Recycling of biomass ashes in The Netherlands

Angelo Sarabèr and Kees Haasnoot

Angelo J. Sarabèr MSc; Vliegasunie, PO Box 265, 4105 JX Culemborg, the Netherlands; asaraber@vliegasunie.nl
Kees Haasnoot; Essent; Amerweg 1 4931 NC Geertruidenberg, the Netherlands; kees.haasnoot@essent.nl

Abstract

Biomass ashes are generated in the Netherlands in various dedicated stand-alone boilers for generation of power and/or heat. A broad desk-study has been performed to assess the potential applications of biomass ashes in the Netherlands (2009/2010). This study was followed by a program where different combinations of biomass were fired in one dedicated boiler. The primary fuel was virgin wood from the region. Secondary fuels were paper sludge, grass and sieve overflow green household waste or sieve overflow compost. The ashes were fired in a test program of one week each. The generated fly ashes ashes were characterized by physical, chemical and mineralogical methods. Also leaching and respirable quartz was assessed (environmental and health aspects). The results of this characterization and assessment are described. Based on this promising applications were assessed.

Keywords: biomass, ashes, recycling, nutrients, filler

INTRODUCTION

Biomass is one of the sustainable sources of energy that is used for today's production of electricity and heat. In the near future its share will increase significant when The Netherlands and Europe fulfil their obligations in the framework of the Kyoto Protocol. In general terms the target of the national government is to secure that the energy supply for the future will be reliable, affordable and sustainable. Biomass will be an important source in the future for power, heat and transport fuels. Sustainable use of biomass for energy production encompasses many aspects. They range from social aspects like security of food supply and workers health to environmental aspects like clean emission and protection of nature. Our study focuses on ash management of biomass fired power plants.

Key themes in ash management are:

- Removal of by-products from the power plants must be assured; otherwise storage.
- Capacity will be the determining factor for the operational period of a power plant. Therefore, sales assurance is an important aspect. In practice, a balance will be found between financial benefits and sales assurance. Sales assurance can be promoted by closing long-term contracts with customers and risk spreading by having different applications and or customers.
- The by-product chain from generation at the power plant to end-user and second generation re-use must comply with the current regulations. This applies to regulations concerning transport, health and safety, environment and technical aspects.
- Utilization must be sustainable, especially in the case of biomass ashes.
- Utilization must generate maximum financial benefits (or minimum of costs).
- Utilization options must be accepted by society and must comply with the power brand (green power, grey power).

POWER GENERATION FROM BIOMASS

Nowadays biomass is an accepted secondary fuel in Dutch coal-fired power plants. Five of the six Dutch power plants are co-firing biomass. Also the three new coal firing power plants that are being built in our country will be equipped for large scale biomass co-firing. These power plants are located near shore for reasons of cooling water, fuel supply and potential for CCS.

The medium scale power plants are located all around the country. The capacity ranges from several kW_{th} up to 115 MW_{th}. There are 5 medium scale biomass fired power plants, which have a capacity 20-50 MWe. These plants are fired with poultry litter (1), demolition wood (3) and a combination of different biomass fuels (1). The latter is the bio energy plant (BEP) in Cuijk, which will be the focus of this paper. Furthermore there are four plants combusting relatively high volumes of biomass namely sewage sludge () and paper sludge (12 and 45 MW_{th}).

Figure 1: Bio energy plant (BEP) Cuijk, the Netherlands

The Netherlands is a densely populated country with 403 inhabitants per km^2. Therefore it is not very easy to get sufficient biomass for the transition to more sustainable power and heat generation. It is expected, which is also practice at present that the main biomass resources for large scale power plants will be from import (wood pellets and occasionally agro residues). The biomass from inland production being used for heat and power generation will be mainly fired in small and medium scale dedicated power plants.

The future availability of inland generated biomass has been studied by Koppejan et al [1]. This study focuses on 2020 using four scenarios. It is thought that wet biomasses like grass and manure as these will be used for fermentation and production of green gas which can be used for gas engines or feeding it into the natural gas grid. Several wastes like industrial waste and municipal waste which will be incinerated in dedicated MWI. Energy crops will be mainly used for bio fuel and chemicals because of the higher added value (like coleseed and energy maize). The survey shows that the main biomasses from inland production are (poultry) manure (2.03-2.35 Mton/year, dry material), old and contaminated wood (1.09-1.82 Mton), wood from forest with and without harvesting (0.06-0.57 Mton), wood from house-built environment (0.28 Mton) and residual wood from wood industry (0.38 Mton).

