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CHEMICAL AND PHYSICAL CHARACTERIZATION OF CYCLONE FLY ASHES FROM FIVE GRATE-FIRED BIOMASS COMBUSTION PLANTS

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Abstract: The fly ash leaves the combustion zone with the off-gas and is separated from the off-gas by dust separators. For the handling and treatment of fly ash its chemical composition and physical properties are important. Fly ashes from biomass combustion slightly contaminated with heavy metal can be utilized as a soil conditioner, thus closing the nutrient cycles for the soil where the biomass was grown. In this study five cyclone fly ashes from grate-fired bio mass combustion plants were investigated. Most of the fly ashes showed poor flowability, especially the fly ashes with small particle size. The flowability of the fly ash from straw combustion was also poor although this fly ash is rather coarse. This is probably caused by longish remainders of incompletely combusted straw stalks in this fly ash. All fly ashes contain valuable nutrients for the soil. However, in all fly ash samples from wood chip combustion the measured concentrations of Cd and Zn were above the limit concentration. Therefore, these fly ashes cannot be used as soil conditioners. The fly ashes from straw combustion and from palm oil residue combustion were much less contaminated by heavy metals and can be utilized as soil conditioner.

Keywords: biomass combustion, cyclone fly ash, nutrients, heavy metals, physical properties

1. INTRODUCTION

Limited availability of fossil fuels and concerns about climate change caused by the carbon dioxide emissions from fossil fuel combustion cause a continuous rise in combustion of biomass for heat and power generation (European Biomass Association, 2013). Biomass combustion is considered to be almost carbon dioxide neutral because the emissions produced during combustion are offset by the carbon dioxide fixed in the biomass during its growth.

The inorganic constituents from the combusted biomass remain as ash. Some of the ash leaves the combustion zone together with the off-gas as so called fly ash. The amount of fly ash produced depends on the kind of biomass combusted and the type of combustion process. The fly ash usually accounts for about one quarter of the total amount of ash (van Loo & Koppejan, 2008). The fly ash has to be separated from the flue gas in a dust collector. Single stage dust collection by a cyclone or by multi-cyclones is only sufficient for biomass combustion plants which have a higher dust emission limit because of the limited collection efficiency of cyclones, especially for fine particles. In order to comply with low dust emission limits (<20mg/m³ (STP)), a fabric filter or an electrostatic precipitator (EP) is often installed downstream of the cyclone.

The fly ash collected in the cyclones is a bulk material that has to be handled, treated and utilized or disposed of at landfill sites. For the decision about the further fate of the fly ash the chemical composition is essential. In Austria bottom ash and cyclone fly ash from the combustion of chemically untreated biomass can be utilized as soil conditioner on agricultural land and forests if the concentrations of pollutants are below the limit concentrations (Bundes-ministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011). The recycling of biomass ashes to the forest soil is proposed to help to close the nutrient cycles for the soil where the biomass was grown (Hallenbarter et al., 2002; Moilanen et al., 2002; von Wilpert et al., 2014). In other European countries the limit concentrations for biomass fly ash utilization can be different. The limit concentrations for Austria and for Scandinavian countries are summarized in table 1.

For the design of the storage bins and other fly ash handling equipment the physical properties of the ash are important. For example, in the calculation of the storage capacity of bins the bulk density of the fly ash and its angle of repose are required. The angle of repose can also be used for a rough categorization of the flowability of the material (Stanley-Wood, 2008).

In the literature only few data are available for biomass cyclone fly ashes. Some data on the chemical composition of cyclone fly ashes were reported by Hansen et al., (2001), Ingerslev et al., (2011), Pöykiö et al., (2009), Rönkkömäki et al., (2008) and van Loo & Koppejan (2008). Data of the density of cyclone fly ash were published by van Loo & Koppejan (2008).

