

## Ash-related Problems during Biomass Combustion and Possibilities for a Sustainable Ash Utilisation

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### Abstract

The chemical composition of biomass fuels and especially the contents of ash forming elements influence the choice of an appropriate combustion and process control technology. They affect deposit formation, fly ash emissions and ash handling as well as ash utilisation/disposal options. Major ash forming elements (Al, Ca, Fe, K, Mg, Na, P, Si) are of relevance for the ash melting behaviour and deposit formation. Volatile ash forming elements such as Cl, S, Na, K, As, Cd, Hg, Pb, Zn play a major role regarding gaseous and especially aerosol emissions as well as concerning deposit formation, corrosion and ash utilisation/disposal.

Aerosols are very small sized particles with diameters  $< 1 \mu\text{m}$  formed during the combustion of biomass fuels. They are mainly composed of alkali and heavy metal salts and cause particulate emissions, which can only be reduced with highly advanced gas cleaning devices such as electrostatic and fibrous filters. Due to fly ash and aerosol depositions on surfaces of boiler tubes, the efficiency of heat transfer decreases. Furthermore, ash depositions and especially those with high chlorine contents may cause corrosion of boiler tubes.

On the other hand, biomass ashes contain relevant amounts of plant nutrients like K, Mg and P. However, they also contain heavy metals and therefore possibilities for a sustainable ash utilisation (recycling to agricultural fields or forests) have to be found.

**Keywords:** Biomass ash, aerosol formation, corrosion, ash utilisation.

### Introduction

The whole process of thermal utilisation of solid biofuels (fuel supply, fuel conversion, solid and gaseous emissions) is influenced by the kind of solid biofuel used, its physical characteristics (e.g. particle size, bulk density, moisture content, gross calorific value) and its chemical composition. Due to high R&D efforts, biomass combustion technologies have already achieved a high level of development in all capacity ranges. The most important advantage of biomass fuels as compared to fossil fuels is that their thermal utilisation is almost  $\text{CO}_2$  neutral. In addition, state-of-the-art biomass combustion and co-firing systems also have achieved low  $\text{CO}$ -,  $\text{NO}_x$ - and TOC-emission levels, which are comparable to the emission levels of fossil fuel fired

systems. However, there is still one disadvantage left, namely ash related problems, which affect the particulate emissions from biomass combustion units and also can cause plant internal problems due to slagging, deposit formation and corrosion.

The paper presented will discuss ash related problems during biomass combustion and will especially focus on the composition of biomass fuels and their influence on ash related problems under special consideration of ash and aerosol formation during biomass combustion, on deposit formation and corrosion as well as on ash characterization and utilisation.

## Composition of biomass fuels and their influence on ash related problems

Different elements are present in solid biofuels at varying concentrations depending on the origin and type of biomass. Table 1 and Table 2 show guiding values for ash contents and element concentrations in wood and herbaceous fuels [1].

The ash content of the fuel is essential for the choice of the appropriate combustion and gas cleaning technologies (see Table 1 and Table 2). Furthermore, fly ash formation, ash deposit formation as well as logistics concerning ash storage and ash utilisation/disposal depend on this parameter [2]. Wood usually contains relatively low amounts of ash, while significantly higher values are typically found in bark, straw, grasses and grains.

Grate or fluidised bed combustion are suitable technologies for ash-rich fuels. Underfeed stokers are not suitable for these fuels due to the formation of ash layers on the surface of the fuel bed which can cause irregular breakthroughs of the gas and combustion air resulting in increased emissions [2].

