

RESULTS AND EVALUATION OF A NEW HEAVY METAL FRACTIONATION TECHNOLOGY IN GRATE-FIRED BIOMASS COMBUSTION PLANTS AS A BASIS FOR AN IMPROVED ASH UTILISATION

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ABSTRACT: In general, three different ash fractions have to be distinguished in biomass grate furnaces, the bottom ash precipitated on the grate or in the furnace, the coarse fly-ash, usually collected in cyclones and the fine fly-ash mainly containing aerosols formed during combustion. Previous work has shown that a mixture of bottom ash and coarse fly-ash (usable ash) from biomass combustion plants fired with chemically untreated woody biomass, usually keeps the limiting values of ecologically relevant heavy metals for the utilisation of biomass ashes on soils. However, the utilisation of new energy crops, like *Salix* has shown that these crops take up and accumulate heavy metals from the soil, especially Cd and Zn, and thus contain significantly higher concentrations of these metals than normal wood (e.g. spruce or beech). Due to this fact, the limiting values for ash utilisation are exceeded. This work shows a new and patented technology, where the coarse fly-ash is re-circulated to the furnace, which enhances the fractionation of the volatile and ecologically relevant elements Cd and Zn, and leads to an increased accumulation of these heavy metals in the fine fly-ash fractions, while the main part of the nutrients remains in the usable ash. Due to this effect the limiting values for the usable ash can be kept and a sustainable ash utilisation can be achieved. The heavy metal rich but small fine fly-ash fraction has to be disposed of. Following this approach a biomass plant can act as an efficient heavy metal filter for the environment.

Keywords: biomass, combustion, heavy metals, ash utilisation

1 BACKGROUND

Thermal utilisation of biomass is considered an environmentally sound way of providing energy, especially for process heat and district heating purposes. The main advantage of energy from biomass is the CO₂-neutrality of this energy production process provided that sustainable forestry is given. However, biomass combustion produces solid by-products, ashes, that have to be considered.

The ashes contain plant nutrients like calcium, magnesium, potassium and phosphorous that should be recycled to forest or agricultural soils, thus closing not only the carbon cycle but also the mineral material fluxes of the overall energy production process. The problem is however, that besides nutrients, the ashes also contain heavy metals. Especially Cd poses a risk to the use of wood ash on soils and is considered as the environmentally most relevant element in wood ashes.

This is especially important in cases when Cd accumulating species like *Salix* are used as fuel. *Salix* is an interesting short rotation crop and has been seen to extract and accumulate Cd from soils, making it suitable for long term phyto-remediation of contaminated agricultural land. This is however only ecologically feasible if the extracted Cd can be separated efficiently from the main part of the ash produced during combustion in order to make a sustainable ash utilisation possible.

The behaviour of environmentally relevant heavy metals during biomass combustion has been investigated for several years by the research group "Thermal Biomass Utilization" at the Graz University of Technology [1, 2, 3, 4, 5]. The following paper summarises the results obtained from these investigations and describes the subsequent development of a new

combustion technology with integrated heavy metal fractionation.

Previous research has shown that bottom ash from fixed bed biomass combustion plants with low concentrations of environmentally relevant and volatile heavy metals (Cd, Pb and Zn) and high concentrations of nutrients (K, Ca) can be produced by keeping on and around the grate the combustion air ratio low ($\lambda < 1.0$) and the temperature high (500 to 900 °C) [2, 3, 4].

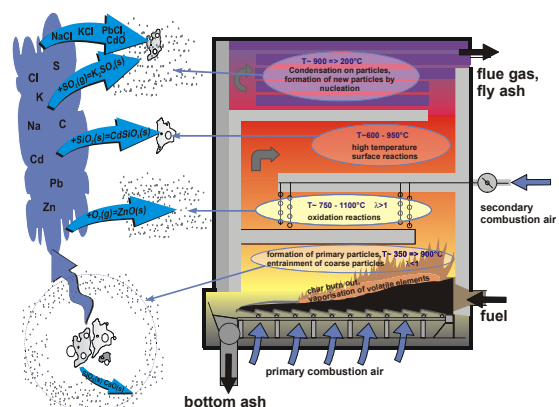


Figure 1: Principle of the behaviour of volatile ash forming species during wood combustion

The main part of the volatile heavy metals is vaporised during combustion under reducing conditions and accumulates in the fly ash due to subsequent condensation or chemical reactions on fly ash particles in the flue gas (see Figure 1). Fine fly-ash particles reveal higher concentrations of these metals compared to coarse fly-ash particles, mainly due to their large specific surface area but also due to formation of new particles by nucleation (Zn). Although the concentration of volatile environmentally relevant heavy metals is lower in coarse

fly-ash particles compared to fine fly-ash particles, significant amounts of these elements are bound in the coarse fly-ash fraction, which can amount from 10 to 35 wt.% of the total ash produced, when conventional combustion technology is used.