The aim of this study was to characterize cyclone fly ashes from five different grate-fired biomass combustion plants. For this purpose the chemical composition of the fly ashes was analyzed and several physical properties were measured. Additionally the suitability of the different cyclone fly ashes as soil conditioner was verified with respect to the Austrian and Scandinavian limits.

2. MATERIAL AND METHODS

2.1. Materials

Cyclone fly ashes from five grate-fired biomass combustion plants were collected for this study. An overview of the thermal capacities of the plants, the type of cyclone installed and the combusted biomass is given in table 2. The fly ash samples of approximately 2dm³ were collected at the discharge system of the dust collectors. The volume of the ash samples was reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Retsch PT100, Quantachrome Micro Riffler).

2.2. Methods

The moisture content of the ash samples was determined gravimetrically. The samples were dried at 105°C for one hour. The particle size distribution was measured using a Sympatec, type HELOS/RODOS laser diffraction instrument with dry sample dispersion. The density (particle density) was determined according to ÖNORM EN ISO 8130-3 (Österreichisches Normungsinstitut, 2011).

Table 1. Heavy metal concentration limits for utilisation of ash from biomass combustion as a soil conditioner in forests and agriculture; in mg/kg d.w.

	Austrian guideline[1] (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011)		Finland cited in Nurmesniemi et al. (2012)	Sweden cited in Emilsson (2006)	Denmark cited in Haglund (2008)
	A	B			
As	20	20	40	30	
Cd	5	8	25	30	5 / 15[2]
Cr	150	250	300	100	100
Cu	200	250	700	400	
Ni	150	200	150	70	30 / 60[3]
Pb	100	200	150	300	120
Zn	1200	1500	4500	7000	
V				70	
B				500	
Hg			1.0	3	0.8

[1] if the concentrations are below limits according to A, no soil analysis is required
[2] left Cd limit for straw ash, right Cd limit for wood ash
[3] dosage limit for values between 30–60 mg/kg

Table 2. Biomass combustion fly ashes investigated

	Thermal capacity in MW_{th}	Type of cyclone	Combusted biomass
Plant A	0.6	Single cyclone	Wood chips, forest residue, 60% softwood
Plant B	1.1	Single cyclone	Wood chips, forest residue, 60% softwood
Plant C	5.0	Multi-cyclone	Wood chips, forest residue, 80% softwood
Plant D	4.0	Multi-cyclone	Residue from palm oil production (empty fruit bunches)
Plant E	2.2	Single cyclone	Wheat straw

This method is based on a determination of the mass and the volume of a test portion using a liquid displacement pyknometer. The capacity of the pyknometers used was approximately 105cm³ and n-heptane (density: 0.681g/cm³) was used for displacement of the air. The bulk density of the samples was determined according to ÖNORM EN ISO 60 (Österreichisches Normungsinstitut, 1999). The measurement is carried out in the following way: the powder stored in the funnel (120cm³) flows by gravity into the coaxial 100cm³ measuring cylinder when the bottom cover of the funnel is removed. The excess material is removed by drawing a straightedge blade across the top of the vessel.

The angle of repose was determined according to DIN ISO 4324 (Deutsches Institut für Normung, 1983). The measurement is carried out in the following way: a cone of material is obtained by passing a given volume of the powder through a special funnel placed at a fixed height above a completely flat and level plate. The base angle of the cone is calculated from the diameter of the base plate and the height of the cone. The angle of repose can be used as a flowability indicator to categorize the flowability of bulk solids and powders. The categories according to the United States Pharmacopeial Convention USP 29-NF24 (as cited in Stanley-Wood, 2008) are "excellent" for an angle of repose of 25°-30°, "good/free flow" for 31°-35°, "fair" for 36°-40°, "passable" for 41°-45°, "poor/cohesive" for 46°-55°, "very poor/very cohesive" for 56°-65° and "very very poor/ non-flow" if the angle of repose is greater than 66°.

