



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 727616.



Bioefficiency

Ash utilisation - Draft for technical regulations (D6.3)

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Version:	Final
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Date:	10.10.2019
Partners involved:	LAB

Grant Agreement No.	727616
Starting Date:	01.11.2016
Duration:	36 months

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Abbreviations and Acronyms

BAT	Best Available Technique / Technology
BFBC	Bubbling Fluidised Bed Combustion
CE	Conformité Européenne
CEN	Comité Européen de Normalisation
CFBC	Circulating Fluidised Bed Combustion
DIN	Deutsche Industrie Norm
EFB	Empty Fruit Bunch
EN	European Norm
FGD	Flue Gas Desulfurisation
LOI	Loss On Ignition
PAH	Poly Aromatic Hydrocarbons
PFC	Pulverised Fuel Combustion
PSD	Particle Size Distribution
REA	RauchgasEntschwefelungsAnlagen
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
TE	Total Equivalent
UBC	UnBurned Carbon
VGB	hist. <i>Vereinigung der Großkesselbesitzer e.V.</i>

1. Introduction

This project started with the goal of writing a draft EU regulation regarding the utilization of biomass ashes (with additives). Next, the EU suggested to go for a CEN standard, by Mr. Kiriakos Maniatis. For writing a standard, the participation of almost all stakeholders is required. One of the stakeholders should be the VGB, which rejected the idea of writing a standard. Besides, writing a standard takes much longer than this EU Bioefficiency project. The VGB suggested to write guidelines, by Mr. Joachim Feuerborn.

So, this deliverable is about guidelines for utilization of biomass ashes (with additives). Some suggestions for improving existing EU legislation are added. This deliverable is also about a draft EU regulation, as initially agreed upon with the EU.

Biomass ashes (with additives) can be applied in top soil. This application is favoured by EU policies regarding the circular economy. However, there is also an EU policy regarding protection of top soils. Biomass ashes (with additives) contain “heavy metals”, which can also be “micro-nutrients”. This means that for application of biomass ashes in top soils, especially agricultural land and/or forests, the EU policies can be or are contradictory. In general, biomass ashes will most likely not meet the limits of the new EU Fertiliser Regulation 2019.

In several EU countries, legislation exists regarding application of biomass ashes in top soils, in general supporting/allowing this application. However, the quality of the biomass ashes for application in top soils is regulated in these countries. According to the NEW EU Fertiliser Regulation 2019, the countries may apply less strict limits for applications of biomass ashes in top soils, but may not export the biomass ashes to other countries as CE marked product for applications in top soils (16).

2. A proposal for EU legislation on the utilisation of biomass ashes

The EU legislation on the valorisation of biomass ash is far from optimal and even absent (1). Similar holds for many, if not all, EU countries. However, improvement is in progress (2).

This proposal regarding valorisation of biomass ash (with additives), consists of 2 parts:

1. For an EU Directive regarding biomass ash
2. Best Available Techniques.

Obviously, the proposal for an EU Directive should meet existing EU legislation, as far as possible and as far as meaningful.

In this chapter, our proposals are in Italic. Especially tables 2.1 and 2.2 are important, which contain our maximum limits for application of biomass ash in top soils.

Within EU countries, there seem to be 2 different types of legislation regarding top soils:

- Non-strict limits, allowing for the use in agriculture and forestry of residues like manure, biomass ash, liquid and solid residue from digestion, biochar, compost, etcetera
- Strict limits, for protection of the soil, not allowing for heavy metals, organic toxins and pathogens.

The strict limits severely limit the use of residues like manure, biomass ash, liquid and solid residue from digestion, biochar, compost, etcetera, in top soils. For instance, the Cd content of unpolluted top soils range from 0.1 to 1.0 mg/kg (3). Should this result in a Cd limit of biomass ash of 1 mg/kg of Cd?

Micro-nutrients are firmly established in EU legislation regarding fertilisers (4). The elements B, Co, Cu, Fe, Mn, Mo and Zn are listed as micro-nutrients (4).

