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# **BYE/03/G31 Project “Biomass Energy for Heating and Hot Water Supply in Belarus”**

## **Fact sheet ash utilisation**

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# 1 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 research and development 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 CO<sub>2</sub> neutral. In addition, state-of-the-art biomass combustion and co-firing systems also have achieved low CO-, NO<sub>x</sub>- and TOC-emission levels, which are comparable to the emission levels of fossil fuel fired systems.

Due to increasing thermal utilisation of biomass, the amounts of residues from the combustion process also increase, given the fact that the ash content of biomass fuels ranges from 0.5 wt.% (related to dry basis - d.b.) (for soft wood) to 4-8 wt.% (d.b.) for bark. Table 1 shows that the quantity of ash is strongly influenced by the bark content in wood fuels. This is a result of higher ash content in bark, on the one hand, and a higher level of mineral impurities (sand, earth, stones) in the bark, on the other hand.

**Table 1:** Fuel-specific ash content of various biomass fuels [1]. Low contents for wood chips and sawdust and higher for hard wood

Explanations: Ash content in wt.% (d.b.), ash content measurement according to ISO 1171-1981 at 550°C.

Biomass fuel used	Ash content
Bark	5.0 - 8.0
Wood chips with bark (forest)	1.0 - 2.5
Wood chips without bark (industrial)	0.8 - 1.4
Sawdust	0.5 - 1.1

Considering the fact that the disposal costs are rising, and that biomass ash volumes are increasing, a controllable ash utilisation has to be established.

For a sustainable biomass 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.

Previous research has shown that the natural cycle of minerals within the process of energy production from 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. By separating a side-stream rich in heavy metals it should be possible to recycle the major part of the ashes produced preferably in the combustion plant.

To make sustainable biomass ash utilisation as practical as possible, ash pre-treatment is necessary in order to offer a usable product to the farmer. The ash must be mixed in a proper way to guarantee the right chemical composition, which makes the installation of a quality

assurance system necessary. Furthermore, the ash must be supplied in a way that makes it possible to distribute it with conventional manure spreaders. The ash-pre-treatment depends on the size of the combustion plant as well as on the kind of biomass fuel used. Also, storage of ash can be important if it is not possible to directly link ash production and ash utilisation.

Besides direct ash utilisation on agricultural or forest soils, indirect utilisation is also possible, by adding biomass ash to agricultural compost. The indirect ash utilisation shows lower dust formation but more manipulation and handling are necessary. For the selection of the right kind of ash utilisation, several factors have to be considered, like the agricultural infrastructure and total costs of a certain ash utilisation process.

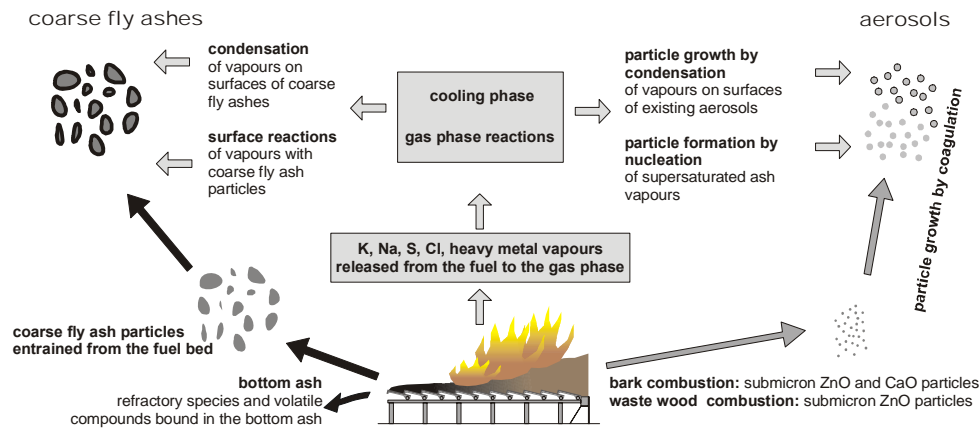
The production of ash granules by hardening the ash with water is a common pre-treatment technology for biomass ashes. It is especially used and being tested in Sweden [2]. Ash granulation has the advantages of dust formation reduction during ash manipulation and spreading. Moreover, the leaching and availability of nutrients from the ash is reduced, which makes the ash more soil-like and decreases possible pH-shock effects on plants.

## **2 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 [3].

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 [4]

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 [4].

### 3 Ash characterisation

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.

#### 3.1 Particle sizes and densities of biomass ashes

Table 2 shows the standard values for the average mass distribution of various ash fractions related to the total amount of ash for fixed-bed combustion plants. The differences are due to

different combustion technologies and different particle sizes of the biomass fuels used. The mass distribution depends also on the geometry of the furnace, combustion air inlet, the process control system, and the dust separation technology applied.

**Table 2:** Percentage of the various ash fractions on the total ash amount.

Explanations: Data source [5, 6, 7]. All furnaces are equipped with cyclones, followed by a second and more efficient dust precipitation unit.