All chemical analyses were determined by testing each sample in duplicate. In the results the average values are presented. The carbon content (TC) was determined with a LiquiTOC system from Elementar Analysensysteme. By combustion with air the carbon is transformed into CO_2 which is subsequently analysed. For the determination of the concentration of metals, sulphur and phosphor in the fly ash the solid samples were dissolved by aqua regia digestion (International Organization for Standardization, 1995) prior to analysis. The metals were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). For the analysis an ICP-OES system Ultima 2 from Horiba Jobin Yvon was used. The concentration of mercury was analysed using cold vapour atomic absorption spectrometry (CV-AAS) according DIN EN ISO 12846 (Deutsches Institut für Normung, 2010). The concentration of alkali and earth alkali metals, sulphate and phosphate was measured by ion chromatography (IC), (Dionex ICS-1000 system; cations: analytical column IonPac® CS12A 4x250mm; eluent: 20mM methanesulfonic acid, flow rate 1.0ml/min; anions: analytical column IonPac® AS14A 4x250mm; eluent: 8.0mM sodium carbonate / 1.0mM sodium hydrogen carbonate; flow rate 1.0ml/min).

Chloride and nitrate cannot be analysed after digestion by aqua regia. However, nearly all components containing these ions are highly soluble in water. Therefore, for the determination of the chloride and nitrate concentration in the samples, approximately 2grams of a sample were leached in 200ml of deionized water for one hour. To aid the leaching process the samples were placed in an ultrasonic bath. After leaching the remaining solids were separated by filtration. The concentration of chloride and nitrate was measured by IC.

3. RESULTS AND DISCUSSION

The fly ash particle size distributions are shown in figure 1. It is obvious that there are considerable differences between the cyclone fly ash samples investigated. All fly ashes from wood chip combustion (plant A, B and C) show a similar course of the size distribution curve.

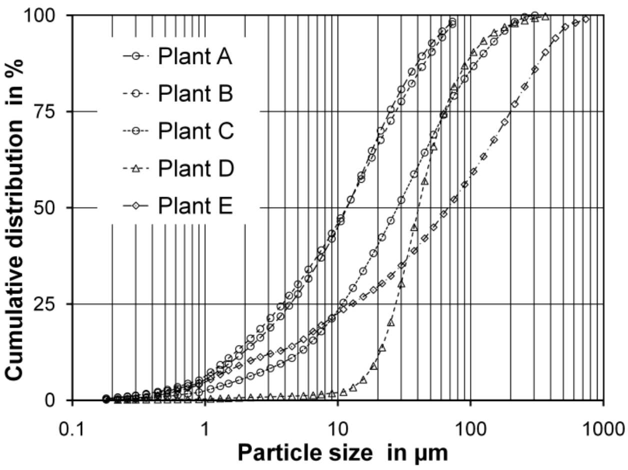

Figure 1. Particle size distribution of various cyclone fly ashes.

However, the size distribution of the fly ash from plant C is a little coarser. The spread of the distribution, defined as the quotient of x_{95} and x_5 (Rumpf, 1990) ranges from 61 to 98. The other fly ashes are coarser and the shape of their size distribution function is different. Fly ash D has a very narrow particle size distribution whereas fly ash E has a wide size distribution. The mass median diameters and the spreads of the size distribution of the various fly ash samples are summarized in table 3.

The results for further physical parameters are also shown in table 3. The humidity of most fly ash samples was far below 1%. In the straw combustion fly ash the water content was a bit higher.

The density of the fly ashes varies between 2270 kg/m³ and 2800 kg/m³. The higher values were found for the fly ashes from wood chips combustion whereas the lowest value was measured for the fly ash from straw combustion. The bulk density of the fly ashes varies within a wide range. The lowest value of 190 kg/m³ was found for the straw combustion fly ash while the fly ash from the palm oil residue combustion reaches a bulk density of about 900 kg/m³. The results of the density measurements for fly ash from wood chips and straw combustion correspond well with the data presented by van Loo & Koppejan (2008).

