Chemical composition and properties of ashes from combustion plants using Miscanthus as fuel

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ARTICLE INFO

Article history:
Received 5 November 2015
Revised 2 March 2016
Accepted 15 March 2016
Available online 4 July 2016

Keywords:
Biomass combustion
Miscanthus
Ash composition
Ash properties

ABSTRACT

Miscanthus giganteus is one of the energy crops considered to show potential for a substantial contribution to sustainable energy production. In the literature there is little data available about the chemical composition of ashes from the combustion of Miscanthus and practically no data about their physical properties. However, for handling, treatment and utilization of the ashes this information is important. In this study ashes from two biomass combustion plants using Miscanthus as fuel were investigated. The density of the ashes was $2230 \pm 35 \text{ kg/m}^3$, which was similar to the density of ashes from straw combustion. Also the bulk densities were close to those reported for straw ashes. The flowability of the ashes was a little worse than the flowability of ashes from wood combustion. The measured heavy metal concentrations were below the usual limits for utilization of the ashes as soil conditioner. The concentrations in the bottom ash were similar to those reported for ash from forest residue combustion plants. In comparison with cyclone fly ashes from forest residue combustion the measured heavy metal concentrations in the cyclone fly ash were considerably lower. Cl$^-$, S and Zn were enriched in the cyclone fly ash which is also known for ashes from wood combustion. In comparison with literature data obtained from Miscanthus plant material the concentrations of K, Cl$^-$ and S were lower. This can be attributed to the fact that the finest fly ash is not collected by the cyclone de-dusting system of the Miscanthus combustion plants.

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Introduction

Concerns about climate change caused by the carbon dioxide emissions from the combustion of fossil fuels lead to a continuous rise in the combustion of biomass for heat and power generation (European Biomass Association, 2013). The combustion of biomass is considered to be almost carbon dioxide neutral because the carbon dioxide emissions produced during the combustion process are almost offset by the carbon dioxide fixed by photosynthesis during the growth of the biomass. Besides forest and agricultural residues energy crops are also used as fuels in biomass combustion plants. Miscanthus giganteus is one of the energy crops being considered to show the potential for a substantial contribution to sustainable energy production (Lewandowski et al., 2003). In Europe the area of agricultural land where Miscanthus was grown in 2011 was approximately 20,000 ha (European Biomass Association, 2013). In 2014, the acreage of Miscanthus in Austria was 1180 ha (Statistik Austria, 2015) with the main production areas being in Upper and Lower Austria. The yield of dry biomass depends on the soil quality, the water supply and the temperature. In upper Austria, the yield on good soil is in the range of 15–22 ton dry mass per hectare (Frühwirth and Liebhard, 2006).
In the combustion of Miscanthus the inorganic constituents remain as ash. Most of the ash is discharged as bottom ash but some of the ash leaves the combustion zone together with the off-gas as fly ash. The amount of produced fly ash depends on the combustion conditions and the type of combustion process. In biomass combustion the fly ash typically accounts for about one quarter of the total amount of ash (van Loo and Koppejan, 2008). In smaller size combustion plants the fly ash is collected in a single de-dusting stage by a cyclone or a multi-cyclone. The collected cyclone fly ash is usually discharged from the combustion process together with the bottom ash as mixed ash. The total ash content of Miscanthus is reported to be in the range of 2.0%–3.5% (European Biomass Association, 2013). Similar values were reported by Baxter et al. (2012) and Michel et al. (2012) for the ash content of samples from the whole plant.

In many countries ashes from the combustion of chemically untreated biomass are utilized as soil conditioner on agricultural land and forests if the concentrations of pollutants are below the limit relevant concentrations. The recycling of biomass ashes to the soil is proposed to help to close the nutrient cycles for the soil where the biomass was grown (von Wilpert et al., 2014). Country-specific limit concentrations for heavy metals can be found in the literature (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011; Emilsson, 2006; Nurmesniemi et al., 2012).