UTILIZATION OF BIOMASS ASHES IN THE NETHERLANDS

Potential utilizations of biomass ashes have been surveyed by KEMA and ECN in 2008 [2]. The survey is based on desk research and interviews. This list is used as starting point for the development of utilizations for biomass fly ashes from BEP Cuijk. The updated list is presented as table 1.

No	Application	Function	Sector
1	Binders alternative for standard cement	Component	Building industry and civil engineering
2	Clinker production (cement)	Raw material	
3	C-fix	Filler	
6	Concrete (products) low quality	(Reactive) filler	
7	Road Construction material	Binder/Raw material	
8	Sand-lime bricks	Filler/lime	
9	Infrastructural works (embankments, fillings)	Filling material	
10	Soil stabilization	Binder/lime	
11	Synthetic aggregates[1]	Raw material	
12	Fuel	Combustion	Energy production[2]
13	Back-filling	Filler	Mining
14	Polymers	Filler	Industry
15	Metals	Filler	
16	Phosphor production	Raw material	
17	Zeolites	Raw material	
18	Metals recovery	Raw material	
19	Mineral fibers	Raw material	
20	Soil improvement and fertilizer	Product/Raw material	Agriculture and forestry
21	Neutralization of waste acids	Product	Environmental technology
22	Adsorption material	Raw material	
23	Mineral barrier disposal sites	Raw material	

Table 1: Overview of (potential) applications for ashes (fly ashes and bottom ashes)

[1]) Including synthetic basalt
[2]) Including indirect energy production in industry

At present several applications of biomass ash are implemented in the Netherlands, namely:

- Fertilizer. Biomass fly ash from poultry litter is exported for use as fertilizer. The high contents of phosphate and potassium make this ash attractive for use in agriculture [3]. Biomass ashes from other sources then poultry litter are not being used for fertilizer.
- Phosphor production. A small share of the generated sewage sludge ash is used for phosphor production by Thermphos in Vlissingen [4].
- Raw material for asphalt filler. An important share of the generated sewage sludge ash is used in asphalt filler [4]. However, the use of phosphate containing ashes in asphalt applications will be run down by the Dutch government. Also paper sludge ashes are used as raw material for this application.
- Mining (back-filling) abroad; so-called Ersatzbau in Germany [4].
- Soil stabilization. Paper sludge ash has a relatively high content of free lime and therefore it can be suitable as a lime replacing material. These ashes are used for stabilization in road construction [5].
- Binder in prefab concrete (up to 10% replacement of cement) and immobilization. This concerns paper sludge ash (TopCrete®).

Bed sand is used as sand replacement in non-reinforced prefab concrete and in civil engineering (replacement of primary sand for fillings, embankments etc). Bed sand from bio energy plants which are produced on the same site as municipal solid waste incinerators (MSWI) are mixed with MSWI bottom ash before using it in civil engineering [6]. There is no clear insight in the utilization of biomass bottom ashes from small scale boilers and stoves.

Generation of biomass ash in Bio Energy Plant Cuijk

In 2010 combustion experiments were performed in the Bio Energy plant in Cuijk, owned by Essent/RWE. This plant has a capacity of 80 MW_{th} and 26 MW_e (gross). The boiler is a bubbling fluidized bed type, designed for 31.4 ton/hr of wood chips. The combustion temperature is about 800 °C. The NOx emissions are reduced by SNCR/SCR and ammonia injection (±100 kg/h). The bed material is quartz sand. The ash is removed from the flue gas by Electrostatic Precipitators. See figure 2.

The combustion experiments were performed using virgin wood as basic fuel and combined with other biomass fuels that were available in the region. In the case of grass from roadsides also an additive for binding potassium was used. An overview of the combustion experiments is presented in table 4. Some basic characteristics of the biomass fuels are presented in Table 5.