Table 1: Typical mean values for the chemical composition of wood fuels

Explanations: data source [1], daf...dry basis, ash free, d.b...dry basis; ash content measured according to ISO 1171 (1997) at 550°

Parameter / Unit		Wood without bark		Bark		Logging residues		Short rotation coppice Willow
		Coniferous wood	Deciduous wood	Coniferous wood	Deciduous wood	Coniferous wood	Deciduous wood	
<b>Ash</b>	w-% d.b.	0.3	0.3	4.0	5.0	2.0	1.5	2.0
<b>Al</b>	mg/kg d.b.	100	20	800	50			-
<b>Ca</b>	mg/kg d.b.	900	1,200	5,000	15,000	5,000	4,000	5,000
<b>Fe</b>	mg/kg d.b.	25	25	500	100			100
<b>K</b>	mg/kg d.b.	400	800	2,000	2,000	2,000	1,500	3,000
<b>Mg</b>	mg/kg d.b.	150	200	1,000	500	800	250	500
<b>Mn</b>	mg/kg d.b.	147	83	500	190	251	120	97
<b>Na</b>	mg/kg d.b.	20	50	300	100	200	100	-
<b>P</b>	mg/kg d.b.	60	100	400	400	500	300	800
<b>Si</b>	mg/kg d.b.	150	150	2,000	10,000	3,000	150	-
<b>Ti</b>	mg/kg d.b.	< 20	< 20					10
<b>As</b>	mg/kg d.b.	< 0.1	< 0.1	1		0.3		< 0.1
<b>Cd</b>	mg/kg d.b.	0.1	0.1	0.5	0.5	0.2	0.1	2
<b>Cr</b>	mg/kg d.b.	1	1	5	5			1
<b>Cu</b>	mg/kg d.b.	2	2	5	5			3
<b>Hg</b>	mg/kg d.b.	0.02	0.02	0.05	< 0.05	0.03	0.02	< 0.03
<b>Ni</b>	mg/kg d.b.	0.5	0.5	10	10			0.5
<b>Pb</b>	mg/kg d.b.	2	2	4	5	3	5	0.1
<b>V</b>	mg/kg d.b.	< 2	< 2	1				
<b>Zn</b>	mg/kg d.b.	10	10	100	50			70
<b>Cl</b>	w-% daf	0.01	0.01	0.02	0.02	0.01	0.01	0.03
<b>S</b>	w-% daf	0.02	0.02	0.1	0.1	0.04	0.04	0.05

Major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and minor (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, Zn) elements form, together with Cl and S, the ash components. These elements are of relevance for ash melting, deposit formation, fly ash and aerosol

emissions as well as corrosion and the utilisation/disposal of the ashes (see Table 1 and Table 2).

Ca and Mg usually increase the ash melting point, while K and Na decrease it [2, 3]. Chlorides and low melting alkali- and aluminosilicates may also significantly decrease the ash melting point [4]. This can also cause sintering or slag formation in the combustion chamber (reduced plant availability and lifetime).

Straw, cereal, grass and grain ashes, which contain low concentrations of Ca and high concentrations of Si and K (see Table 4), start to sinter and melt at significantly lower temperatures than wood fuels. This fact must be considered when selecting the appropriate combustion and temperature control technology [3].

Table 2: Typical mean values for the chemical composition of herbaceous fuels  
Explanations: data source [1], daf...dry basis, ash free ; d.b...dry basis; ash content measured according to ISO 1171 (1997) at 550°

Parameter / Unit		Straw from wheat, rye, barley	Straw from oilseed rape	Grains from wheat, rye, barley	Miscanthus	Virgin reed canary grass	Grass, in general
<b>Ash</b>	w-% d.b.	5.0	5.0	2.0	4.0	6.4	7.0
<b>Al</b>	mg/kg d.b.	50	50				200
<b>Ca</b>	mg/kg d.b.	4,000	15,000	500	2,000	3,500	3,500
<b>Fe</b>	mg/kg d.b.	100	100		100		600
<b>K</b>	mg/kg d.b.	10,000	10,000	5,000	7,000	12,000	15,000
<b>Mg</b>	mg/kg d.b.	700	700	1,500	600	1,300	1,700
<b>Na</b>	mg/kg d.b.	500	500			200	1,000
<b>P</b>	mg/kg d.b.	1,000	1,000	4,000	700	1,700	3,000
<b>Si</b>	mg/kg d.b.	10,000	1,000			12,000	15,000
<b>As</b>	mg/kg d.b.	< 0.1	< 0.1	< 0.1	0.2	0.1	0.1
<b>Cd</b>	mg/kg d.b.	0.1	0.1	0.05	0.1	0.04	0.2
<b>Cr</b>	mg/kg d.b.	10	10	0.5	1		1
<b>Cu</b>	mg/kg d.b.	2	2	4	2		5
<b>Hg</b>	mg/kg d.b.	0.02	0.02	< 0.02	0.03	0.03	< 0.02
<b>Ni</b>	mg/kg d.b.	1	1	1	2		2
<b>Pb</b>	mg/kg d.b.	0.5	2	0.1	2	1	1
<b>V</b>	mg/kg d.b.	3			< 1		3
<b>Zn</b>	mg/kg d.b.	10	10	30	10		25
<b>Cl</b>	w-% daf	0.4	0.5	0.1	0.2	0.6	0.8
<b>S</b>	w-% daf	0.1	0.3	0.1	0.2	0.2	0.2