<b>Biomass fuel / ash fraction</b>	<b>Bark</b>	<b>Wood chip</b>	<b>Sawdust</b>
Bottom ash	65 – 85	60 – 90	20 – 30
Cyclone fly ash	10 – 25	10 – 30	50 – 70
Filter fly ash	2 – 10	2 – 10	10 – 20

The average amount of ash produced depends primarily on the fuel and is shown in Table 1. Fluidised bed combustion systems produce higher amounts of ash than fixed-bed units due to the fact that, in addition to the biomass ash, bed material is also discharged from the furnace. The share of bottom ash in the total amount of ash produced in fluidised bed combustion plants is considerably lower than in fixed-bed combustion systems and amounts to 20-30%. The remaining 70-80% of the ash produced is fly ash, which is entrained with the flue gas and separated in the boiler sections and dust precipitators placed behind the boiler sections.

The particle density decreases from the bottom ash to the filter fly ash (Table 3) and can be explained by the decreasing amount of mineral impurities within the ash fraction and the increasing salinity. The bulk density decreases with the fineness of the ash fraction

**Table 3:** Average particle and bulk densities of biomass ashes.

Explanations: Data source [8, 9]. All data refer to dry matter.

<b>Ash fraction</b>	<b>Particle density</b>	<b>Bulk density</b>	
	<b>Average [kg / m<sup>3</sup>]</b>	<b>Mean value [kg / m<sup>3</sup>]</b>	<b>Standard deviation [kg / m<sup>3</sup>]</b>
<b>Bark combustion (moving grate and underfeed stoker)</b>			
Bottom ash	2,600 - 3,000	950	200
Cyclone fly ash	2,400 - 2,700	650	120
Filter fly ash	2,300 - 2,600	350	120
<b>Wood chips combustion (moving grate and underfeed stoker)</b>			
Bottom ash	2,600 - 3,000	950	200
Cyclone fly ash	2,400 - 2,700	500	150
Filter fly ash	2,300 - 2,600	--	--
<b>Sawdust combustion (underfeed stoker)</b>			
Bottom ash	2,600 - 3,000	650	150
Cyclone fly ash	2,400 - 2,700	300	100
Filter fly ash	2,300 - 2,600	--	--

Particle dimension depends on the particle size of the fuel used, the ash content, the chemical composition of the ash, and the amount of mineral impurities within the fuel. The particle size

of the bottom ash is influenced by ash sintering while the particle size of the fly ash depends on the dust separation technology applied as well as on the chemical composition of the biomass fuel (amounts of aerosols formed).

### 3.2 Concentrations of plant nutrients in various biomass ashes

Table 4 shows the mean values of plant nutrients in ashes from bark, wood chips, sawdust. The ashes analysed contain considerable amounts of plant nutrients, which makes an ash utilisation economically interesting. The only missing plant nutrient in biomass ash is nitrogen. During combustion of the fuel, nitrogen turns to vapour and escapes almost completely with the flue gas.

**Table 4:** Average concentrations of plant nutrients in various ash fractions of bark, wood chips, and sawdust combustion plants.

Explanations: Data source [5, 6, 7]. Concentrations in wt.% (d.b.). Type of biomass used: Wood chips and bark from spruce. St.dev.: Standard Deviation.

Nutrient	Bottom ash		Cyclone fly ash		Filter fly ash	
	Mean value	St.dev.	Mean value	St.dev.	Mean value	St.dev.
CaO	41.7	8.7	35.2	11.8	32.2	6.9
MgO	6.0	1.2	4.4	0.9	3.6	0.7
K <sub>2</sub> O	6.4	2.1	6.8	2.3	14.3	7.2
P <sub>2</sub> O <sub>5</sub>	2.6	1.0	2.5	0.9	2.8	0.7
Na <sub>2</sub> O	0.7	0.2	0.6	0.3	0.8	0.6

The Ca concentrations in ashes from bark and wood chips combustion plants are considerably higher than for instance in ashes from straw and cereal combustion plants. For K it is the other way round. The Mg concentrations are similar in the ashes of all biomass fuels investigated. Table 5 shows the chemical composition of ashes from wood residues. The ash composition of wood residues is similar to that of ashes from fresh wood.

**Table 5:** Average concentrations of plant nutrients in various ash fractions of combustion plants using wood residues.

Explanations: Data source [10, 11, 12]. Concentrations in wt.% (d.b.).

Nutrient	Bottom ash	Cyclone fly ash	Filter fly ash
CaO	32.6	32.3	--
MgO	3.0	3.2	--
K <sub>2</sub> O	6.6	7.5	--
P <sub>2</sub> O	0.9	1.3	--
Na <sub>2</sub> O	--	--	--

### 3.3 Concentrations of heavy metals in various biomass ashes

Table 6 shows the average heavy-metal concentrations in various ash fractions of wood bark combustion plants (fixed-bed combustion). The concentrations of highly volatile and ecologically relevant heavy metals (Zn, Cd, Pb) increase from the bottom to the filter fly ash due to the fact that volatile heavy metals turn to vapour phase during combustion and then condense or react, forming new and very fine fly-ash particles (aerosols), or accumulate on

the surface of existing fly-ash particles. The smallest ash fraction – the filter fly ash – considerably exceeds the respective limiting values for utilisation of ashes on agricultural fields or in forests for certain heavy metals. Consequently, this ash fraction has to be disposed of or industrially treated. The remaining ash fractions (the bottom ash and the cyclone fly ash – usually representing more than 90 wt.% of the entire ash) should be mixed in a plant-specific ratio – the so-called usable ash – and utilised on agricultural land or in forests as a secondary raw material with fertilising and liming effects.