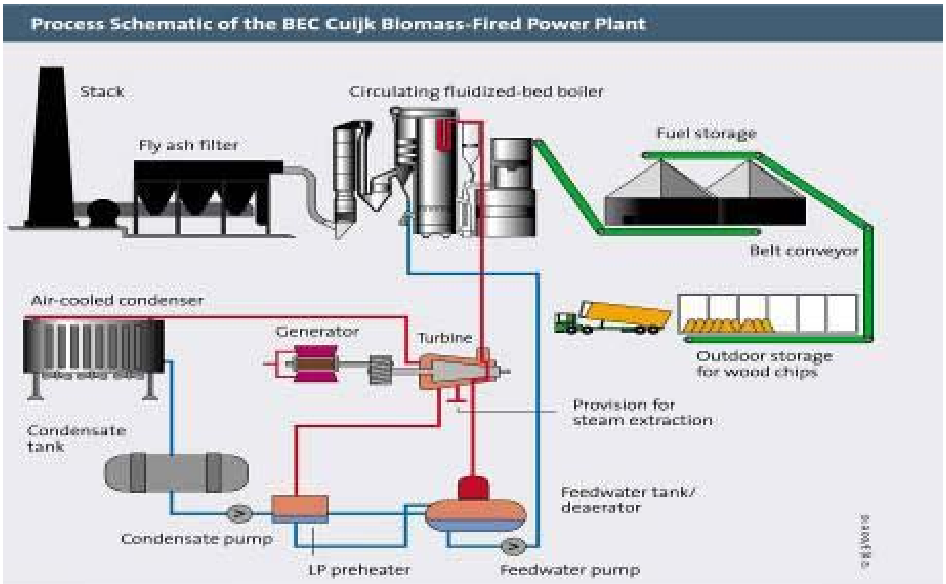

Figure 2: Process scheme of bio energy plant Cuijk

Code	Fuel combination	Additive
HP	92 % Wood + 8 % paper sludge	No
HZ	84 % Wood + 16 % sieve overflow compost	No
HG	87 % Wood + 13 % sieve overflow organic waste	No
HB	93 % Wood + 7 % grass from roadsides	Yes
HBZ	88 % Wood + 12 % grass from roadsides	No

Table 4: Combustion experiments at Bio energy plant Cuijk

Parameter		paper sludge	sieve overflow compost	sieve overflow organic waste	wood
C	% m/m	32.3		33.4	
H	% m/m	3.44	5.30	3.97	6.19
N	% m/m	0.20		1.44	
S	% m/m	0.10		0.22	
O	% m/m	17.90		18.40	
moisture content	% m/m	48.1	52.4	38.8	44.6
ash content	% m/m	46.1	21.5	42.6	3.1
LHV (wet) AR	MJ/kg	3.98	6.10	5.77	9.16

Table 5: Some characteristics of the combusted biomass fuels

Characteristics of generated fly ashes

The generated biomass fly ashes were analyzed with ICP after total digestion by TLR Laboratories in Rotterdam. The chemical composition of the fly ashes is presented in table 6 and 7. The composition of the fly ashes is dominated by SiO_2 en CaO (78-81 % m/m). The amount of Al_2O_3 varies between 3.2 and 7.2 % m/m and is outside the range of ashes, from 100% virgin wood firing in Cuijk. The content of Na_2O and SO_3 are at a low level and not significant for many applications. The amount of MgO is the range1.9-2.5% m/m. The loss on ignition (LOI) is <6% m/m. The fly ash contains pieces of pyrolized wood with a length of a few millimeters and a diameter of about 1 mm. It seems that this is a significant part of the LOI.

The concentrations of the trace elements As, Ba, Br, Cu en Ni are in the same range as with pure wood, while the concentrations of Cr, Mn and Zn are somewhat lower. Sb, Se and V are above the range of 100% virgin wood fly ash.

	Virgin wood			Combustion experiments 2010				
	Av.	min	Max	HP3	HZ4	HG3	HB3	HBZ3
Al_2O_3	4.6	2.75	6.52	7.19	4.92	5.01	4.63	3.24
CaO	25.7	12.45	39.00	42.9	22.1	21.1	16.1	20.0
Cl	0.6	0.06	1.17	0.33	-	-	-	-
Fe_2O_3	2.9	1.97	3.92	1.62	2.55	2.39	2.17	1.47
K_2O	8.2	4.46	11.98	4.37	6.27	6.14	5.46	5.98
MgO	3.6	1.77	5.34	2.48	2.46	2.28	1.88	2.33
Na_2O	0.6	0.42	0.84	0.05	0.78	0.89	0.61	0.75
P_2O_5	3.4	1.80	5.06	0.20	2.90	3.50	2.63	3.70
SiO_2	45.8	23.84	67.68	40.19	52.7	52.8	60.8	57.5
SO_3	4.2	0.37	7.95	2.79	0.5	0.2	1.0	0.9
TiO_2	0.3	0.22	0.45	-	-	-	-	-
LOI	9.4	1.32	17.42	0.00	4.8	5.6	4.7	4.2