The angle of repose is in the range of 35° to 53°. The corresponding flowability categories are "good/free flow" for the fly ash from plant D and "poor/cohesive" for all other fly ashes. In figure 2 the ratio of the bulk density to the density is shown as a function of the angle of repose. The worse the flowability of the material expressed in the form of the angle of repose, the lower is the ratio of bulk density to density. This can be explained by the reduced ability of poorly flowing material to fill gaps between the particles. For a free flowing material with a typical porosity of 0.4 the ratio of bulk density to density would be 0.6. The fly ash from wood chips combustion showed a tendentiously higher ratio than the fly ash from other biomass.

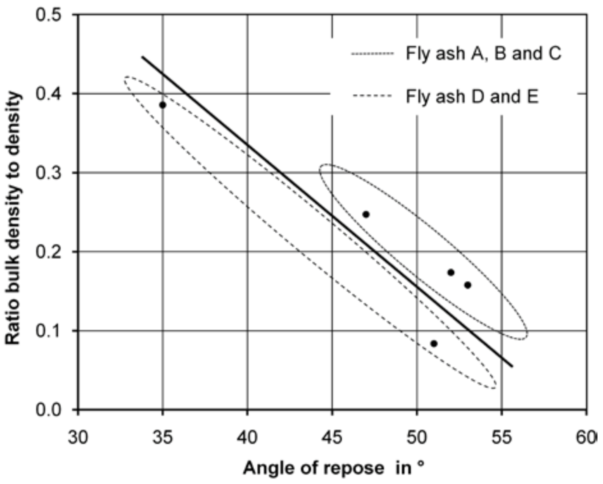

Figure 2. Density ratio versus angle of repose

The good flowability of fly ash D results from its relatively large particle size, the small spread of the size distribution and the close to spherical particle shape (Fig. 3).

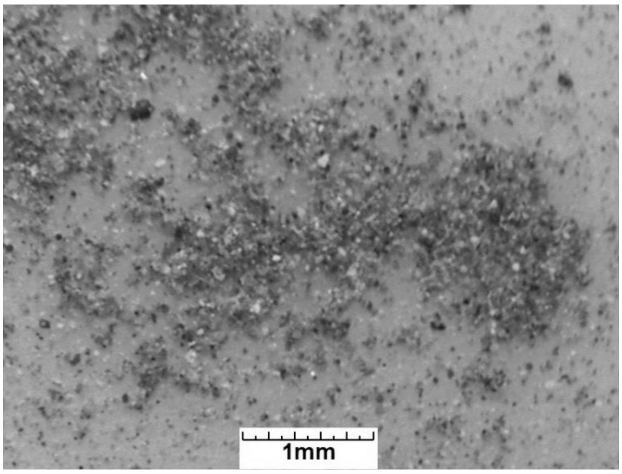

Figure 3. Microscopic image of the fly ash from plant D

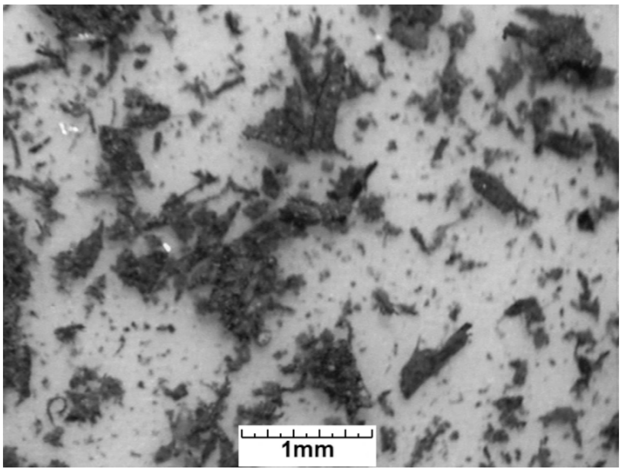

Figure 4. Microscopic image of the fly ash from plant E

The average particle size of the fly ash from plant E is even larger, however, the spread of the size distribution is wide and the bigger particles are far from being spherical (Fig. 4). It has to be mentioned that these large particles are over-represented by number in the shown image. The bigger particles are presumably remainders of incompletely combusted straw stalks.