2.1. EU Directives on biomass ash

2.1.1. Fertiliser Regulation 2019

According to Laborelec, interesting and relevant aspects of this Regulation are (16):

- (Biomass) ashes are not considered yet, but will be added to Annex II without delay.
- Countries are allowed to have their national legislation, with less strict limits. However, fertiliser / liming agent / soil improver which do not meet the EU limits may not be exported to other countries as CE marked product for application in top soils. This is very exceptional for EU legislation.
- Differentiation between application in agriculture and in forestry is not made.
- Most likely (biomass) ashes will not meet the EU limits.
- (Biomass) ashes suitable for application in top soil lose their status as waste.

2.1.2. Waste legislation

In agreement with the EU waste legislation (5), biomass ash should be re-used or recycled. The biomass ash should certainly not be land filled. This re-use or recycling also holds for biomass ash with residues from additives used in the combustion process or in the process of flue gas treatment.

2.1.3. UnBurned Carbon (UBC)

Biomass ash with more than 30 wt.% UBC must be re-used as a fuel.

However, its use as biochar in top-soil can be considered, assuming it meets the requirements of the standard (6, 7), at least according to this standard. Usually, the UBC content of the biomass ash will be low, compared to biochar from pyrolysis. The biochar should meet the limits indicated in table 2.1 regarding “soil improver”, with the exception of the UBC content, as the limits according to the “International Biochar Initiative” does not hold specifically for the EU. However, there is a proposal of an EU standard regarding biochar (7), which has limits which are often more stringent than those indicated in table 2.1. Alternatively, the biochar should meet the limits indicated in tables 2.1 and 2.2 regarding “soil improver”, corrected for the UBC content. For example, when the UBC content is 50 wt.%, the limits are reduced by a factor 2.

The use of biomass ash with high UBC content as biochar in other applications than in top soil can be considered (8, 9).

2.1.4. Phosphor

Some types of biomass should be combusted applying mono combustion. This holds especially for biomass:

- With a high P content of more than 2 wt.% = 4.6 wt.% P₂O₅, on dry base.
- Producing biomass ash with a high P content of more than 4.3 wt.% = 10 wt.% P₂O₅, on dry base and UBC free.

For example, dry municipal sewage sludge contains about between 0.2 to 5.5 wt.% P and about 40 wt.% ash, on dry base (10). This results in ash with about between 1 and 32 wt.% P₂O₅. Next, at least the P should be recovered from the ash. Alternatively, this biomass ash with high P content can be applied as a fertiliser, when it meets the requirements and the P is available for plants. Alternatively, this ash is applied in products which require this type of ash, like bone china. Some examples of biomass with a high P content are:

- Meat- and bone meal
- Municipal sewage sludge
- Solid residue from anaerobic digestion (= digestate)
- Chicken manure.

2.1.5. Mixing and blending

It is allowed to mix the different types of biomass ash from one unit firing biomass, like bottom ash and fly ash.

It is allowed to mix biomass ash, combined with storage, for obtaining a large quantity of known composition. This allows for making marketing of biomass ash easier.

It is allowed to mix biomass ash with other compounds (organic fertilisers and/or synthetic fertilisers) for manufacturing mixed fertilisers. However, each compound must meet its specification and its upper limits regarding toxic elements/compounds.

It is allowed to mix biomass ash with compost.

It is not allowed to mix biomass fly ash and the residue from flue gas purification from one unit, when a dedicated biomass fly ash filter is available.

Mixing the biomass ash (with additives) with other materials is not allowed, for meeting the limits presented in tables 2.1 and 2.2, as this is considered as dilution.