The Cl content of wood is generally very low, while significantly higher amounts are present in herbaceous biofuels (see Table 1 and Table 2). During combustion, the Cl contained in the biofuel mainly forms gaseous HCl, Cl<sub>2</sub> or alkali chlorides such as KCl and NaCl. Due to the subsequent cooling of the flue gas in the boiler section of the combustion plant, large parts of Cl salts form particles or condense on the heat exchanger surfaces or on fly ash particles. Investigations have shown that 40 to 80% of the total Cl released are embedded in the ash in the case of wood chip or bark combustion, and 80 to 85% in the case of straw or cereals combustion if baghouse filters are applied.

The S contained in the solid biofuel (see Table 1 and Table 2) forms mainly gaseous SO<sub>2</sub> and alkali as well as earth-alkali sulphates. Due to the subsequent cooling of the flue gas in the boiler section of the combustion plant, SO<sub>x</sub> forms sulphates and condenses on the heat exchanger surfaces or forms fine fly ash particles, or reacts directly with fly ash particles deposited on heat exchanger surfaces (sulphation). Investigations have shown that 40 to 70% or 60 to 90% of the fuel S were integrated in the ash in the case of wood chip or bark combustion and only 40 to 55% in the case of (wheat) straw or cereal combustion (plants equipped with baghouse filters) [2]. The efficiency of S fixation in the ash depends on the concentration of alkali and earth-alkali metals (especially Ca) in the fuel.

## Ash and aerosol formation during biomass combustion

Ashes formed during biomass combustion can be divided into bottom ashes and fly ashes. The fly ash fraction typically consists of a coarse and a fine mode. While the coarse mode (particles larger than some  $\mu\text{m}$ ) is simply due to ash entrainment from the fuel bed, the formation pathways of the fine mode (so-called aerosols with a particle diameter  $<1\ \mu\text{m}$ ) are much more sophisticated.

The basic mechanisms concerning aerosol formation in combustion processes are, in general, well known from former research work [5]. Volatile ash forming compounds, which are in the specific case of biomass combustion K, Na, S, Cl as well as easily volatile heavy metals (Zn and Cd), are released from the fuel into the gas phase and subsequently undergo gas phase reactions. As soon as the vapour pressure of a compound exceeds the saturation pressure, which can either happen due to a high formation ratio of this compound or by cooling of the flue gas, particle formation by nucleation or condensation of these vapours on existing surfaces takes place. Nucleation and condensation are always competing processes, and, if enough surface for condensation is available, nucleation can partly or even totally be suppressed. Otherwise, very small (some nm) aerosol particles are formed. As soon as these particles are formed, they start to coagulate with other aerosols or with coarse fly ashes.