Moreover, previous research showed that in most cases the Austrian limiting values for heavy metals regarding the recycling of biomass ashes on soils [6], can be kept by a mixture of coarse fly-ash and bottom ash (usable ash) from the combustion of chemically untreated wood fuels. However, in cases with elevated concentrations of heavy metals in the biomass fuels, e.g. Salix, the limiting values for the usable ash are exceeded.

The fine fly-ash, which usually only represents 5-15 wt% of the overall ash amount in fixed bed biomass combustion systems has to be separately collected and must not be recycled to soils, due to its high heavy metal content.

Consequently, a new technology had to be developed in order to ensure a sustainable ash utilisation for fuels with higher concentrations of heavy metals as well. The idea behind the and new improved fractionation technology is to re-circulate coarse fly-ash (e.g. precipitated in a multi-cyclone), into the reducing atmosphere on the grate (see Figure 2) and thus re-vaporise the volatile heavy metals in this ash. The refractory part of the ash (mainly nutrients) stays on the grate and is precipitated with the bottom ash (usable ash). The concentration of volatile heavy metal vapours in the flue gas rises and consequently the fine fly-ash particles get enriched in Cd and Zn. Following, the fine fly-ash fraction will contain the main part of the heavy metals which has to be precipitated by an effective fine fly-ash filter (wet ESP or baghouse filter) in order to minimise particulate emissions. Due to its high content of heavy metals this fine fly-ash fraction has to be disposed of (ash for disposal).

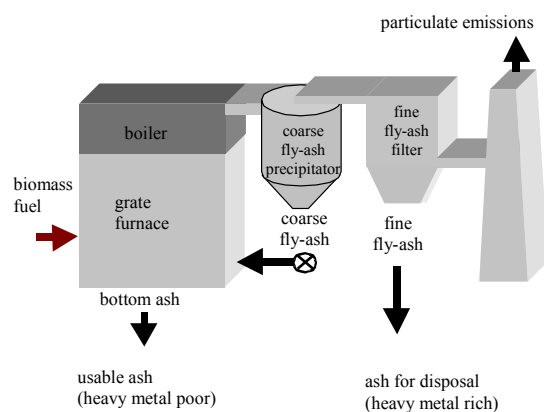


Figure 1: Schematic outline of the new biomass combustion technology with integrated fractionated heavy metal separation by coarse fly-ash re-circulation

This new and patented combustion technology was realised and tested in a pilot-scale grate combustion plant using Salix as fuel and later on applied in a large-scale grate combustion plant burning a mixture of wood chips and veneer residuals in Austria.

2. OBJECTIVES

The objective of the work was to investigate the potential of an improved heavy metal fractionation technology in grate fired biomass combustion plants by a two stage fly-ash precipitation and re-circulation of coarse fly-ash to the furnace. A second aim was to test and evaluate the efficiency of this technology for different biomass fuels with varying heavy metal concentrations.

3. METHODOLOGY

Test runs with coarse fly-ash re-circulation to the grate were conducted in a pilot-scale plant (nominal boiler capacity 400 kW_{th}) burning Salix fuels containing elevated Cd concentrations (0.8-2.6 mg Cd/kg dry basis) and later on in a full-scale grate combustion plant (nominal boiler capacity 6 MW_{th}) burning a mixture of wood chips and veneer residuals (0.13 mg Cd/kg fuel, dry basis). In both units test runs were performed with and without the application of the new fractionation technology. Moreover, the results obtained were compared with data gained from full-scale biomass combustion plants using conventional grate combustion technology.