2.1.6. Recycling, fertilisers, etcetera, and toxins

For application of biomass ash (with additives) in agriculture, forestry, etcetera, we propose to follow the EU legislation which is already developing. Tables 2.1 and 2.2 present proposals for some limits. This table 2.1 is based on (2, 11, 12, 16). We do not suggest limits regarding pH-value and salt content. *When the biomass ash (with additives) meets the limits of table 2.1 or 2.2 it loses its status as waste and is considered as the product fertiliser, when applied as or in fertiliser.*

Two subgroups of biomass ash may be considered:

- For application in forestry
- For application in agriculture

With non-identical upper limits for each group. With agriculture, the biomass ash may be applied each year, as with forestry the biomass ash may be applied about each 10, 15, 20 or 25 years.

Table 2.2 presents practical limits, allowing for the application of biomass ash in top soil.

Regarding the micro-nutrients, reference (13) provides easy access to information, and discrimination between toxins and nutrients.

Table 2.1: A proposal for upper limits for application of biomass ash (with additives) on and in top soils, following EU proposals for maximum concentrations of heavy metals in inorganic macro-nutrient fertilisers, liming material and inorganic soil improver, especially reference (16). dm = dry matter

Element / compound	Unit	Application			
		Fertiliser, <5wt.% P ₂ O ₅ dm	Fertiliser, >5wt.% P ₂ O ₅ dm	Liming material	Soil improver
B	mg/kg dm	500	500	500	500
Cd	mg/kg dm	3	60	2	1.5
Cr(VI)	mg/kg dm	2	2	2	2
Cr	mg/kg dm	100	100	100	100
Hg	mg/kg dm	1	1	1	2
Ni	mg/kg dm	100	100	90	50
Pb	mg/kg dm	120	120	120	120
As	mg/kg dm	40	40	40	40
Zn	mg/kg dm	1500	1500	800	800
Cu	mg/kg dm	600	600	300	300
UBC	g/kg dm	50	50	50	50
Cl	g/kg dm	30	30	30	30
Dioxins and furans	ng TE/kg	100	100	100	100
PAH	mg/kg	100	100	100	100

The maximum Cl content is far from established and open for discussion. Copper and zinc are essential trace elements, at least for humans and plants. Cr(VI) is water-leachable Cr(VI)? The Cd limit of 60 will be reduced with time, for instance to 20.

The results of analyses as presented in Deliverable 6.2 show that in practise biomass ash cannot meet these EU limits as presented in table 2.1. For allowing biomass ashes to be used in top soil, these limits must be modified.

The results of analyses as presented in Deliverable 6.2 show, that ash from fresh wood chips contain much more Zn than 800 and 1500 mg/kg. As Zn is an essential trace element for humans, plants and animals, one can consider to modify these limits in table 2.1 to practical values, which allow for application of biomass ash in top soil: table 2.2. However, the EU limits of Cd and Cr(VI) are also strict, regarding the application of biomass ashes in top soils. Table 2.2 is mainly based on Swedish limits (14).

Fly ash from EFB and straw will contain more Cl than 3 wt.%. For instance a limit value of Cl of 20 wt.% could be selected. An UBC content of 100 g/kg dm could be acceptable as well. However, in this project we did not encounter ashes with more than 50 g/kg dm UBC.

Regarding Cr(VI) this should be water leachable Cr or Cr(VI). For obtaining a limit value of 2 mg/kg special measures are required. This value of 2 possibly originates from REACH for cement.

With table 2.2, some possible adaptations are suggested in red, based on the remarks above.

Table 2.2: A proposal for upper limits for application of biomass ash (with additives) on and in top soils. For comparison the EU limits are presented as well. dm = dry matter

Element / compound	Unit	Biomass ash (with additives)	EU Fertiliser (16)
B	mg/kg dm	1000	-
Cd	mg/kg dm	30	3
Cr(VI)*	mg/kg dm	2	2
Cr	mg/kg dm	2	-
Hg	mg/kg dm	3	1
Ni	mg/kg dm	100	100
Pb	mg/kg dm	300	120
As	mg/kg dm	50	40
Zn	mg/kg dm	10 000	1500
Cu	mg/kg dm	1000	600
V	mg/kg dm	70	-
UBC	g/kg dm	50 or 100	-
Cl	g/kg dm	200	-
Dioxins and furans	ng TE/kg	100	-
PAH	mg/kg	100	-

*Water-leachable Cr(VI)

For table 2.2 it is proposed to have a limit for Zn of 10 000 g/kg dm and to have a limit for Cl of 200 g/kg dm. Obviously, the limits of table 2.2 do not meet the limits of the EU for inorganic macro fertiliser (16).

