash is favourable liming material because of relatively high consistence of alkali metals. By using 1 tonne of sieved wood ash, it is possible to bring in soil 170 kg of liming material (150 kg Ca and 20 kg Mg) (Figure 2).

Liming properties are defined by alkali compounds which could be carbonates or oxides and hydroxides. It was found that between ash moisture and proportion of Ca and Mg expressed as carbonates there was a moderate and positive correlation ($r_{act} = |0.785| > r_{(0.05;30)} = 0.361$) (Figure 3). The dryer is the ash, the higher proportion of Ca and Mg is expressed as hydroxides, which can cause plant damage during fresh ash spreading. To prevent negative effect on vegetation, stabilisation (moisturising or hardening) of dry ash before spreading is required. Results show that wood ash taken from furnaces with water beds are more suitable as forest fertilizer.

Since coarse ash is not favourable as fertilizer, further only fine and medium ash fractions are analysed. Higher K content was found in ash produced by small and medium (less than 10 MW) furnaces (Table 2), which could be explained by higher temperature regime in large scale furnaces. Boiling point of potassium is at 760 °C. Above this

temperature evaporation of K compounds increases (Misra, Ragland, & Baker, 1993; Vassilev, Baxter, & Vassileva, 2013). Content of organic carbon also differs significantly between combustion systems and level of this element is lower in high capacity furnaces because of higher combustion rates. When temperature decreases volatile elements adsorb on finest ash particles (Saqib & Bäckström, 2014) which explains higher content of K in fine ash fraction.

Phosphorus is a non-volatile element (Vassilev, Baxter, & Vassileva, 2013) that is why the content of P in wood ash from different furnaces is not significant and depends more on other factors like biomass type. Determined elements form about 30 % of total ash. While ash also consists of chemically bounded oxygen, composition of ash from biomass is dominated by Si (silicon) (Nunes, Matias, & Catalão, 2016). High silicon content in wood biomass ash is a reason of coarse fraction formation.

Like K also cadmium (Cd) is a volatile element (boiling point 767 °C) and its content in wood ash highly depends on combustion temperature and is one of the elements whose concentration is not multivariate as high as other heavy metals (Table 2). Other heavy metal content is less stable, which is a problem if ash is considered as a fertilizer. Concern of environmental pollution is the main obstacle of wood biomass ash use for soil amendment.

In Latvia, no restrictions have been set about wood-based ash use for forest soil amendment, however, in other countries maximum content of heavy metals is limiting biomass ash use as fertilizer (Eijk, Obernberger, & Supancic, 2012) (Table 3). During some studies no significant impact or trace element accumulation by wood-based ash application in living organisms has been found yet (Perkiomäki *et al.*, 2003; Perkiömäki & Fritze, 2005; Omil, Piñeiro,

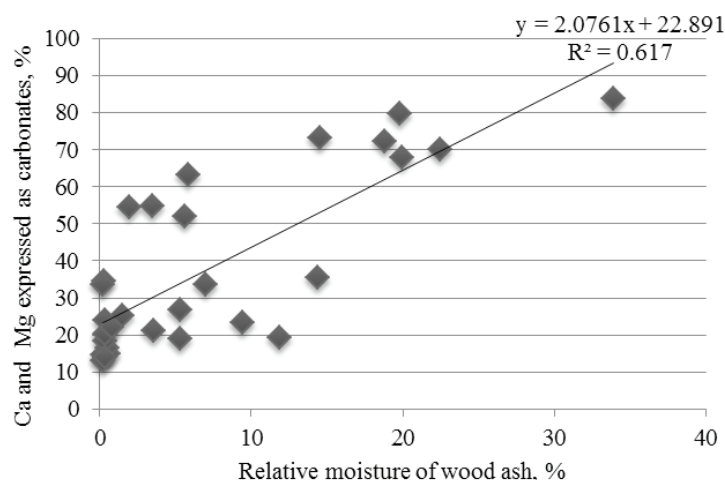


Figure 3. Relation between relative moisture of ash and alkali metals expressed as carbonates.