The ashes from the combustion processes are bulk materials that have to be handled, stored, treated and utilized or disposed of at landfill sites. The chemical composition of ashes is essential in determining its utilization. For its use as a soil conditioner the country-specific limits are decisive. The physical ash properties like the bulk density and the flowability are important parameters for the design of the handling and storage facilities (Schulze, 2008).

In the literature there is only little data available for the chemical composition of ashes from the combustion of Miscanthus. Baxter et al. (2012) and Michel et al. (2012) reported the concentrations of main ash components in ashes produced by combustion of small samples of Miscanthus in a muffle furnace at 550°C for 3 hr and 400°C for 8 hr, respectively. The ash content and concentration data for main ash components and some heavy metals for Miscanthus plants are available in Obenberger et al. (2006). From this data the expected content of the components in the ash can be calculated. No data was found in the literature for the physical properties of ashes from the combustion of Miscanthus.

The aim of this study was to characterize bottom ash and cyclone fly ash from the combustion of Miscanthus in full scale combustion plants with respect to their chemical composition and their physical properties.

1. Materials and methods

1.1. Material

The ashes investigated in this study were collected from two grate-fired biomass combustion plants using M. giganteus as fuel. The thermal capacity of plant A and plant B was 400 KWth and 750 KWth, respectively. The biomass for the two combustion plants was grown in Lower Austria (250 m a.s.l.) and Upper Austria (350 m a.s.l.), respectively. In April, the culm material was harvested leaving the leaves out on the soil. The material was chopped and stored under open air roof. In both plants the combustion temperature measured about 1 m above the combustion grate was approximately 600°C. Each plant was equipped with a cyclone for the de-dusting of the combustion off-gas. Ash samples of 1 dm³ were collected at the ash discharge systems. From plant A only a combined bottom ash and cyclone fly ash sample could be obtained, whereas, in plant B the bottom ash and the cyclone fly ash were collected separately. The volume of the ash samples was reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Haver&Boecker HAVER RT and Quantachrome Micro Riffler).

1.2. Analytical methods

The moisture content of the dust samples was determined with an OHAUS, type MB 45 moisture analyser. The dust samples were dried at 105°C until the weight of the sample was constant. The particle size distribution of the ash samples was determined using a Fritsch ANALYSETTE 3 PRO laboratory sieve shaker with sieves from 10 to 500 μm. The undersize material of the 500 μm sieve was analysed using a Sympatec, type HELOS/Rodos laser diffraction instrument with dry sample dispersion. The calibration of the instrument was verified with a SiC-P600/06 standard from Sympatec. The target value for the mass median diameter x50 is 25.59 μm and the acceptable range is 24.82 to 26.36 μm. The measured value for the x50 was 25.64 μm.

The density of the ashes ρs (particle density) was determined according to EN ISO 8130-3 (European Committee for Standardization, 2011). The mass and the volume of a test portion of ash were determined using a 100 cm³ liquid displacement pyknometer. N-heptane (density: 0.681 g/cm³) was used for the displacement of the air. The bulk density ρB of the ash samples was determined according to EN ISO 60 (European Committee for Standardization, 1999). For the measurement 120 cm³ of the powder stored in a funnel flow by gravity into the coaxial 100 cm³ measuring cylinder. The volume of the certified measuring cylinder is 100 ± 0.5 cm³ and the precision of the balance was ±0.01 g. The excess material is removed by drawing a straight blade across the top of the cylinder. The voidage was calculated as 1 – ρB / ρS.

The angle of repose can be used as a flowability indicator for bulk solids and powders. It was measured according to ISO 4324 (International Organization for Standardization, 1977). For the measurement a cone of material is obtained by passing the powder through a special funnel placed at a fixed height above a completely flat and level circular plate. The base angle of the cone is calculated from the diameter of the base plate and the height of the cone. The reproducibility of the measurements was ±1°.

