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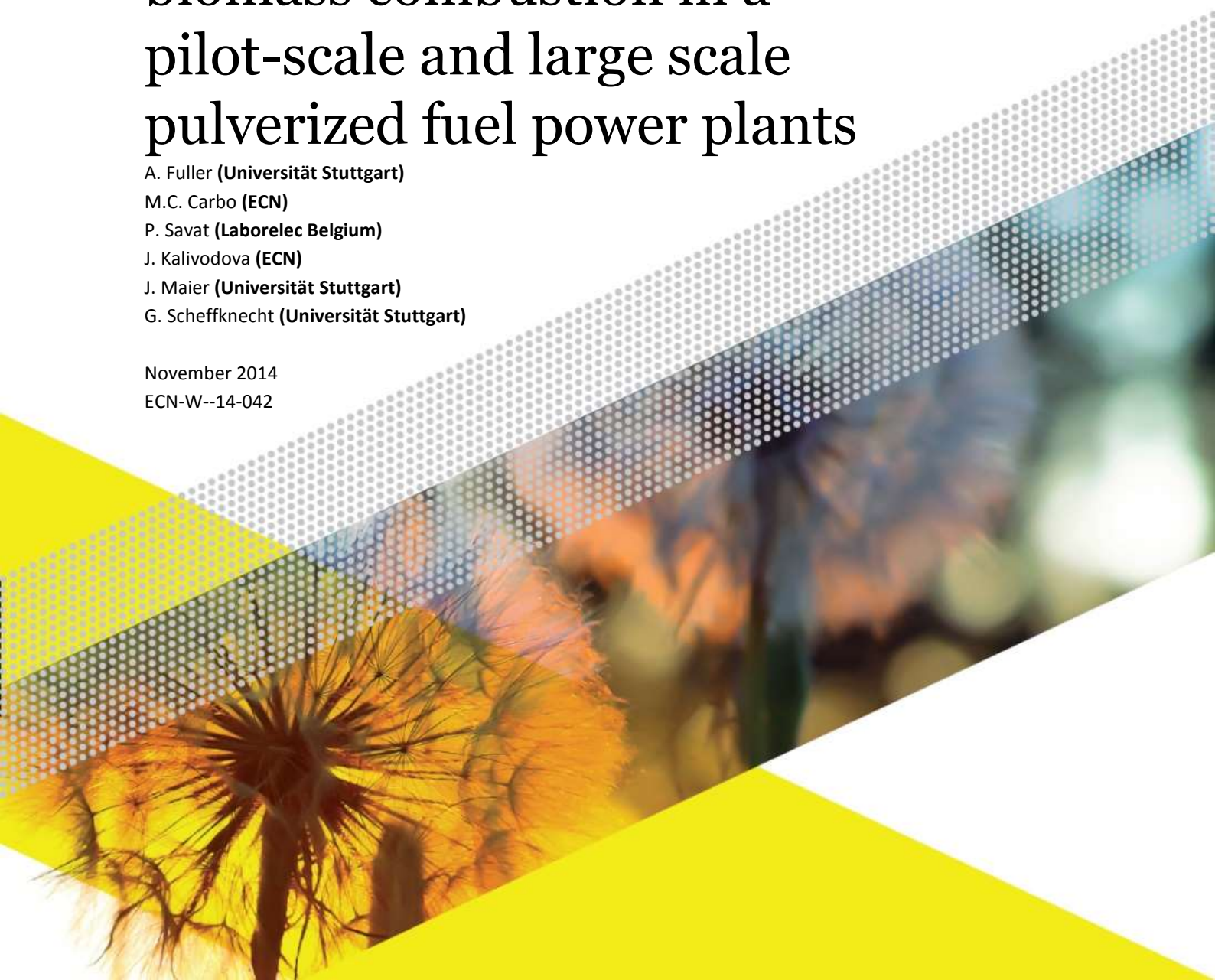
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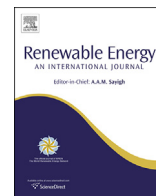
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## ABSTRACT