During the test runs all fuel and ash streams (including dust emissions) were measured and samples were collected for subsequent chemical analyses. Ash and biomass fuel samples collected during the test runs were analysed for their content of heavy metals, Cd, Zn, Pb, Cu and As as well as the main ash forming elements Ca, Mg, K, Na, Si, S, and Cl, using proven methods [7, 8, 9]. However, in this paper only the influence of the new heavy metal fractionation technology on the most relevant elements (Cd, Zn, K and Ca) regarding biomass ash utilisation will be discussed. In addition, the total ash and water contents of the biomass fuels were determined.

The amount of fuel combusted during each test run was calculated by means of energy balances over the plant. The balances were performed considering the heat produced, the gross calorific value of the fuel, the water content of the fuel, the average O₂ and CO concentration in the flue gas as well as the flue gas temperature at boiler outlet during each test run.

Mass flows of ashes as well as the concentration of the heavy metals and the ash forming elements in the fuels, in the bottom ashes (including the ash collected in the furnace), the coarse fly-ash, and the fine fly-ashes (dust in the flue gas at the outlet of the coarse fly-ash precipitator) were determined. From these mass flows and analysis data, mass and element balances over the plant were calculated for each test run. From the results achieved transfer factors for the different elements from the fuels into the different ash fractions could be calculated for each fuel and technology investigated.

The pilot-scale test runs were conducted in a horizontally moving grate-fired pilot plant equipped with controlled air staging and flue gas re-circulation, which allows for an efficient control of temperature and combustion air ratio conditions on the grate, which are important factors for an efficient heavy metal

fractionation. The coarse fly-ash was precipitated in a rotational particle separator (RPS). This fly-ash precipitation stage has a smaller cut diameter (about 1µm) than ordinary multi-cyclones [1] and ensures an almost complete precipitation of coarse fly-ash particles. The dust remaining in the flue gas after the RPS (aerosol fraction) forms the fine fly-ash which was also measured and analysed. Based on the results achieved, fine fly-ash precipitation in a baghouse filter was estimated considering a dust emission of 2 mg/Nm³ (13% O₂) in the flue gas at the outlet of the filter.

Reference test runs without ash re-circulation and test runs with ash re-circulation were performed for each fuel. Coarse fly-ash collected during the reference test runs was added by a vibrating feeder to the fuel in the subsequent test runs with ash re-circulation. By this way a direct internal re-circulation of coarse fly-ash was simulated.

In the full-scale grate fired biomass combustion unit a direct internal re-circulation of coarse fly-ash was installed. The coarse fly-ash is precipitated in 4 parallel cyclones and continuously fed back into the primary combustion chamber by pneumatic transport. Mass flows and transfer factors of ash and ash forming elements were measured and calculated with and without this internal re-circulation. The fine fly-ash is precipitated in an electrostatic precipitator (ESP) placed behind the cyclones.

The data and results obtained from the pilot- and full-scale test runs were compared with previous results achieved from test runs in a conventional full-scale grate combustion plants (equipped with a multi-cyclone and a flue gas condensation unit) utilising wood chips and bark from spruce as fuels.

Table I: Chemical composition of the fuels investigated

Plant	Fuel	Cd	Zn	K	Ca	ash
		mg/kg d.b.				
Full scale (conventional technology)	wood chips (Spruce)	0.29	60.2	1,218	5,179	16,209
Full scale (conventional technology)	bark (Spruce)	0.57	144.4	2,743	10,090	35,809
Full scale (new technology)	wood chips + vener residual	0.13	18.9	896	3,370	10,191
Pilot scale (new technology)	wood chips (Salix 1)	2.57	177.5	3,269	6,316	36,167
Pilot scale (new technology)	wood chips (Salix 2)	0.85	138.8	2,527	4,409	18,734

4. RESULTS

The chemical compositions of the fuels investigated are compared in Table 1. The two Salix fuels used in the pilot-scale test runs contain significantly higher concentrations of primarily Cd and secondarily Zn than the other fuels. The Salix fuels do also contain the highest concentrations of the nutrient K. Furthermore, the varying concentrations of ash forming elements between the different kinds of biomass fuels investigated become evident. Spruce wood chips and bark contain higher concentrations of Cd, Zn and K and significantly higher concentration of Ca than the mixture of wood chips and veneer residuals, which is due to the fact that the veneer residuals have been treated in hot water during the processing of the veneer (leaching effects).