**Table 6:** Average concentrations of heavy metals in various ash fractions of bark, wood chips, and sawdust incinerators.

Explanations: Data source [5, 6, 7]. Concentrations in mg/kg (d.b.). Type of biomass used: Wood chips and bark from spruce. St.dev.: Standard deviation.

Element	Bottom ash		Cyclone fly ash		Filter fly ash	
	Average	St.dev.	Average	St.dev.	Average	St.dev.
Cu	164.6	85.6	143.1	46.7	389.2	246.4
Zn	432.5	305.2	1,870.4	598.5	12,980.7	12,195.9
Co	21.0	6.5	19.0	7.3	17.5	5.2
Mo	2.8	0.7	4.2	1.4	13.2	9.8
As	4.1	3.1	6.7	4.3	37.4	41.4
Ni	66.0	13.6	59.6	19.0	63.4	35.4
Cr	325.5	383.0	158.4	61.0	231.3	263.7
Pb	13.6	10.4	57.6	20.5	1,053.3	1,533.0
Cd	1.2	0.7	21.6	8.1	80.7	59.2
V	43.0	10.0	40.5	16.6	23.6	9.1
Hg	0.01	0.03	0.04	0.05	1.47	2.05

### 3.4 Organic contaminants and organic carbon in biomass ashes

The concentrations of organic contaminants (PCDD/F, PAH) in bottom ashes and cyclone fly ashes from biomass combustion plants meeting the current technological standards and using chemically untreated biomass are generally low and ecologically harmless (see Table 7). In filter fly ashes, organic contaminants are enriched considerably. Consequently, this ash fraction should be collected separately and should not be used on soils.

Investigation of ashes from bark and wood shows a correlation between the organic carbon content in the cyclone fly ash and the PAH content. This underlines the importance of a good burnout of fly ashes. The content of  $C_{org}$  within biomass ashes should be below 5 wt.% (d.b.) in order to remain within current guidelines for biomass ash utilisation on agricultural land and in forests in various countries (e.g. Austria and Denmark). Higher  $C_{org}$  concentrations require extra determination of PCDD/F and PAH in the ashes.



**Table 7:** Organic carbon, chlorine and organic contaminants in biomass ashes.

Explanations: Data source [5, 6, 7]. TE – toxicity equivalent; PCDD/F – polychlorodibenzo-p-dioxin and dibenzo-furan; PAH - polycyclic aromatic hydrocarbons according to US-EPA (16 compounds); B[a]P – benzo[a]pyrene (carcinogenic PAH compound and therefore separately listed).

Ash fraction	C <sub>org.</sub> [wt.% d.b.]	Cl <sup>-</sup> [wt.% d.b.]	PCDD/F [ng TE/kg d.b.]	PAH [mg/kg d.b.]	B[a]P [µg/kg d.b.]
<b>Bark combustion</b>					
Bottom ash	0.2 - 0.9	<0.06	0.3 - 11.7	1.4 - 1.8	1.4 - 39.7
Cyclone fly ash	0.4 - 1.1	0.1 - 0.4	2.2 - 12.0	2.0 - 5.9	4.7 - 8.4
Filter fly ash	0.6 - 4.6	0.6 - 6.0	7.7 - 12.7	137.0 - 195.0	900.0 – 4,900.0
<b>Wood chips combustion</b>					
Bottom ash	0.2 - 1.9	<0.01	2.4 - 33.5	1.3 - 1.7	0.0 – 5.4
Cyclone fly ash	0.3 - 3.1	0.1 - 0.5	16.3 – 23.3	27.6 - 61.0	188.0 - 880.0
Filter fly ash	--	--	--	--	--
<b>Sawdust combustion</b>					
Bottom ash	0.2 - 3.4	<0.1	1.3 - 2.1	14.7 - 21.1	21.0 - 40.5
Cyclone fly ash	3.2 - 15.3	0.1 - 0.6	1.5 - 3.7	11.2 - 150.9	180.0 - 670.0
Filter fly ash	--	--	--	--	--

The formation of organic contaminants can be impeded by a high degree of flue gas and ash burnout and by the use of fuels with low Cl content.

Ashes from the combustion of wood residues show a concentration of PCDD/F ranging from 3 to 5 ng TE / kg (d.b.) (Content of chlorides in the ash: 0.01 to 0.6 wt.% (d.b.)) [11].