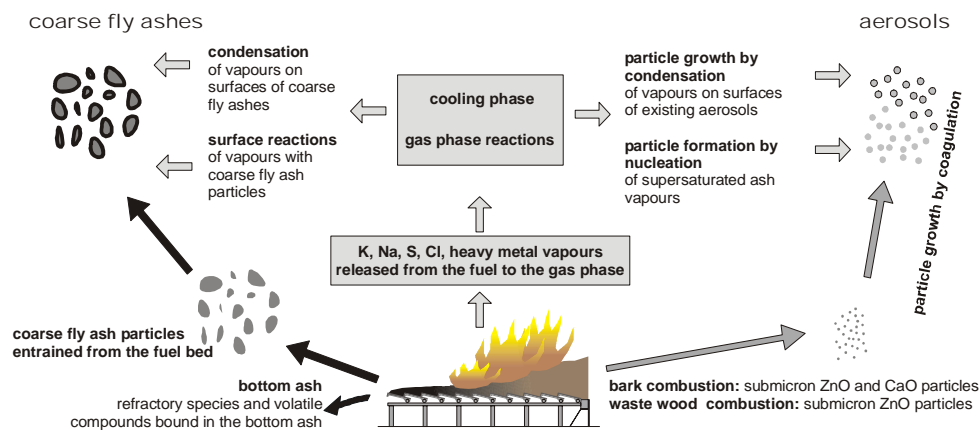


Figure 1 Mechanisms involved in ash formation during biomass combustion

Explanations: data source [6]

Due to the different formation pathways of coarse fly ashes and aerosols as well as due to their different chemical composition and behaviour, these two fly ash fractions have always to be treated separately. However, since the presence of coarse fly ashes influences the formation and behaviour of aerosols, the interactions between these two fractions have to be considered. Figure 1 gives an overview over the different ash and aerosol formation processes, for more details see [6].

## Deposit formation and corrosion

Cl, S, K and Na in biofuels play a major role in deposit formation and corrosion mechanisms. Table 3 gives an overview over guiding values and guiding ranges of different elements in solid biofuels and ashes for unproblematic combustion. The main influences of Cl are its corrosive effect on metal surfaces in furnaces and boilers [7], as well as HCl and particulate (KCl, NaCl,  $\text{ZnCl}_2$ ) emissions. Cl induced corrosion

problems are to be expected at fuel concentrations above 0.1 w-% (d.b.) and can therefore be of relevance for straw, cereals and grasses (see also Table 1 and Table 2) [8]. Measures against corrosion include automatic heat exchanger cleaning systems, coating of the boiler tubes, appropriate material selection as well as optimised combustion and process control technologies (see Table 3). Leaching of the fuel in order to decrease its Cl content (leaching) is an additional measure.

Table 3: Guiding values and guiding ranges of different elements in solid biofuels for unproblematic combustion

Explanations: data source [8]; d.b....dry basis; solid biofuels in brackets can exceed guiding values in special cases but usually keep them

element in the fuel w-% (d.b.)	guiding conc. w-% (d.b.)	limiting parameter	if guiding concentr. ranges are not kept problems can occur for	technological possibilities if the guiding values are not fulfilled
Cl	< 0.1	corrosion	straw, cereals, grasses, waste wood	fuel leaching automatic heat exchanger cleaning coating of boiler tubes appropriate material selection
S	< 0.1	corrosion	straw, cereals, grasses, waste wood, (bark)	see Cl
element in the ash w-% (d.b.)	guiding conc. w-% (d.b.)	limiting parameter	if guiding concentr. ranges are not kept problems can occur for	technological possibilities if the guiding values are not fulfilled
K	< 7.0	ash melting, depositions, corrosion	straw, cereals, grasses	against ash melting: temperature control on the grate and in the furnace against corrosion: see Cl
	--	aerosol formation	straw, cereals, grasses	efficient dust precipitation, fuel leaching
Na	<2.0	ash melting, depositions, corrosion	waste wood	fuel pre-treatment

The importance of S does not primarily result from SO<sub>2</sub> emissions but from its role in corrosion processes. Higher SO<sub>2</sub> concentrations in the flue gas cause sulphation of alkali and earth-alkali chlorides with decreasing flue gas temperatures (see Figure 1). This leads to the release of Cl. If these reactions take place in ash particles precipitated on the surface of heat exchanger tubes, the released Cl can cause corrosion by FeCl<sub>2</sub> or ZnCl<sub>2</sub> formation at the metal surfaces [9].