Table 6: Chemical composition of biomass fly ash / macro-elements

	Virgin wood		Combustion experiments 2010				
	Av	Range	HP3	HZ4	HG3	HB3	HBZ3
As	20.8	<3-40	9.58	46.6	14.6	10.3	8.98
Ba	740	490-1400	338	1300	457	398	464
Br	36.9	19-52	29	39.8	-	-	-
Cd	14.4	3-42	9.92	3.09	9	7.32	7.95
Co	-	-	9.13	43.0	46.7	23.7	19.0
Cr	176	110-370	60.4	113	86.6	70.8	65.0
Cu	162	68-280	233	72.1	174	92.0	111
F	-	-	97	190	257	186	307
Hg	-	-	0.09	0.401	0.30	0.16	0.11
Mn	3948	1600-8500	1200	672	1220	1319	1685
Mo	39.3	0-90	9.8	30.7	13.6	9.3	9.3
Ni	72.1	41-110	29.3	108	39.3	40.5	27.3
Pb	270	110-480	75.0	23.3	171	92.6	75.0
Sb	< 3	<3-4	2.7	18.5	12.3	4.2	3.6
Se	< 3	<3-4	1.08	36.5	1.37	2.92	<1.0
Sn	-	-	5.7	2.9	6.9	2.3	2.4
V	25	13-36	41.2	234	41.8	46.6	34.7
Zn	1326	500-2100	715	142	840	723	749

Table 7: Chemical composition of biomass fly ash / trace elements

X-ray diffraction analyses were performed by University of Leuven. The patterns were quantified using Rietveld's method. The results are presented in table 8. Calcium is present mainly as calcite, free lime and Ca_2SiO_4, and to a small extent as gypsum and anhydrite. Silicium is mainly present as quartz and Ca_2SiO_4.

	HP3	HZ4	HG3	HB3	HBZ3
Quartz	12.7	28.2	18.8	42.8	12.3
Ca2SiO4 alfa	9.5	1.9	6.5	2.3	10.4
Rutile	1.0	<1	<1	<1	<1
Ca3Al2O6	7.6	1.8	4.4	1.0	7.5
Calcite	8.1	4.7	8.9	5.1	11.2
Portlandite	<1		<1	<1	<1
Free lime	12.4	4.2	9.8	4.1	12.1
Periklase	<1	<1	<1	<1	<1
Gehlenite	4.0	1.5	3.1	1.4	3.6
Ca2SiO4 beta	5.2	1.2	3.2		4.5
Mayenite	1.1		<1		1.4
Sylvite		1.7	<1	<1	
Anhydrite		<1	<1	<1	
Feldspar		4.2	1.3	2.0	
Cristoballite		<1			
Gypsum		<1			
Hallite			<1		
Not identified	37	47	40	38	35
Total	100.0	100.0	100.0	100.0	100.0

Table 8: Mineralogical composition fly ashes

Health and safety aspects characteristics of generated fly ashes

Additional analyses were performed for assessing health and safety aspects of the generated fly ashes. As expected, the concentrations of PAH's, PCB's, dioxins and furans were below detection level or in negligible levels. Further, the concentration respirable quartz was measured by TCKI [7]. They improved an existing method with FTIR. A sample of biomass fly ash HB3 was dispersed in the air of a closed container, where the respirable fraction was sucked and analyzed by FTIR (Fourier Transform Infrared spectroscopy). The concentration of respirable quartz and the maximum concentration of compounds in the fly ash were examined in relation to the Dutch regulations for exposure of workers [8] and the old Threshold Limit Values (TLV). In this examination it is assumed that the maximum dust concentration in the air is 5 mg/m^3, which is the limit value for nuisance dust. In that situation no other limit values were exceeded. This implies that it is justified to classify the generated biomass fly ashes as nuisance dust.