We propose some changes to the EU waste codes list like:

- 10 01 03: fly ash from peat, untreated wood and other untreated biomass fuels, with and without combustion additives.
- 10 01: calcium based reaction wastes from flue gas cleaning, from peat, untreated wood and other untreated biomass fuels, with and without combustion additives.

2.2. Best Available Techniques (BAT)

2.2.1. Recycling & Co.

At present (2016) we consider as BAT:

- *Recycling of biomass ash back to the top soil, when it meets the criteria presented in (table 2.1 or) table 2.2.*
- *Application of biomass ash in or as fertiliser for forests and agriculture.*
- *Mono-combustion of biomass fuels with a high P content and biomass fuels producing ashes with a high P content. This allows for recovery of P from the biomass ashes*
- *Chicken manure is best converted to a suitable fertiliser, and not used as fuel.*

Accumulation of Cd in top soil can be prevented by good soil management, at least in Europe (3). Cd is a natural constituent of soil parent material. The addition to and removal of Cd from top soil must be balanced, at least. It seems even possible to reduce the Cd content of top soil with time, as Cd is removed with the harvest and with seepage water (3). It is suggested that with the application of mineral P fertilisers in agriculture, the Cd concentrations must be below 50 mg/(kg P).

2.2.2. Other BAT

Safety aspects with handling and transport of biomass ash (with additives) requires much attention. This holds especially for the presence of dust, CaO, UBC and the high pH-value. With storage, attention is required for hardening.

The UBC content of the biomass ash can be reduced by improving the existing combustion process and/or by re-burning. The UBC content should be less than 10 or 5 wt.%, except when UBC is favourable for a certain application. Ash with a high UBC content is combustible. Especially fine fly ash with a high UBC content is a hazardous substance, as dust explosions and fires may occur (15).

The content of lime can be reduced by hydration and/or carbonation of the ash. Granulation / agglomeration improves the handling of fine ash as well.

Leaching of biomass ash with an aqueous solution, acid or base is possible. With this leaching valuable elements can be recovered, such as P and K. Heavy metals can be removed from the aqueous solution by ion exchange, membrane separation and/or (co-)precipitation.

Biomass ash is suitable for traditional ceramics and traditional glass, when it meets certain criteria. When needed it can be leached prior to valorisation. Carbonation can be considered as well, for reducing the solubility of calcium. Examples of traditional ceramics are: fired bricks, fired roof tiles, fired tiles and expanded clay pellets.

Biomass ash (with additives) can be used in geo-polymers. When needed it can be leached prior to valorisation.

Biomass ash can be used in silica-lime blocks. When needed it can be leached prior to valorisation.

Especially bottom ash (with additives) can be purified by applying techniques such as: magnetic separation, eddy current separation, screening, air classification, etcetera. Techniques such as grinding and agglomeration can be applied as well with biomass fly ash (with additives).

3. Towards a standard / guideline for BAT regarding utilisation of biomass ashes

3.1 Coal fly ash and gypsum

For residues of pulverised coal firing 2 “standards” apply regarding valorisation. The first standard is EN-450, for using fly ash from pulverised bituminous coal firing as partial replacement of cement in concrete. In this standard limited co-combustion is included. The second “standard” is about FGD gypsum: VGB-TW 710, 2005, Vom Rauchgasentschwefelungsrückstand zum Qualitätsrohstoff REA-Gips, and VGB-TW 707 e, 1990, Comparison of natural gypsum and FGD gypsum. Finally, both materials are used as or in construction materials.

CFBC coal fly ashes can meet the criteria of EN-450, but are not mentioned in this standard. CFBC fly ashes are not spherical, which is related to the lower combustion temperature, compared to fly ashes from pulverised coal-firing.