Table 2

Wood ash chemical composition according to furnace power

Element	Capacity of combustion system, MW and wood ash fraction					
	< 1		1 - 10		> 10	
	Fine	Medium	Fine	Medium	Fine	Medium
C _{carb.} , g kg ⁻¹	31.09± 8.35	20.71± 6.87	26.00± 3.41	17.14± 3.60	15.00± 3.96	10.88± 3.23
C _{org.} , g kg ⁻¹	148.73± 127.55	213.5± 122.35	57.52± 29.61	122.41± 45.82	20.84± 8.61	52.46± 34.00
S _{tot.} , mg kg ⁻¹	27.00± 9.28	17.49± 7.11	13.80± 4.96	31.76± 10.15	11.37± 4.25	20.90± 6.28
N _{tot.} , g kg ⁻¹	-	1.72± 0.58	0.34± 0.06	0.60± 0.15	0.26± 0.09	0.25± 0.08
P, g kg ⁻¹	10.75± 2.67	6.64± 1.58	11.12± 0.76	8.00± 0.60	7.82± 0.91	5.73± 0.62
K, g kg ⁻¹	46.34± 10.88	42.50± 11.96	43.01± 3.39	38.96± 3.50	24.05± 2.86	20.64± 3.07
Ca, g kg ⁻¹	155.95± 25.67	138.78± 24.12	186.98± 10.00	159.81± 9.75	128.95± 12.54	114.88± 11.33
Mg, g kg ⁻¹	28.11± 8.16	27.63± 11.34	25.76± 1.53	26.05± 2.00	18.41± 1.75	19.05± 2.12
Mn, g kg ⁻¹	3.81± 0.93	3.04± 0.86	3.72± 0.31	2.98± 0.33	2.10± 0.26	1.76± 0.25
Fe, g kg ⁻¹	11.58± 4.12	13.58± 4.74	6.60± 1.91	11.82± 3.82	4.72± 0.25	4.52± 0.52
Cd, mg kg ⁻¹	15.06± 4.53	12.83± 2.71	15.6± 2.14	14.95± 2.43	9.20± 1.54	8.79± 1.20
Pb, mg kg ⁻¹	70.09± 24.86	73.7± 15.35	60.76± 7.76	62.67± 7.86	45.54± 8.25	88.75± 11.42
Cr, mg kg ⁻¹	143.36± 24.46	215.9± 59.06	103.26± 11.58	208.77± 28.89	229.99± 35.70	298.01± 59.13
Ni, mg kg ⁻¹	28.08± 6.40	29.85± 7.19	38.00± 7.28	49.80± 11.39	23.84± 2.29	36.46± 4.70
Zn, mg kg ⁻¹	-	-	286.29± 56.65	192.44± 53.1	490.40± 159.79	409.42± 165.26
Cu, mg kg ⁻¹	203.97± 39.35	219.76± 71.22	218.09± 31.49	232.38± 47.76	99.86± 17.03	72.30± 10.88

Table 3

Existing limiting values of heavy metals in biomass ash for the application on forest lands, mg kg⁻¹

Trace element	Germany	Denmark	Sweden	Finland
Cd	1.5	20	30	25
Cr	2.0	100	100	300
Cu	-	-	400	700
Ni	80	60	70	150
Pb	150	250	300	150
Zn	-	-	7000	4500

& Merino, 2007). High differences of limiting heavy metal contents between countries, evidence for hazardous effect of heavy metal contamination has not been studied sufficiently yet. Some of trace elements are favourable for plant growth as microelements, for example, Cu and Zn.

Conclusions

Coarse ash fraction is more often found in higher capacity furnaces and is less valuable as fertilizer, so particles larger than 16 mm should be sieved off before transportation to treatment sites.

Between ash moisture and proportion of Ca and Mg attached to carbonates is moderate and positive correlation ($r = 0.79$) which suggests that fresh ash are not suitable for spreading in forest at vegetation period.

Qualitative composition of wood ash depends on volatilization of elements in high temperatures, higher concentrations of potassium have been found in ash from lower capacity furnaces, which makes wood ash more valuable as fertilizer, but also cadmium concentration is higher, which might cause higher contamination risk.

This is more likely preliminary overview of wood-based ash chemical composition from Latvia plants, no precise ash determining values could be set while wood based ash content depends on many factors. Capacity of furnaces could not be used for ash chemical content prediction and classification, because of high variation of element content, further investigations should be made.

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