TESTING POTENTIAL APPLICATIONS

General

Based on the desk study, several potential applications for the generated biomass fly ashes were selected to be assessed more in detail, namely:
- Filler in asphalt.
- Filler in concrete.
- Infrastructural works (embankments, fillings).
- Sludge stabilization.
- Soil improvement/fertilizer in agriculture and forestry.
- Mineral barriers for top sealing disposal sites (Hydrostab®).

Filler in asphalt

In the Netherlands asphalt fillers are produced from primary and combinations of primary with secondary materials; namely MSWI fly ashes, sewage sludge ashes, paper sludge ashes and coal fly ashes. Water solubility and fineness are important properties for this application. In general, water solubility should be less than 10% in the final filler product. It should be noted that the water solubility of the tested ashes is higher than 10% with exception of HP3 (see table 9). This presence of 12% free lime is able to bind 4% water; so this can not explain the difference with the other ashes. The requirements for passing 125 µm and/or 63 µm are not met by three of the five fly ashes. This implies that these fly ashes are less attractive for use in asphalt filler than for instance coal fly ashes. In fact the generated biomass fly ashes have to compete more with MSWI fly ash and sewage sludge ash than coal fly ash.

Parameter	Water solubility	D_{10}	D_{50}	D_{90}	Passing 125 µm	Passing 63 µm	Soundness NEN-EN 450-1
Unit	% m/m	µm	µm	µm	%	%	Mm
Requirement	≤10	-	-	-	85-100	70-100	≤ 10
Coal fly ash	±5	±2	±18	±42	>95	-	<5
HG3	17	4	35	120	91	75	-
HP3	3	4	35	120	96	51	13
HZ4	11	7	60	>250	71	53	-
HB3	10	7	60	>250	56	36	-
HBZ3	-	10	35	140	90	76	21

Table 9: Characteristics of biomass fly ash relevant for use in asphalt filler and concrete

Filler in concrete

The use of fly ash in concrete is a regular application since many decades. The properties of fly ash are well defined for standard and high performance concrete in the EN 450-1 [9]. However, there is also a broad range of concrete or concrete-like products where less strict requirements are possible as the main function of fly ash is to act as inert filler to improve grain size distribution, to increase the paste content and/or to improve workability. The low alumina content points to the presence of low contents of phases like metakaolinite, meta illite or glassy alumino silicates in the fly ash. This means that the biomass fly ash will have low pozzolanic and hydraulic properties. Therefore the ash has to be used in concrete primarily as inert filler. The SO_3 content and the Na_2O equivalent of the biomass fly ashes are lower than the limit values of the EN 450 (respectively 3.0 and 5.0% m/m). The chloride content exceeds the limit value of the EN 450-1 but meets the limit of 1.0% m/m for non-reinforced concrete in the European standard for concrete. The LOI content meets the requirements of a so-called category A coal fly ash.

The soundness (Le Chatelier test) has been tested according to the EN 450-1 for use of fly ash in concrete and exceeds the limit value; especially HBZ3. The limit value for fly ash is 1:1 taken over from the cement standard. In our opinion this limit can be too stringent for coal fly ash. In the case of biomass fly ash soundness should be tested on the concrete (expansion test).

Infrastructural works (embankments, fillings)

Coal fly ash is used as a substitute for sand in embankments and fillings in many countries. Fly ash has to be moistened to avoid dust emissions during transport and on site. Also, it has to be available directly in large quantities when the project is being performed. This means that sufficient ash has to be in stock. The leaching behavior of one biomass fly ash was tested using the Dutch percolation test (see table 10). The leaching of Ba, Cl, Cr, Mo and SO_4 exceeded the limit values for non-bound building materials for use without restricted conditions, but meet the limit values for building materials with restricted conditions. It implies that it competes with secondary materials like MSWI bottom ash, which has a negative price. The limited quantities and the lack of storage facilities make the use in embankments and fillings not feasible for biomass fly ashes.

component	leaching		Limit value Free applicable	Limit value Restricted
As	≤	0.20	0,9	2
Ba		44	22	100
Br		10	20	34
Cd	≤	0.0070	0,04	0,06
Cl		1600	616	8800
Co	≤	0.070	0,54	2,4
Cr		3.5	0,63	7
Cu	≤	0.10	0,9	10
F	≤	1.0	55	1500
Hg	≤	0.0050	0,02	0,08
Mo		1.8	1	15
Ni	≤	0.2	0,44	2,1
Pb	≤	0.30	2,3	8,3
Sb	≤	0.0090	0,16	0,7
Se		0.14	0,15	3
Sn	≤	0.020	0,4	2,3
SO_4		4800	1730	20000
V	≤	0.30	1,8	20
Zn	≤	0.70	4,5	14

Table 10: Leaching characteristics of biomass fly ash [mg/kg]

Sludge stabilization

Several industrial sludges are used for immobilization in the Netherlands. These sludges have to be stabilized to be able to store them. Biomass fly ashes, especially with some free lime are able to bound water physically and chemically. Tests are running to assess the potential.