### 3.5 pH value and electric conductivity of biomass ashes

The pH values of wood ashes normally range from 12 to 13 (see Table 8)

**Table 8:** pH value and electric conductivity of biomass ashes.

Explanations: Data source [5, 6, 7]. El. cond.: Electric conductivity.

	Bottom ash		Cyclone fly ash		Filter fly ash	
	pH value in CaCl <sub>2</sub>	El. cond. [mS/cm]	pH value in CaCl <sub>2</sub>	El. cond. [mS/cm]	pH value in CaCl <sub>2</sub>	El. cond. [mS/cm]
Bark	12.7	8.9	12.7	10.8	12.7	35.6
Wood chips/sawdust	12.8	10.2	12.7	13.1	12.6	39.5

After the ash is spread on the soil, a rapid conversion of hydroxides into carbonates will occur due to the CO<sub>2</sub> content of the air in soils. Following this, the pH value of the ash will decrease to a neutral value and the pH value of the soil will increase. Parallel to this carbonate formation, the electric conductivity will also decrease within days to normal values for soils (below 0.75 mS/cm). So far, no negative effects of biomass ash applications on soils or plants due to pH shocks have been detected.

### 3.6 Si, Al, Fe, Mn, and carbonate concentrations in biomass ashes

Table 9 shows the average concentrations of Si, Al, Fe, Mn, and carbonate (expressed as CO<sub>2</sub>) in mixtures of bottom ash and cyclone fly ash (so-called ‘usable ash’) for different kinds of biomass fuel. The ecological impact of recycling these ashes to soils is presented below for the various ash components.

**Table 9:** Si, Al, Fe, Mn, and carbonate concentrations in biomass ashes (mixture of bottom ash and cyclone fly ash) for various fuel types

Explanations: Data source [1].

<b>Property [wt.% d.b.]</b>	<b>Bark combustion</b>	<b>Wood chips combustion</b>	<b>Sawdust combustion</b>
SiO <sub>2</sub>	26.0	25.0	25.0
Al <sub>2</sub> O <sub>3</sub>	7.1	4.6	2.3
Fe <sub>2</sub> O <sub>3</sub>	3.5	2.3	3.8
MnO	1.5	1.7	2.6
SO <sub>3</sub>	0.6	1.9	2.4
CO <sub>2</sub>	4.0	3.2	7.9

Si is neutral from an ecological point of view, insoluble, and can improve the structure of soils [13].

The content of Al in the upper layer of soils in e.g. Austria ranges from 15,000 to 60,000 mg/kg (d.b.) [14]. Therefore, only ashes from bark show Al concentrations higher than those usually occurring in soils. If the pH values of the soil are above 5, the Al is not soluble and therefore neutral in an ecological sense (bound as oxides or hydroxides). If the pH value is below 3.8 (forest soils), the release of Al<sup>3+</sup> ions will increase and plant damage will occur. Therefore, the Al content of biomass ashes is not a threat to soils with pH values above 3.8. The alkaline effects of biomass ashes will further increase the pH value of the soil and impede the release of Al.

Fe and Mn are essential nutrients for plants. Due to the low concentration of S in biomass ashes, S can also be evaluated as a nutrient [13].

The concentrations of Fe and Al in the bottom ash and cyclone fly ash are in the same range. S is highly volatile and therefore concentrates in the cyclone fly ash. Si and Mn are concentrated in the bottom ash.

The elements in the bottom ash and cyclone fly ash are mainly available as oxides, but hydroxides, carbonates, and sulphates also occur. The amount of carbonates (calculated as CO<sub>2</sub>) in the various ash fractions strongly depends on the time the ash was exposed to a moist and CO<sub>2</sub>-rich atmosphere (flue gas channel, ambient air) as well as on the furnace temperature. This means that if furnace temperatures are high and residences times of the fly ash in the flue gas channels are low (full load operation of the combustion plant), the carbon content of the ashes will be lower. The second influencing factor for the formation of carbonates is the concentration of Ca and Mg in the ash. This is why the carbonate content is low in straw combustion plants, in spite of relatively low furnace temperatures (Si forms oxides; K forms oxides, chlorides, or sulphates).

## 4 General aspects for ash utilisation

Ashes from combustion of solid biofuels contain considerable amounts of plant nutrients, which make an ash utilisation on soils interesting (see Section 3.2). 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 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.

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 [15]. Wood and bark ashes are Ca rich, whereas straw and cereal ashes contain high amounts of K.

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 fertiliser 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. 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.

## **5 Biomass ash utilisation in Austria**

### **5.1 Current situation**

Austria is the first European country that introduced clear legislation for the utilisation of biomass ashes. These regulations are briefly outlined below.

Wood ash is defined as ash from the thermal utilisation of chemically untreated woody biomass like wood chips, bark, and sawdust. The wider terminus biomass ash also includes ashes from the thermal utilisation of straw, cereals, hay, and other agricultural residues.

Bottom ash, cyclone fly ash, and filter fly ash from biomass combustion plants are legally considered industrial waste and not hazardous waste. The utilisation of waste materials makes them a secondary raw material, provided the process is ecologically friendly and meaningful. Moreover, ashes from biomass combustion are not regarded as fertilisers as their chemical composition varies too much. The utilisation of biomass ashes as a secondary raw material must be regulated.