The results of the test runs carried out clearly reveal that the volatile heavy metals Cd and Zn are mainly bound in the coarse- and fine- fly-ash fraction in all plants investigated (Figure 2). By re-circulating the coarse fly-ash fraction and thus eliminating this ash fraction as an output flow, the transfer of Cd and Zn from the usable ash fraction (bottom ash + coarse fly-ash) to the fine fly-ash is considerably increased, while the amount of usable ash is kept high at about 80 - 90 % of the total ash.

By applying coarse fly-ash re-circulation about 75 to 95 % of Cd and Zn are bound in the fine fly-ash fraction, while without coarse fly-ash re-circulation only 40 to 60% of Cd and Zn are bound in this fraction.

K as a semi-volatile element is also bound to a certain extent in the fly-ash fractions. As K represents the most important plant nutrient in wood ashes, it is the effort of fly-ash re-circulation to keep as much of K in the usable ash as possible. The results obtained show, that fly ash re-circulation does not significantly enhance the K accumulation in the fly ash due to the fact that K is also bound in the bottom ash by reactions with less volatile ash forming elements (Si, Al, Mg and Ca). It has, however, to be noticed that although the volatile heavy metals are accumulating in the fine fly-ash fractions (aerosol particles) its main mass consist of KCl and K₂SO₄.

Ca is important as a soil improving agent in biomass ashes. Ca is not volatile during biomass combustion and thus mainly found in the usable ash (bottom ash and entrained coarse fly-ash particles).

Moreover, the results show that the Austrian limiting values for heavy metals in biomass ashes regarding their utilisation on soils can in most cases be kept by utilising a mixture of bottom ash and coarse fly-ash (usable ash) from combustion of fuels with low concentrations of heavy metals like chemically untreated woody biomass (wood chips and bark from Spruce). However, fuels containing higher concentrations of heavy metals, like Salix, make this technique fail, because the limiting values are exceeded (Figure 3).

By using the new combustion technology with coarse fly-ash re-circulation, the concentrations of Cd and Zn in the usable ash can be significantly reduced and the limiting values for ash utilisation are kept for all fuels investigated (Figure 3).

The results reveal that re-circulation of coarse fly-ash increases the amount of fine fly-ash as well as the heavy metal concentrations in the fine fly-ash fraction. Following, in order to keep the emissions of fine particulates and heavy metals as small as possible, it is of great importance that the fine-fly-ash remaining in the flue gas after coarse fly-ash precipitation is effectively precipitated by using an ESP or baghouse filter as a second dust separation stage.

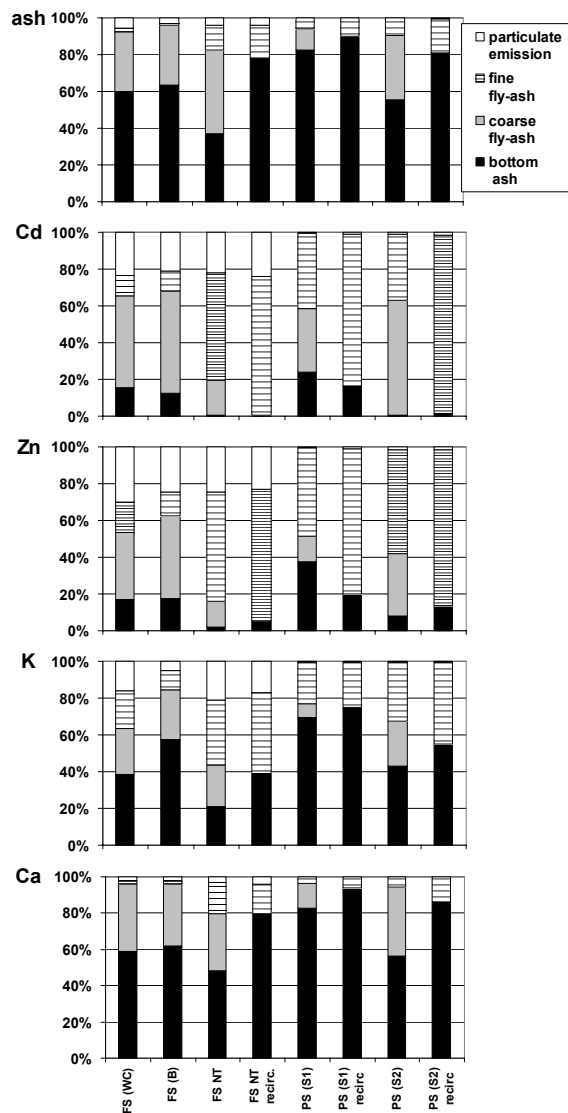


Figure 2: Distribution of ashes and elements among the different ash fractions in the plants investigated