Table 3. Physical properties of the cyclone fly ashes

		Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E
Humidity	%	0.6	0.5	0.4	0.4	3.3
Density	kg/m³	2750	2800	2670	2320	2270
Bulk density	kg/m³	480	445	660	895	190
Mass median diameter d_{50}	µm	11.7	11.6	27	41	68
Spread of the size distribution	-	61	73	98	10	440
Angle of repose	°	52	53	47	35	51

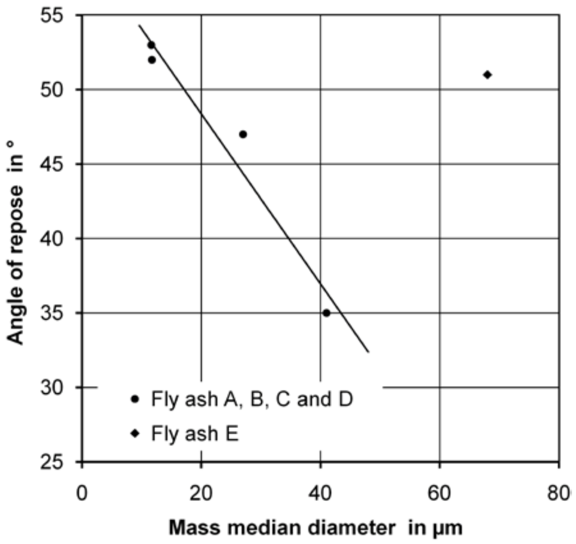

Figure 5. Angle of repose versus mass median diameter

The total carbon (TC) content of the oversize material obtained by sieving the fly ash with a 200µm sieve was 21%, which is nearly twice the average TC content of the fly ash. The effect of these irregular, longish particles can also be seen in a diagram where the angle of repose is shown as a function of the particle size (Fig. 5).

For the fly ashes A to D a good correlation between the angle of repose and the mass median diameter was found. Deviating from this correlation the angle of repose of fly ash E is comparatively much too high.

The results of the chemical analysis are summarized in table 4. The total carbon content of the fly ash characterizes the completeness of the combustion in the furnace. The average value for the fly ashes from wood chips combustion is 2.0±0.5%. This is in the range of the published values (van Loo & Koppejan, 2008). In the straw combustion fly ash sample the total carbon content was much higher (13.1 %).

For the utilization of the cyclone fly ash as a soil conditioner two items are important: a high content of nutrients, especially Ca, Mg, K, P and N, and heavy metal concentrations below the limit concentrations. The average concentration of Ca, Mg and PO_4^{3-} in the fly ash from wood chips combustion was 255±16g/kg, 16.6±1.6g/kg and 51±5g/kg, respectively.

Table 4 Chemical composition of the cyclone fly ashes (all concentrations based on dry weight); measured values exceeding the Austrian limit concentration for utilization of the fly ash as soil conditioner are printed in bold type