### **5.2 Austrian Guidelines**

On the basis of comprehensive research results, the Austrian Ministry for Agriculture and Forestry has worked out two guidelines [16, 17] for the proper utilisation of biomass ashes on agricultural fields and in forests.

These guidelines regulate

- which kind of biomass ash can be used as a fertilising and liming agent for agricultural and forest soils (the guidelines cover the kind of ash fractions as well as the concentration of heavy metals in the ash);
- how and when ash spreading is possible (spreader technology, climatic and weather conditions);
- the maximum amounts of ash to be applied; and
- the demands on the composition of the soil (kind of soil, chemical analysis).

The use of filter fly ash on soils is forbidden. This ash fraction must be treated as industrial waste

### **5.3 Recommended procedure and quantitative limits for biomass ash recycling in Austria**

The following recommendations are based on comprehensive ash analysis, field tests, and material balances concerning the “Ash-Soil/Ground Water – Plant” system for agricultural land, green land, and forests in Austria. These recommendations are also incorporated in the Austrian guidelines for the use of biomass ashes on soils.

From the ash fractions produced in biomass combustion plants (bottom ash, cyclone fly ash, and filter fly ash), a mixture of bottom ash and cyclone fly ash in the plant-specific ratio

(usable ash) is usually applied as a secondary raw material with fertilising and liming effects on soils.

To avoid ecological incompatibilities and damage, the following procedure should be regarded:

- Only ashes from the combustion of chemically untreated biomass fuels are allowed to be utilised.
- The filter fly ash and the cyclone fly ash should be collected separately. The filter fly ash has to be disposed of or industrially utilised (after an appropriate treatment).
- The usable ash of a biomass combustion plant has to be analysed for its content of nutrients and its content of ecologically relevant heavy metals before it is used on soils. Ash analysis should be repeated at regular intervals.
- The following quantitative limits are recommended for the utilisation of usable ash from bark, wood chips, and sawdust combustion on soils [16, 17]: 1.000 kg per ha and year on agricultural land, 750 kg per ha and year on greenland, 3.000 kg per ha ones in 50 years in forests.
- The amounts of usable ash from straw and cereal combustion should be determined according to the nutrient demand of the plants and the soil. Due to the low heavy-metal concentrations of these ashes, there should be no environmental limitations on their utilisation on soils as long as the filter fly-ash fraction is separated.

The Austrian limits for utilisation of biomass ashes on agricultural land and in forests as well as the guiding values for soils are shown in Table 10.

The limits on the amounts of ash used for agricultural land and green land are based on the heavy-metal content of the ash. As long as the heavy-metal content of the ash used is lower than the limiting value in the guideline, the amount of ash can be increased [17].

The limit for the amount of ash to be used in forests is based on the content of Cd in the ash. This limit guarantees that the input of Cd into the forest due to ash recycling does not exceed the output of Cd from forest due to wood harvesting [16].

Ashes from the combustion of bark or wood should be used in forests or in short rotation stands, while ashes from the combustion of straw or cereals should be used on agricultural land.

Due to the high content of Ca and Mg in wood and bark ash, the effects of using wood ash as a fertiliser are similar to fertilising the forest with lime (similar ratio  $\text{CaO}/\text{CaCO}_3$ , high pH value of wood ash). The larger particle size of wood ash lowers its aggressiveness in comparison to lime. Therefore, wood ash is recommended for forest soils where an increase of the pH value is desirable.

**Table 10:** Limiting values for concentrations of heavy metals in biomass ashes used on agricultural land and in forests according to existing Austrian regulations.

Explanations: Data source: Limiting values [16, 17]. Concentrations in mg/kg d.b. \* - According to quality class I.

Element	Limiting values forest	Limiting values agriculture*
Cu	250	250
Zn	1,500	1,000
Ni	100	100
Cr	250	250
Pb	100	250
Cd	8	5

In general, the amount of ash used for fertilising depends on the specific cultivation, the soil as well as on the additional fertilisers used, and should be calculated annually by nutrient balance.

Concerning the availability of K, biomass ashes are similar to industrial fertilisers. Therefore, biomass ashes are suitable for plants which are sensitive to Cl (trees, bushes, several kinds of vegetables) and which can stand an increase of the soil pH. Furthermore, biomass ash can be used for annual energy crops substituting fertilisers with high Cl content in order to decrease the Cl uptake of the plants [18].

As for P, wood and bark ashes can only keep the P level in soils stable. The concentration as well as the availability of P is higher in straw and cereal ashes. If soils lack P, industrial fertilisers should be used.

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## **6 Biomass ash utilisation in Sweden**

### **6.1 Current situation**

Bioenergy is a significant energy source in Sweden. Fuels from forests dominate. Forest fuels are, for instance, black liquor (a residue in pulp production), other by-products from the pulp industry, sawmill by-products, fire wood and logging residues from harvesting [20].

With the ambition to create a sustainable energy system, the use of renewable energy in Sweden is expected to grow further and biofuels are expected to account for a large part of this increase.