3.2 Construction materials

Within the EU there is legislation regarding the quality of final products (construction materials) for different and many applications. This legislation also holds for final products made with biomass ashes. So, this type of legislation is not required anymore. In general, construction materials should not leach, should not emit vapours and should not radiate. As indicated in this EU Bioefficiency project, especially the leaching is of interest for final products made with biomass ashes.

As with FGD gypsum, the purchaser(s) (and supplier(s)) of biomass ashes for construction materials (or other applications) will make a specification, and for marketing the biomass ashes must meet this specification. The specification may depend on the construction material: fired ceramics, geo-polymers, calcium silicate blocks, etcetera. For meeting the specifications, water-leaching of the biomass ashes may be required.

Regarding application of biomass ashes in construction materials, following aspects are of interest:

- Chemical composition, especially the free lime content and the content of unburned carbon
- Pre-treatment of the biomass ashes, like reaction with water, carbonation and granulation. This pre-treatment may improve handling.
- Pre-treatment of the ashes, like water leaching and reduction of Cr(VI)
- Pre-treatment of ashes, like screening, magnetic separation, eddy current separation, grinding, grinding and mixing of bottom ashes and mixing with fly ashes
- Chemical composition, the main compounds: moisture, carbonate, hydroxide, LOI, CaO, K₂O, SiO₂, MgO, Na₂O, Al₂O₃, Fe₂O₃, P₂O₅, Cl and SO₃. Also free lime and free hydrated lime are of interest.
- Health and safety aspects: PSD, pH-value, free lime, UBC, hazardous waste regarding heavy metals, quartz
- Sources of the biomass ashes: bottom ash, fly ash, from one unit, from 1 plant? Note that 1 plant can consist of more than 1 unit.

- The type of combustion (PFC, BFBC, CFBC, grate firing), including additives used (limestone in the bed, kaolin, coal fly ash, hydrated lime with flue gas cleaning)
- The type(s) of biomass fired.

An example is presented as table 3.1.

Table 3.1: Aspects of interest of biomass ash (with additives) for application in construction materials.

Property	Unit	Quantity / example
Chemical composition		
Free lime, CaO	wt.%, dry	
Hydrated lime, Ca(OH) ₂	wt.%, dry	
UBC	wt.%, dry	
Moisture	wt.%, as received	
LOI, 550°C	wt.%, dry	
Carbonate, as CO ₂	wt.%, dry	
Hydroxide, as H ₂ O	wt.%, dry	
Salt / water-soluble	wt.%, dry	
Water-leachable Cr(VI)	wt.%, dry	
Oxides	wt.%, dry	
CaO	wt.%, dry	
K ₂ O	wt.%, dry	
SiO ₂	wt.%, dry	
MgO	wt.%, dry	
Na ₂ O	wt.%, dry	
Al ₂ O ₃	wt.%, dry	
Fe ₂ O ₃	wt.%, dry	
P ₂ O ₅ ,	wt.%, dry	
SO ₃	wt.%, dry	
Cl	wt.%, dry	
Combustion		
PFC, CFBC, BFBC, grate		
Type of ash		
Bottom, fly		
Additives used		
Bed material	Y/N	Y, quartz sand
Flue gas cleaning	Y/N	Y, hydrated lime Y, limestone to the bed
Combustion additive	Y/N	Y, clay Y, coal fly ash, 90% of ash
Treatment		
Screening	Y/N	Y, over 1mm screen
Water-leaching	Y/N	
Grinding	Y/N	
Carbonation	Y/N	
Granulation	Y/N	Y, > 10mm
Reduction of Cr(VI)	Y/N	Y, ascorbic acid Y, Fe(II)SO ₄
Magnetic separation	Y/N	
Eddy current separation	Y/N	
Air classification	Y/N	

The water-soluble content of the ash can be determined by:

- Mixing 100 g of ash with 1 kg of water for 24 hours
- Filtration of the ash
- Analyses of the filtrate for Na, K, Ca, Cl, sulfate, carbonate, (others ?) followed by calculating as KCl, K_2SO_4 , $Ca(OH)_2$, Na_2SO_4 , K_2CO_3 , $CaCl_2$, (others ?)
- Alternative: evaporation of the filtrate (for instance at about 105°C in air) and measuring the remaining salt / dissolved solids. Hydroxides and hydrates may have formed, like gypsum.
- Calculating the water-soluble fraction of the ash.