		Fly ash A	Fly ash B	Fly ash C	Fly ash D	Fly ash E
TC	%	1.8	1.7	2.7	1.7	13.1
Cl^-	g/kg	10.7	8.9	10.2	26	122
NO_3^-	g/kg	0.6	0.2	0.7	0.6	0.3
PO_4^{3-}	g/kg	54	55	46	36	22
SO_4^{2-}	g/kg	72	60	84	28	47
Na	g/kg	1.6	1.7	2.8	0.6	2.2
K	g/kg	89	88	88	103	275
Mg	g/kg	15	18	16	10	9.2
Ca	g/kg	255	271	240	191	39
Al	g/kg	6.8	7.9	11.8	9.0	1.5
Fe	g/kg	5.1	5.8	12.2	11.8	9.6
Mn	g/kg	10.1	10.8	12.3	0.4	0.2
As	mg/kg	9	11	15	17	8
B	mg/kg	546	547	583	105	21
Ba	mg/kg	355	360	244	35	257
Bi	mg/kg	132	141	135	101	4
Cd	mg/kg	**38**	**30**	**108**	1	2
Co	mg/kg	39	39	50	< 25	< 25
Cr	mg/kg	33	39	67	13	22
Cu	mg/kg	35	51	47	< 5	< 5
Hg	mg/kg	0.22	0.23	0.13	< 0.05	0.21
Mo	mg/kg	78	31	33	< 5	< 5
Ni	mg/kg	27	30	48	15	< 5
Pb	mg/kg	157	92	247	27	< 25
Sb	mg/kg	15	12	10	10	< 25
Sr	mg/kg	428	460	663	115	97
V	mg/kg	43	40	43	43	< 25
Zn	mg/kg	**2560**	**2000**	**4780**	198	145

In the straw fly ash the concentration of Ca especially is much lower and also the PO_4^{3-} concentration is less than half. On the other hand, the K concentration in straw fly ash is 275g/kg, which is about three times the concentration measured for the wood chips fly ash. The nutrient content of the fly ash from the palm oil residue combustion is between that of the fly ash from wood combustion and that of the fly ash from straw combustion. The concentration of NO_3^- is very low in all fly ash samples.

The measured concentrations of the nutrients in fly ash from wood chips combustion compare quite well with the data reported by Hansen et al. (2001), Ingerslev et al. (2011), Pöykiö et al., (2009) and van Loo & Koppejan (2008). In the fly ash from straw combustion the concentration of K was more than twice the concentration reported by van Loo & Koppejan (2008), whereas the concentrations of the other nutrients did not differ that much.

There is a higher concentration of most heavy in the fly ash samples from wood combustion (plant A, B and C) compared to the fly ashes from straw and palm oil residue combustion. In all three ash samples from wood combustion the Cd concentration is above the Austrian limit concentration and also above the limit concentrations in Finland and Denmark, which are substantially higher than the Austrian limit. For Sweden the limit for Cd is still higher but even there only the fly ash sample from plant B would fulfil the requirements. In the fly ashes from straw and palm oil residue combustion the Cd concentration is very low. The Zn concentrations of the wood fly ashes are also above the Austrian limit. However, only the fly ash from plant C exceeds the Finnish limit and no fly ash exceeds the Swedish limit. All other heavy metal concentrations are below the given limits.

For the concentrations of the heavy metals in cyclone fly ash from wood chips combustion considerable differences are found in the published studies. The values measured in this study are in the range of the published values. The measured heavy metals concentrations for the straw combustion ash fit very well with the data published by van Loo & Koppejan (2008).

Thus, none of the investigated fly ashes from wood combustion can be utilized as soil conditioner but have to go into landfills or must be treated to reduce the concentrations of Cd and Zn. The fly ash from straw combustion and the fly ash from palm oil residue are much less contaminated by heavy metals and therefore can be utilized as soil conditioner.

4. CONCLUSIONS

Five cyclone fly ashes from grate-fired biomass combustion plants were investigated. The three fly ashes from wood chips combustion are quite similar in physical properties and in chemical composition. The fly ash from palm oil residue combustion and the fly ash from straw combustion are quite different. Most of the fly ashes exhibit poor flowability. The angle of repose increases with decreasing particle size. An exception from this correlation is shown by the fly ash from straw combustion which is probably caused by the longish remainders of incompletely combusted straw stalks.

All fly ashes contain valuable nutrients for the soil, especially K, Ca, Mg and PO_4^{3-}. However, the concentration of the various nutrients depends on the type of biomass combusted. In the fly ash from wood chips combustion the measured concentrations of Cd and Zn were above the limit concentration. Therefore, these fly ashes cannot be used as soil conditioners. The fly ashes from straw and from palm oil residue combustion were much less contaminated with heavy metals and therefore can be utilized as soil conditioner.

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