The growing use of biofuels over the past decades has led to an increased production of wood ash.

Approximately 40 % of the ashes originate from combustion of bark, wood chips and sawdust in boilers located at sawmills, wood-working factories and pulp and paper industries. Another 35 % are produced in district heating plants. The remaining part comes from wood firing in the domestic sector, basically property owners in agricultural or rural areas.

Ash from the industrial or the district-heating sector is normally available for large-scale recycling. Wood ash from the domestic sector is produced in small units from numerous households, and is not readily accessible.

### **6.2 Ash treatment, transportation and spreading – Swedish approach**

The handling of dry, untreated ash is not recommended. Apart from the salt and pH effects it may generate in the forest, the dust problems during handling and spreading are severe and the ashes are highly corrosive [21].

Thus, stabilisation of wood ash is needed before it is recycled. The treatment must facilitate handling, transportation and spreading. It must also ensure that the recycled material has the desired leaching properties. With a slow release of the ash contents drastic changes in pH and salt content in the soil are avoided. In some cases, the ash must be reburnt in order to reduce the content of unburned carbon. It also seems possible to reduce the level of heavy metals in the ash.

The ash is stabilised by adding water and by a slow reaction with carbon dioxide in the air. Its chemical composition is then changed to a much less soluble form. After mixing with water, the ashes are agglomerated. Three techniques have primarily been studied to agglomerate ash after mixing it with water: self hardening, granulating and pelletising.

Self-hardening involves conditioning the ash and subsequent compaction in a pile. This simple method has been successfully applied to different ashes, all with a content of unburned carbon below 10 %. Normally, the ash has to be stored for a number of weeks or months to reach its proper compressive strength. Ashes from co-combustion of peat and wood have less good self-hardening properties than pure wood ash and are less suited for this method. Drawbacks of the method include the large storage capacity needed, and sometimes an excessively high fraction of fine particles in the ash product. Good control of leaching properties can not always be achieved. The main advantage is the simplicity and the low costs.

Moistened ashes can also be granulated in a rotating drum. The process can be fully automated but requires that the content of unburnt carbon is not more than 10 %. The main advantage of granulating is that better control is achieved of the final product quality (a low fraction of fine particles and low solubility). The drawback is the higher cost compared with self-hardening.

Pelletising by forcing moist ash through a matrix has also been tried. The method is less sensitive to the content of unburnt carbon in the ash, but energy consumption is high and the equipment suffers from serious erosion and plugging of the matrix.

In Sweden, wood ash is mainly produced during the cold period of the year. The ash often has to be stored for some time at the plant, either in hardened form or as dry ash, before spreading during the summer months. Some protection against snow and rain is advisable.

The hardened ashes can be transported to the forest by bulk lorries. Other systems such as containers and big bags have also been tried. Spreading methods suitable for agglomerated ash comprise helicopter, forest tractor, special vehicles or even horses for small-scale applications.

The energy required to treat, transport and spread the ash corresponds to approximately 0.3 % of the energy in the fuel from which it is derived [22].

The responsibility for ash recycling has not been established. One possibility is that the ash-producer is responsible for treatment and quality declaration of the ash, while the owner of the forest or the fuel supplier is responsible that the ash is spread in an appropriate way, on appropriate sites and at the right time.

### **6.3 Environmental aspects**

Ideally, recycling of wood-ash to forest should be performed in a way that produces all the desired benefits but minimises negative impacts on fauna, ground vegetation and surface waters. Non-hardened loose ashes are known to dissolve relatively quickly and affect both the soil condition as well as certain organisms, while hardened and/or granulated ash is generally less soluble and gives a slower response. In principle, non-hardened ashes or large doses should be avoided, especially on clear-cuts or sites with sensitive vegetation. However, virtually no negative ecological effects have been noted at sites where well-stabilised ashes have been applied in moderate doses (3 tonnes per hectare).

Wood-ashes can be applied both to well-drained forest soils and to forested peat lands. In well-drained mineral soils, nitrogen is generally the limiting nutrient for tree growth, and nitrogen-free fertilisers will have no effect on forest production. On such soils, ash recycling is not a suitable method to increase forest growth but rather a way to conserve the soil fertility. The overall aim is to maintain the nutrient status in a long-term perspective, and in some cases, notably for strongly acidified soils in southern Sweden, to improve the soil conditions. On forested, drained peat lands the situation is somewhat different. These forests are often deficient in phosphorus and potassium, and thus supply of wood-ash will normally stimulate growth considerably. In fact, forestry on peat lands is often not sustainable without a nutrient supply, even if forest residues are not harvested.

Field experiments have shown that concentrations of many nutrients, especially of potassium, magnesium, and phosphorus, normally increase in soils amended with wood-ash. Hardened,



slowly-soluble ash types give rise to moderately increased pH levels, while soil pH may rise several units if high doses (>5 tonnes/ha) of unhardened ashes are added.