Comparing the results with the weight loss of the sample after water-leaching and drying at 45°C. The drying temperature must be limited, as gypsum may be present.

Potential reactions with water-leaching of the biomass ash are:

- Formation of calcium hydroxide from calcium oxide
- Formation of gypsum from calcium sulfate, potassium sulfate or sodium sulfate and calcium compounds
- Formation of calcium carbonate from potassium carbonate.

3.3 Application in top soils, aspects of interest

For application of fertilisers, liming agents, soil improvers, etcetera, EU legislation is in progress (16). This should / will include biomass ashes for application in top soils. In some countries there is national legislation. The base of EU legislation should be either protection of top soil quality or allowing for recycling biomass ash from “pure” biomass back to top soils. One can discriminate between forestry and agriculture, but the EU legislation does not. In general, biomass ashes will not meet the limits of the new EU Fertiliser Regulation 2019.

4. Letter of the VGB

Version improved by Laborelec.

VGB comment on standards for biomass ash

Based on a report of ENGIE/Laborelec about the Bioefficiency project and a direct request we would like to explain our concerns about the need for "standards" as outcome of research projects. Our concerns are mainly to avoid misunderstandings with the phrase "standard", to a missing scope and to the already existing standards and regulations covering biomass or wood ash.

In the scope of product and application standards the final use is defined. This is by now not addressed in the outcome of the project. From our experience a standard works beneficially to support the supply and use of materials on "existing" or "developed" markets for well-developed applications. It is based on experience to make sure that market partners accept the properties of the product for the specific use and understand why quality control procedures are needed. In this way a standard creates an easy access to the market, but it will never create a market or application!

In the pre-standard phase, experiences has to be shared between the stakeholders in the supply chain to develop a common understanding about nomenclature, essential characteristics and quality assessment procedures. Well-founded best-practice guidelines are very useful in this phase. Later on these can be the starting point to develop standards.

Furthermore, there are already standards existing where biomass ashes are covered for certain applications e.g. the aggregate standards for use in bound and unbound conditions (e.g. EN 12620 for aggregates for concrete). The "source materials" are defined in Annex A (i.a. biomass ash). Please note that the list will be separated from the standards into a CEN Technical Report within the ongoing revision of the aggregate standards. Also for applications in earthworks (TC 396) a CEN Technical report on the national experiences (based on European and national regulations) is under preparation.

Also there national experiences – based on existing regulations - will be described.

A part of biomass ash is further addressed in the fertiliser act as "wood ash" covering the use in or as fertiliser in agriculture. For other applications, especially nutrient recycling in forests, national regulations or guidelines exist.

As the development of a standard is time and cost consuming and, when implemented, cost expensive for producers as they have to perform a quality control without the guarantee that the material is accepted on the market, the decision to start the development of a standard as outcome of research projects has to be well considered.

Based on decades of experience with standards and guidelines for coal ashes and gypsum, VGB concludes that at this moment there is no need for standards (without proper defined scope), but for a better and active sharing of experiences and developing best practice guidelines.

Essen, 02.09.2018, J. Feuerborn

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Based on decades of experience with standards and guidelines for coal ashes and gypsum, VGB concludes that at this moment there is no need for standards (without proper defined scope) but for a better and active sharing of experiences and developing best practice guidelines.

Remark of ENGIE Laborelec to this VGB letter.

Biomass (fly) ash itself is not an aggregate, but can be used for making an aggregate. Biomass fly ash is very fine, with an average diameter $< 63\mu\text{m}$, and can be considered as a filler, at least related to the standard DIN EN 12620.

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