Straw, cereal, grass and grain ashes, which contain low concentrations of Ca and high concentrations of Si and K (see Table 4), start to sinter and melt at significantly lower temperatures than ashes from wood fuels. Melts occurring in fly ash particles may cause hard deposit formation on cooled furnace walls or heat exchanger tubes [2]. Hard deposit formation due to sticky fly ash particles can be accelerated by alkali and heavy metal salt mixtures (mixtures of alkali chlorides and sulphates with Zn chlorides) [7, 9]. The influence of heavy metals is of special relevance when waste wood is utilised.

### Ash characterization and utilisation

In biomass combustion plants three different ash fractions must normally be distinguished: bottom ash, cyclone fly ash and filter fly ash.

The bottom ash is produced on the grate and in the primary combustion chamber. This ash fraction often is mixed with mineral impurities contained in the biomass fuel like sand, stones and earth. These mineral impurities can, especially in fixed-bed combustion plants using bark, cause slag formation (due to a lowering of the melting point) and sintered ash particles in the bottom ash. The cyclone fly ash contains fine, mainly

inorganic, ash particles entrained with the flue gas from the grate and precipitated primarily in multi-cyclones placed behind the combustion unit. This ash fraction mainly consists of coarse fly ash particles. The filter fly ash is the second and finer fly ash fraction precipitated in electrostatic filters, fibrous filters or as condensation sludge in flue gas condensation units (normally placed behind the multi-cyclone). This ash fraction mainly consists of aerosols.

Ashes from combustion of solid biofuels contain considerable amounts of plant nutrients, which make an ash utilisation on soils interesting (see Table 4). Of course ecological ash utilisation is only applicable for ashes from chemically untreated biofuels (no ashes from contaminated biofuels, like waste wood, should be utilised on soils). For a sustainable biofuel utilisation it is essential to close the material fluxes and to integrate the biomass ashes within the natural cycles. Therefore, the cycle of minerals (soil/nutrients - root/plant - combustion - ash - soil) should be closed as completely as possible.

However, previous research has shown that the natural cycle of minerals within the process of energy production from chemically untreated biomass is disturbed by depositions of heavy metals on the forest ecosystem caused by environmental pollution. Therefore, it is not possible to recycle the total amount of ashes produced during the combustion process in most cases. This is mainly of relevance for wood fuels such as bark, wood chips and sawdust. Ashes from straw, cereals (whole crop) and grasses usually contain significantly lower amounts of heavy metals (see Table 4).

The environmentally most relevant heavy metals in biomass fuels (Zn and Cd), are mainly recovered in the fly ash while the nutrients (K, Mg and P) and liming agents (Ca) are primarily recovered in the bottom ash [10]. Wood and bark ashes are Ca rich, whereas straw and cereal ashes contain high amounts of K (see Table 4).

The reason for the higher amounts of heavy metals in the fly ash compared to the bottom ash is that the volatile heavy metals Cd and Zn mainly vaporise during combustion and are subsequently precipitated on the surface of fly ash particles or form aerosols. A part of smaller ash particles is entrained with the flue gas from the fuel bed and forms the coarse mode of the fly ash. Due to the fact that these coarse fly ash particles are entrained from the grate, their mineral core has a similar chemical composition to that of bottom ash.

Consequently, a mixture of bottom ash and cyclone fly ash (mainly coarse fly ash particles), the so-called “usable ash” with low amounts of heavy metals should be utilised as a fertilizer and the filter fly ash fraction (which usually covers only 10% of the overall ash amount) with high amounts of heavy metals should be deposited or industrially treated.

For an efficient heavy metal fractionation it is suggested that a biomass combustion plant should be equipped with a well working air staging system allowing low combustion air ratios on the grate and in the primary combustion chamber. Furthermore, the flue gas temperatures in this zone should be high. A combustion air ratio below 1 (reducing atmosphere) and high temperatures enhance heavy metal devolatilisation in the fuel bed. Furthermore, an optimised plant should contain a two stage fly ash precipitation technology with a coarse fly ash precipitator and a highly efficient fine fly ash precipitator. The general guidelines for an effective heavy metal fractionation described above are summarised in Figure 8.