One drawback is that elevated pH levels may stimulate microbial activity in soil and may also enhance nitrate formation. Nitrate, which is formed by microbial oxidation of ammonium, is highly mobile in soil and may, if leached, cause eutrophication of surface waters. Thus, when adding ash in areas with high nitrogen deposition it is important to use a moderate dose of a well-hardened and slowly dissolvable product. Furthermore, before further investigations are made, it is not recommended to supply ashes to fresh clear-cuts, since inorganic nitrogen is often abundant and pH is elevated soon after clear-cutting. This provides ideal conditions for nitrate formation. However, stabilised ashes added to mature forests or to clear-cuts a few years after felling do not seem to increase nitrate concentrations in soil water.

Some experimental results indicate that by harvesting forest residues after clear-felling, nitrogen availability and nitrate leaching might be reduced as compared with conventional logging. Thus, the net effect of harvesting of bio-fuel combined with recycling of well-hardened wood-ashes might well be a reduced risk for nitrogen leaching from forest areas [23].

Spreading non-hardened wood-ashes, or hardened ashes with a high content of fine particles, implies some risk that the vegetation might be affected. Sensitive plants, especially mosses and lichens, can be damaged in the short term by high pH and high salt concentrations. Elevated levels of inorganic nitrogen may cause vegetation changes. Hardened and crushed wood-ashes give less clear effects, but a high fraction of fine particles has been observed to affect certain mosses temporarily. Granulated ashes in appropriate doses have not been shown to affect the vegetation significantly [24].

According to recommendations from The Swedish Environmental Protection Agency and the Forestry Board, wood-ashes should be returned to forest sites in quantities approximately corresponding to the content in harvested biomass [25]. Thereby an accumulation of heavy metals in soil is avoided, unless the ash has been contaminated. It is important to use "clean" wood fuel if the ash is to be returned to the forest.

There is some concern that the heavy metals present in ashes might affect the ecosystem and especially berries and mushrooms. Heavy metals are released slowly from well-hardened and granulated ashes, more or less at rates observed with decomposing needle biomass. Most heavy metals have low solubility at normal forest soil pH, and this prevents excessive uptake by plants and mushrooms. However, cadmium is more soluble than most other heavy metals and, therefore, great attention has been paid to the cadmium effects.

Tendencies for heavy metal contents in mushrooms and berries to increase have been observed a few (2-10) years after ash application (1-10 tonnes per hectare), but generally the effects were not significant, and smaller than the natural variation between species and sites. No, or very moderate elevated levels of heavy metals have been observed in mushrooms and berries as a result of supplying granulated ashes. Even loose unhardened ashes resulted in insignificant effects, with one exception where the cadmium content was significantly elevated in a *Cortinarius* species.

Wood-ash recycling can be considered a prerequisite for sustainable use of forest fuel. Pure biofuel ashes can be recycled without disturbing environmental effects, provided that they are well hardened and spread in doses that correspond to the amount of harvested felling residues.

The fraction of fine particles in the ash should be rather low. The ashes can be spread in forest stands, as well as in plantations that are a few years old.

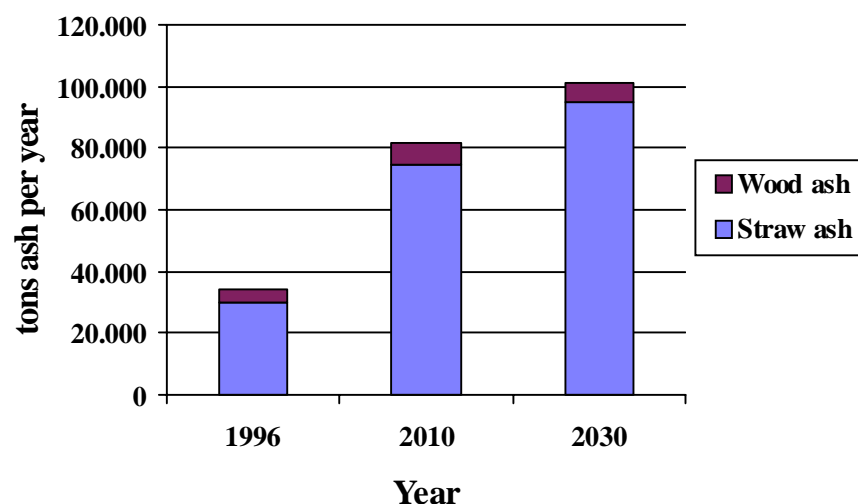
## 7 Biomass ash utilisation in Denmark

### 7.1 Current situation / Danish energy policy

The Danish energy action plan Energy 21 has outlined a significant increase in biomass consumption for energy production. Consequently, energy producers using biomass as fuel will end up with large quantities of biomass ash. By 2030, when *Energy 21* is fully implemented a yearly production of 100,000 tons of biomass ash is expected. Biomass ash contains both valuable nutrients as well as environmentally harmful heavy metals and organic compounds e.g. polycyclic aromatic hydrocarbons (PAH). If the biomass ash is not recirculated to arable soil the nutrient have to be applied as artificial fertiliser while the ash has to be placed at refuse dumps. This solution is both economically and ecologically undesirable. Recirculation of biomass ash to agricultural fields, taking the environmental risks into consideration, will be the only viable solution.