Explanations: FS...full-scale conventional combustion technology; FS NT...full-scale new combustion technology; PS...pilot-scale new combustion technology; WC...wood chips; B...bark; S...Salix; recirc...test runs with coarse fly-ash re-circulation; distributions are calculated based on the total amount of ash and elements in the fuel and thereby assuming a 100% rate of recovery

5. CONCLUSIONS

The results achieved reveal that the heavy metal fractionation potential of the new technology developed and tested depends on the combustion technology used, the technology of fly ash precipitation applied as well as on the concentration of ash and heavy metals in the biomass fuel.

The Austrian limiting values for heavy metals in biomass ashes regarding their utilisation on soils can usually be kept by a mixture of bottom ash and coarse fly-ash (usable ash) when biomass fuels with low

concentrations of heavy metals like wood chips and bark are used.

For biomass fuels containing elevated concentrations of heavy metals (especially Cd and Zn), like the heavy metal accumulating energy crop Salix, the limiting values for Cd and Zn are exceeded following this approach.

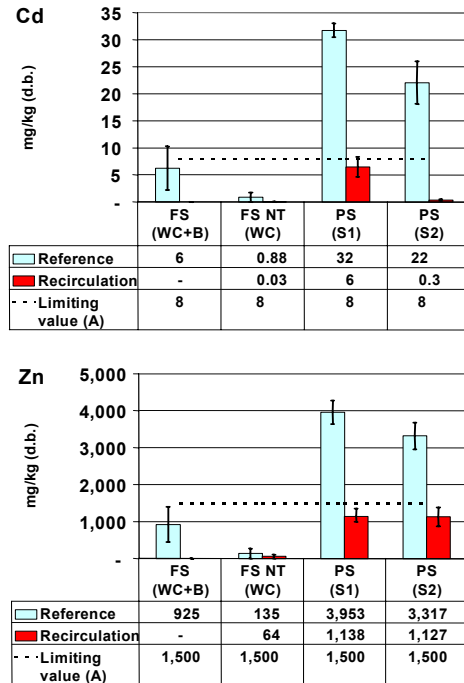


Figure 3: Concentrations of Cd and Zn in the usable ash from test runs performed with and without coarse fly-ash re-circulation compared to Austrian limiting values for ash utilisation

Explanations: usable ash...mixture of bottom ash and coarse fly-ash; FS...full-scale conventional combustion technology; NT...full-scale new combustion technology; PS...pilot-scale new combustion technology; WC...wood chips; B...bark; S...Salix; limiting value...limiting values for biomass ash utilisation on agricultural and forest soils in Austria [6]

The new heavy metal fractionation technology showed, that by re-circulating the coarse fly-ash to the grate and by keeping a reducing atmosphere and high temperature in the grate section, an efficient fractionation of heavy metals can be achieved. 75 to 95 % of Cd and Zn can be bound in the fine fly-ash fractions, which means a considerable improvement in comparison to the fractionation of heavy metals in conventional biomass grate furnaces, which show 40 to 60% recovery of Cd and Zn in the fine fly-ash fraction. The total amount of usable ash can also be kept high at 80 to 90% of the total ash produced.

Following, the new heavy metal fractionation technology offers a good solution for the realisation of a sustainable biomass ash utilisation on soils by significantly reducing the heavy metal concentrations in the usable ash for all biomass fuels investigated.

As the re-circulation of coarse fly-ash to the furnace increases the amount of fine fly-ash produced as well as the heavy metal concentrations in the fine fly-ash

fraction, an efficient precipitation of this ash by using ESP or baghouse filter technology is necessary in order to keep the particulate emissions into the atmosphere as small as possible. Consequently, an important requirement of the new heavy metal fractionation technology is the use of an effective two-stage fly-ash precipitation.

Due to its high concentrations of heavy metals, the precipitated fine fly-ash fraction has to be disposed of or industrially utilised.

6. ACKNOWLEDGEMENT

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