Based on comprehensive ash analysis, field trials and material balances, guidelines for a sustainable utilisation of ashes from chemically untreated biofuels on agricultural land,

green land, and forests were developed in Austria [11, 12]. They cover the kind of biomass ash to be used, limiting values for heavy metals in the ashes and quantitative limits for an utilisation of biomass ashes on different soils. The Austrian guidelines for a sustainable utilisation of biomass ashes could form a good basis for the development of a common regulation on an European level in future.

Table 4: Concentration ranges of selected elements in biomass ashes  
Explanations: data source [3, 13]; d.b...dry basis, for P only average values are available

ash/element	wood chips (spruce) [w-% d.b.]	bark (spruce) [w-% d.b.]	straw (wheat, rye) [w-% d.b.]	cereals (wheat, tritiale) [w-% d.b.]
Ca	26.0 - 38.0	24.0 - 36.0	4.5 - 8.0	3.0 - 7.0
Mg	2.2 - 3.6	2.4 - 5.6	1.1 - 2.7	1.2 - 2.6
K	4.9 - 6.3	3.5 - 5.0	10.0 - 16.0	11.0 - 18.0
Na	0.3 - 0.5	0.5 - 0.7	0.2 - 1.0	0.2 - 0.5
P	0.7	1.6	1.0	4.3
	mg/kg d.b.	mg/kg d.b.	mg/kg d.b.	mg/kg d.b.
Zn	260 - 500	300 - 940	60 - 90	120 - 200
Cd	3.0 - 6.6	1.5 - 6.3	0.1 - 0.9	0.1 - 0.8

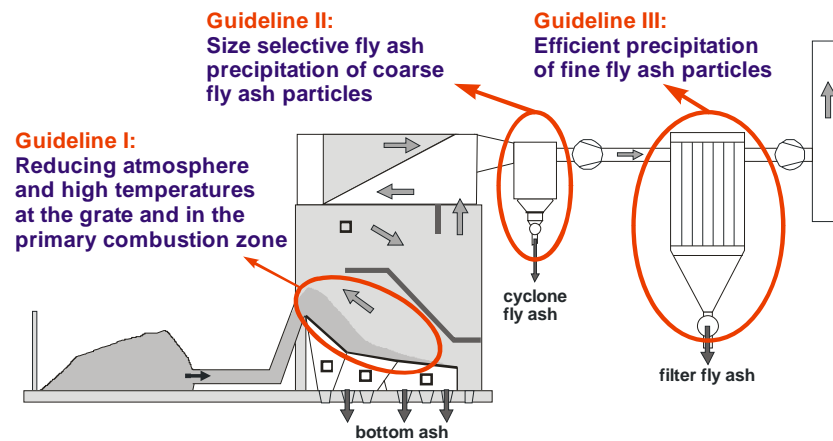


Figure 2 Guidelines for the design of a fixed-bed combustion technology with integrated fractionated heavy metal separation

## Summary and conclusions

The chemical properties of the different kinds of solid biofuels and the ashes produced affect the combustion and flue gas cleaning technologies needed.

Wood fuels (coniferous and deciduous wood, bark, logging residues and short rotation coppice) are characterised with the exception of bark by a low ash content. Their ash usually contains comparatively high concentrations of heavy metals, which is of importance in respect to the utilisation/disposal of ashes but also in respect to aerosol formation and fine particulate emissions. Straw, cereals, grasses and grains can contain relatively high levels of Cl, S and alkali metals which are of special relevance in respect to corrosion and deposit formation. They are usually also characterised by a high ash content. Therefore, grate combustion should be applied for the thermal utilisation of these fuels preferably. Their ashes contain comparatively low Ca but high K and Si contents and therefore start to sinter and melt at significantly lower temperatures than ashes from wood fuels.

Ashes from biomass combustion contain considerable amounts of plant nutrients which make an utilisation on agricultural or forest soils interesting. However, the ideal natural cycle of minerals in ashes from the combustion of chemically untreated biomass is disturbed by the deposition of heavy metals on plants and soils by environmental pollution. Therefore, it is recommended to separate a small and heavy metal rich side-stream of the ashes (filter fly ash) from the process and to utilise the major part of the ashes produced as a secondary raw material with fertilising and liming effects on agricultural and forest soils.

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