Straw and wood typically contain 3-5% and 0.5-2% ash respectively. The growing exploitation of biomass for energy production, according to Energy 21, will obviously lead to a very significant increase in biomass ash production. Ash from private boilers is normally recirculated on agricultural fields or private gardens whereas recirculation of ash from straw- and wood fired district heating plants requires permission from the local county. Especially these fractions will increase significantly (see Figure 2).

If this growing amount of biomass ash (or part of it) cannot be recirculated, the economical and ecological impact will be significant.



**Figure 2:** Expected production of ash from straw- and wood-fired district heating and CHP plants

Explanations: Data source [21]

## 7.2 Danish legislation regarding biomass ash

Agricultural application of ash requires permission from the County. Applications to the county are considered, thereby having regard to the Department of Environment and Energy Executive Order No. 823 of September 16, 1996 on residual products for agricultural application. This order stipulates that the content of heavy metals in the ash should not exceed the limit values (Table 11) stated in the Executive Order.

The Danish Environmental Protection Agency may, however, grant an exemption. It is optional whether the content of heavy metals in the ash is calculated on basis of the dry matter content of the ash or its phosphorus content.

**Table 11:** Limit values for heavy metals in ash for agricultural applications

	Limit values in force 01.10.1996 - 30.06.2000		Limit values in force 01.07.2000	
	mg per kg dry matter	mg per kg total phosphorus	mg per kg dry matter	mg per kg dry matter
Heavy metals				
Cadmium	0.8	200	0.4	100
Mercury	0.8	200	0.8	200
Lead	120	10,000	120	10,000
Nickel	30	2,500	30	2,500
Chromium	100		100	
Zinc	4,000		4,000	
Copper	1,000		1,000	

This Executive Order No. 823 of September 16, 1996 was originally meant for regulation of recycling of sewage sludge, compost a.o. and is therefore not well suited for regulation of recycling biomass ash. Besides heavy metals the Executive Order includes limit values for other products with potential injurious effects on the environment, including polycyclic aromatic hydrocarbons (PAH) and other organic compounds (Table 11).

If the biomass ash cannot meet the requirements of the Executive Order the ash must not be applied as fertiliser. The alternative is often to deposit the material at a refuse dump.

As seen in Table 12 the concentration of Cadmium and to some extend Lead will exceed the limit values stated in the Executive Order. So far exemptions normally have been granted. However, with the increasing amount of biomass ash this solution will not be viable.

An obvious solution is to fractionate, if possible, the biomass ash into 1) a less contaminated ash fraction that could be used on agricultural fields without environmental risks and 2) a smaller, heavier contaminated fraction that can be placed at a refuse dump.

**Table 12:** Concentration of nutrients and heavy metals in ashes from 9 wood-fired and 26 straw-fired district heating plants

Explanations: data source [21]

	Wood Ash			Straw Ash		
	Median	Variation 25%-75% fractile	Number of observations	Median	Variation 25%-75% fractile	Number of observations
Nutrients % in dry matter						
Total Nitrogen	0,1	<0,1-0,3	11	0,09	0,05-0,14	21
Total Phosphorus	1	0,8-1,6	14	1	0,67-1,4	36
Total Potassium	5	2,8-7	6	11	6,7-20	10
Heavy metals, mg per kg dry matter						
Cadmium	4	0,8-9,7	20	2	<1-3,8	41
Mercury	<0,07	<0,05-0,4	18	0,1	<0,1-0,3	36
Lead	40	8-75	18	9	<8-22	36
Nickel	20	18-32	18	5	<5-12	36
Chromium	20	10-74	10	2	1-5	5
Zinc	240	91-880	9	140	96-460	6
Copper	80	49-185	10	30	23-125	9

Biomass not only contains harmful heavy metals but also significant amounts of valuable plant nutrients (see Table 12). If the biomass ash is not recirculated, the agricultural fields and the forestry will lack the nutrients embedded. Artificial nutrients must then be applied. Although the nutrient concentrations are by far lower than in artificial fertiliser the biomass ash produced in 2030 will contain approximately 100 tons of nitrogen, 1000 tons of phosphorus, and 10.000 tons of potassium.

Heavy metals are introduced to agricultural soil in many ways. One of the important is artificial fertiliser. A general reduction in artificial fertiliser application will therefore lead to a lower load of heavy metals. If straw is not used for livestock production or for energy purposes it is typically recycled directly to the soil after harvest. As straw contains the same amount (or more) of heavy metals as is later found in the ash, the load of heavy metals to the soil will not change significantly whether straw is recycled directly to the soil or recycled as ash.

Therefore, a new Executive Order on biomass ash for agricultural application is under consideration. This new Order may be based on a “recycling principle”. This means that it, under definite conditions, will be possible to recycle ash containing the same amount of heavy metals, as was removed when harvesting the straw. The legal impediments for an increased energy use of biomass may thereby be removed, and pave the way for significant achievements.

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