Soil improvement/fertilizer

In the Netherlands there are no specific regulations for the use of biomass ash or wood ash in forestry. This means that the use in forestry should be qualified as spreading of waste, which is forbidden without permission. A first study has been performed to assess the influence of long term harvesting on the mineral balance of the forest. Depending on the conclusions further steps will be taken.

If biomass ash is used as fertilizer it has to meet the Dutch law on fertilizer. As biomass ash is classified as waste it has to pass the regulation concerning the implementation of this law. (so-called ‘Uitvoeringsregeling Meststoffenwet’). The agricultural capability has to be proven; probably field tests will be necessary. Further minimum content of nutrients must be present in the waste material. The minimum limits in so-called ‘other inorganic fertilizers’ are:

- MgO at least 15% or
- CaO at least 25% or
- SO3 at least 25% or
- Na O at least 50%.

Only fly ash HP3 meets one of the limits, namely for CaO. Further, the limit values for several metals, PAH’s dioxins and mineral oil have to be passed. If the concentrations of trace elements in the fly ash are compared with the limit values for CaO fertilizer the limits are exceeded with exception of Hg. See Table 11. Another way is to use biomass fly ash as raw material for production of fertilizers like in PK fertilizers. There is a basic interest in the Dutch fertilizer industry for using biomass ashes, but the concentrations in the generated fly ashes are too low.

	limit	total	on CaO
As	30	9.6	37
Cd	2.5	10	38
Cr	150	60	232
Cu	150	233	896
Hg	1.5	0.09	0.35
Ni	60	29	113
Pb	200	75	288
Zn	600	715	2750

Table 11: Limit values for CaO fertilizer (calculated to CaO), concentrations in fly ash HP3 and calculated to CaO [% m/m]

Mineral barriers for disposal sites (Hydrostab)

Hydrostab is a mixture of residues with certain properties to which soluble alkali silicates have been added. It is used as a mineral barrier in the top sealing of waste disposal sites. Sewage sludge, MSWI fly ashes and other fly ashes are used as raw materials. The biomass fly ash has to have a certain amount of free lime. The demand depends highly on the number of projects, where mineral barriers are foreseen. This together with the winter stop each year make that this utilization will only be attractive if it is combined with other applications to guarantee sales assurance the whole year.

EVALUATION AND CONCLUSIONS

A lot of potential applications for ashes can be found in literature. However, practice is stubborn, especially for biomass ashes, due to relatively small volumes and variations in quality. Applications of biomass fly ash in the Netherlands are based on the physical properties, nutrient concentration or free lime content (in combination with metakaolinite). The most important applications (based on volume) are asphalt filler and fertilizer, mainly fly ash from poultry litter combustion in Moerdijk.

The ash from the experiments in Cuijk was applied as asphalt filler. This application has a negative price because it has to compete with MSWI fly ash and sewage sludge fly ash. New applications with better prices have to be developed to reduce the costs for ash management and to increase the feasibility of power generation by BEP Cuijk. The use as fertilizer in agriculture will only be possible of the concentration of critical trace elements is reduced and/or the CaO content will increase. Another route is to increase the content of K_2O and/or P_2O_5 to get an interesting secondary raw material for fertilizer industry. The latter is probably more feasible than the former. The use in forestry will only have a chance if the nutrient balance of the forests is significantly disturbed by harvesting. Application of biomass fly ashes as inert filler for certain concrete products may only be possible if soundness is secured. Further testing is necessary.

Another approach is to generate a fly ash with high free lime for applications where paper sludge ash is used nowadays. Besides that other applications have to be assessed like use in sand-lime bricks and several niche applications.

The challenge is to reduce the costs for ash management or even to develop positive value for the biomass fly ash. This will only be possible if there is a clear added value by which primary materials or products are replaced like phosphate ores, potassium salts, lime(stone) and cement.

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