The yield locus for the ash samples was determined using a Schulze RST-XS ring shear tester with a 30 cm³ shear cell. The test procedure was conducted in accordance with ASTM D 6773 (2008) at four values of the normal stress (600, 2000, 6000 and 20,000 Pa). A quantitative characterization of the
flowability of a bulk solid is possible with the flowability $f_{fc}$ which is calculated as the ratio of the consolidation stress $\sigma_1$ and the unconfined yield strength $\sigma_c$. The flow category can be in the range from not flowing with $f_{fc} < 1$ to free flowing with $f_{fc} > 10$ (Schulze, 2008). Other results obtained in the shear test are the effective angle of internal friction and the bulk density, both as a function of the stress. The kinematic angle of wall friction with structural steel S235JR (1.0038) was determined using a shear cell where the bottom ring was formed by a sample of this material. Details on the performance of a shear tests can be found elsewhere (Lanzerstorfer, 2015a). The calibration of the shear tester was verified at a normal stress of 3000 Pa at pre-shear using the certified reference material BCR-116 from the Community Bureau of Reference (Limestone Powder), which was also used in a round robin test on ring shear testers (Schulze, 2011). The measured values of the shear stress were in the range of $\tau_{\text{measured}} \pm 0.6$ (SD).

All chemical analyses were determined by testing each sample in duplicate. In the results the average values are presented. The average relative standard deviation calculated from the duplicate measurements was 5.6%. For the determination of the concentration of metals and sulphate in the ashes the solid samples were dissolved by aqua regia digestion according to ISO 11466 (International Organization for Standardization, 1995) prior to analysis. For determination of the Cl$^-$ and NO$_3^-$ concentration the ash samples were leached in deionized water. The concentrations of Na, K, Ca, Mg, C1$^-$, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$ were measured by ion chromatography (Dionex ICS-1000 system). The other metals were measured by inductively-coupled plasma optical emission spectroscopy (Horiba Jobin Yvon Ultima 2 system). The details of the analytical methods can be found elsewhere (Lanzerstorfer, 2015b). The concentration of Si was analysed gravimetrically according to ISO 439 (International Organization for Standardization, 1994). The total carbon (TC) content of the dusts was determined using an Elementar Analysensysteme LiquiTOC system with a solids material extension. By combustion with air organic and inorganic carbon is transformed into CO$_2$ which is subsequently analysed.

2. Results and discussion

2.1. Physical properties

The particle size distributions of the ashes are shown in Fig. 1. For the finer fraction the distributions are very similar for all three ashes. On the coarse end the size distributions of the bottom ash and the mixed ash extend to particle sizes of several mm while the maximum particle size of the cyclone fly ash is approximately 300 $\mu$m. The mass median diameters of the fly ashes and the other physical properties are summarized in Table 1. In contrast to cyclone fly ash from forest residue combustion plants the cyclone fly ash was somewhat coarser (Lanzerstorfer, 2014a, 2014b).

The density of the Miscanthus ashes varied in a small range. The average density of the ashes was $2230 \pm 35$ kg/m$^3$. This is considerably lower than the density of ashes from forest residue combustion but similar to the density of ashes from straw combustion (van Loo and Koppejan, 2008). The bulk density of the cyclone fly ash was also much lower than the bulk density of the bottom ash and the mixed ash. It was in the range of the bulk density reported for cyclone fly ash from straw combustion while the bulk density of the bottom ash was between those reported for wood ash and for straw ash (van Loo and Koppejan, 2008). As a result of the low bulk density the voidage of the cyclone fly ash was much higher.

Fig. 2 shows the dependence of the bulk density of the ashes on the consolidation stress measured in the shear tests. The density of all ashes increased with the increasing consolidation stress. When the axis for the consolidation stress is in the logarithmic scale the measured values for the density almost follow a straight line. In the diagram also the values for the bulk density measured according to EN ISO 60 (1999) are shown at a consolidation stress of 1.0 kPa. These values fit quite well to the density function.

The angles of repose were in a small range from 48° to 52°. Therefore, the corresponding flowability category is “poor/cohesive” for all three ashes (Stanley-Wood, 2008). The value of the angle of repose for the cyclone fly ash is similar to those of fly ashes from the combustion of other biomass (Lanzerstorfer, 2015b) while the value for the bottom ash is much higher than those reported for the bottom ash from forest residue combustion (Lanzerstorfer, 2014b). Similar results for the flowability characterization were obtained in the shear tests. The results for the flowability are shown in the left of Fig. 3. The flowability improves with increasing stress. When both axes are in the logarithmic scale the measured values for the $f_{fc}$ almost follow a straight line. For the lower values of the consolidation stress the flowability $f_{fc}$ was in the range from 2 to 4. This corresponds with a flowability category of “cohesive” (Schulze, 2008).

At higher values of the consolidation stress the flowability of the bottom ash and the mixed ash improved to “easy
flowing”, thus reaching nearly the flowability reported for forest residue combustion bottom ash (Lanzerstorfer, 2014b). The flowability behaviour of the cyclone fly ash was similar to those reported for cyclone fly ash from forest residue combustion, only the ff was somewhat lower (Lanzerstorfer, 2014b).

In the right of Fig. 3 the effective angles of internal friction and the wall friction angles are shown as a function of the normal stress. Generally, the effective angle of internal friction was higher for the cyclone fly ash. For all ashes, the effective angle of internal friction decreased with increasing normal stress. For the wall friction angles similar observations were made: with increasing wall normal stress the wall friction angles decrease. But in contrast to the effective angles of internal friction the wall friction angles for the cyclone fly ash were a bit lower than for the bottom ash and the mixed ash.

In summary, it can be noted that the flow relevant properties of the ashes from Miscanthus combustion are quite similar to those from combustion even though the particle size and the values for density showed noticeable differences. Thus, the design of dust handling and storage equipment for Miscanthus combustion plants can be the same as for the wide spread wood combustion plants.

2.2. Chemical composition

The TC content and the concentrations of the main ash forming components are summarized in Table 2. There was still some TC in the bottom ash and the mixed ash. This was also reflected in the dark grey to black colour of these ashes. In the cyclone fly ash the TC content was significantly higher. The value of 12.6% is much higher than in typical cyclone fly ash from forest residue combustion plants but in the same range as reported for a small straw combustion plant (Lanzerstorfer, 2014a).

Another significant difference between the cyclone fly ash and the bottom ash was found in the Cl− concentrations. It was about ten times higher in the cyclone fly ash compared to the bottom ash. The same effect but less pronounced was found for S. This can be explained by the higher volatility of Cl− and S components. A similar difference is also found in the ashes from forest residue combustion (Pöykiö et al., 2009).

Considering the fact that the mixed ash from plant A is a mixture with bottom ash as the major component and cyclone fly ash as the minor component the overall composition of the ashes from plants A and B do not differ very much. Increased concentrations of the ash from plant A were found for Ca, Mg and S while in the ash from plant B the Al and Si content was higher.

Although the N content of the whole Miscanthus plant is approximately 0.7% (Obernberger et al., 2006) practically no

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**Fig. 2** - Bulk density of the ashes as a function of the consolidation stress.

**Fig. 3** - Flow ability of the ashes as a function of the consolidation stress (left) and effective angle of internal friction and wall friction angle (right).
NO₃ was found in the ash samples. This means that practically all N contained in the plant material leaves the combustion process in the gaseous phase.

In ashes produced in laboratory analysis from Miscanthus plant material the concentrations of K, Cl⁻ and S were considerably higher (Baxter et al., 2012; Michel et al., 2012; Obernberger et al., 2006). This difference might be explained by the fact that the finest fly ash fraction is not collected by the cyclone of the de-dusting system in the biomass combustion plant while K, Cl⁻ and S are especially enriched in the finest fractions of the fly ash from biomass combustion (Lanzerstorfer, 2011, 2015c). Therefore, the bottom ash and the cyclone fly ash are depleted in these components.

The concentrations of heavy metals and other minor ash components are summarized in Table 3. The measured heavy metal concentrations were below the usual limits for ash utilization as soil conditioner (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2011; Emilsson, 2006). This difference might be explained by the fact that the finest fly ash fraction is not collected by the cyclone of the de-dusting system in the biomass combustion plant (Lanzerstorfer, 2014a).

Thus, recycling of the ashes including the fly ashes from Miscanthus combustion to the soil is highly recommendable in contrast to the fly ashes from wood combustion plant, which has to be excluded from recycling in many cases because of exceeding some heavy metals limit concentrations.

### Table 3 - Concentrations of heavy metals and other minor components in the ashes (all concentrations in mg/kg based on dry weight).

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<td>785</td>
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</table>

* Calculated from reported ash content and concentration data for the plant.

** Calculated average of reported values.

Thus, recycling of the ashes including the fly ashes from Miscanthus combustion to the soil is highly recommendable in contrast to the fly ashes from wood combustion plant, which has to be excluded from recycling in many cases because of exceeding some heavy metals limit concentrations.

### 3. Conclusions

The investigation of ashes from combustion plants using Miscanthus as fuel revealed some differences and some similarities in the properties of the ashes compared to the well investigated ashes from forest residue combustion and straw combustion.

The particle size of the bottom ash and the mixed ash was in a typical range but the cyclone fly ash was somewhat coarser than cyclone fly ash from forest residue combustion.

The densities of the ashes from Miscanthus combustion were similar to those reported for straw ashes and, therefore, significantly lower than the densities of ashes from wood combustion. The measured bulk densities for the bottom ash and the mixed ash were between those reported for wood ash and for straw ash and the bulk density of the cyclone ash was close to that of cyclone fly ash from straw combustion.

The angles of repose for the three ashes were all close to 50°, the corresponding flowability category is "poor/cohesive". This value compares well with the angle of repose of other biomass combustion fly ash but is significantly higher than reported for bottom ash from forest residue combustion. Similar results for the flowability characterization were obtained in the shear tests. The flowability of all ashes improved with increasing stress, especially the flowability of the bottom ash and the mixed ash.

In the bottom ash and the mixed ash there was still some TC content, but in the cyclone fly ash the TC content was significantly higher. The value of 12.6% is much higher than in typical cyclone fly ash from forest residue combustion plants but it was in the same range as found for a small straw combustion plant (Lanzerstorfer, 2014a).
The Cl⁻ and S concentrations in the cyclone fly ash were considerably higher compared to the bottom ash. The same effect is known for the ashes from wood combustion. The overall composition of the ashes from plants A and B do not differ very much. Increased concentrations of the ash from plant A were found for Ca, Mg and S while in the ash from plant B the Al and Si content was higher.

The literature values obtained from ashes produced in the laboratory from Miscanthus plant material show considerably higher concentrations of K, Cl⁻ and S. This difference might be explained by the fact that the finest fly ash was not collected by the cyclone of the de-dusting system in the Miscanthus combustion plant and K, Cl⁻ and S are especially enriched in the finest fractions of the fly ashes from biomass combustion.

The measured heavy metal concentrations were below the usual limits for utilization as soil conditioner. The concentrations in the bottom ash and in the mixed ash were similar to those reported for bottom ash from forest residue combustion plants. In the cyclone fly ash the heavy metal concentrations were a bit higher, but only for Zn a significant enrichment was found in the cyclone fly ash. In comparison with cyclone fly ashes from forest residue combustion the measured heavy metal concentrations were considerably lower.

Acknowledgments

The Si measurements carried out by G. Kastner and proof-reading by D. Moser are gratefully acknowledged.

REFERENCES