This work evaluated fly ash quality from combustion of high thermal shares of biomass fuels. Woody biomass was (co)combusted in an industrial scale pulverized fuel power plant, and a herbaceous biomass was co-combusted in a pilot-scale test facility. Ashes from the electrostatic precipitator were collected and evaluated for chemical compounds, leaching behavior, and mechanical properties. Results from the large-scale industrial pulverized fuel showed the ashes still had good reactivity and mechanical properties according to EN450-1, which is a good unexpected occurrence regarding strength development. Results from the pilot-scale test facility showed that a herbaceous biomass co-fired up to 50% thermal share does not seem to have any negative impact on existing fly ash utilization routes. It is concluded that co-firing clean woody biomass at a very high thermal share and co-firing a high thermal share of a herbaceous biomass with lignite would not change current utilization practices. In practice ashes from high thermal shares are not used due to safeguards in standards form a lack of experience from enough performance testing. Thus, the findings can lead to support for standards that incorporate other assessment methods for biomass fly ash utilization requirements.

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## 1. Introduction

Depleting natural resources and damage to the natural environment necessitates alternatives to utilizing fossil fuels. The increase in environmental awareness worldwide over the recent decades has resulted in countries shifting energy policies to include renewable energy sources in their energy mix to produce heat and electricity. Estimations show that after 2042 the only fossil fuel with significant remaining reserves is coal [1]. Thus, coal combustion, the traditionally essential energy supply system, will continue to play a role, either as an indigenous source or as an imported raw material, in the

European energy mix and its diversification [2], as the energy demand is likely to continue to increase. Out of concern for the environment, the European Commission has a binding target to increase the level of renewable energy sources in the EU's overall energy mix to 20% by 2020 [3]. Those renewable energy sources include, but are not limited to, biomass fuels. Noted is the potential of biomass to make a significant contribution to an increasing sustainable energy production globally [4]. Biomass is a renewable and CO<sub>2</sub>-neutral energy source, which continues to gain increasing importance worldwide, aiding to the diversification of renewable energy sources as a fuel for energy production, leading to various reduced emissions besides CO<sub>2</sub> [3–5]. Atmospheric concentrations of CO<sub>2</sub> have increased from pre-industrial era levels to date [6], arguably contributing to higher global temperatures, the greenhouse effect, and ocean acidification. Thus, the increase in environmental awareness has led to the growth of environmental legislation, driven by a rising interest in environmental protection and sustainability.

It is noted that in Europe, most notably in Eastern Europe, both hard coal and lignite are available as indigenous sources, whereas in the future the Southern and Western European countries will

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have to continue to import coal or switch to other energy sources [2]. Among the renewable energy options considered for GHG emission mitigation, biomass is currently the most important, being the fourth largest energy source following coal, oil, and natural gas [7]. Biomass is considered to be the most promising source of renewable energy regarding the use of alternatives to using fossil fuels, with all countries having a trend of increasing their share of biomass in the process of industrial combustion. A reported goal of EU regulations is 14% of biomass in the process of coal combustion by the year of 2020 [8]. Biomass generally belongs to one of the six categories: woody and woody biomass, herbaceous and agricultural biomass, aquatic biomass, animal and human biomass wastes, contaminated biomass and industrial biomass wastes (semi-biomass), and biomass mixture [9]. Interest in biomass combustion has increased during the last decades, as one of the major renewable energy sources [10–12]. Biomass has the potential to make a large contribution to an increase in sustainable energy production globally [4]. The majority of the energetic uses of biomass are in the heating sector, but the production of electricity from biomass is rapidly growing. Dedicated biomass power plants are a technological option; however, their typical conversion efficiency is quite low, near 25% [13]. Biomass co-firing in existing coal-fired power plants is another technological alternative, which combines the high efficiencies of coal power plants (at least 43% for the newest facilities [14]) with installation costs lower than dedicated biomass combustion facilities and comparable or lower to other renewable energy sources options [15]. Many biomass fuels, such as residues, energy crops, herbaceous, and woody biomasses have been co-fired in pulverized fuel, stoker, and cyclone boilers, ranging in proportions from (1 to 20) % [3]. In most cases, the quick adoption of co-firing relies on the availability of relatively high quality wood biomass fuels, often in the form of pellets or chips. In addition, the biomass thermal shares are typically below 20%. Competition with the heating sector, price increases, as well as the overall policy direction, lead to a push for a more extensive utilization of other biomass types, such as agricultural residues and dedicated energy crops [16]. Energy crops in particular are considered as very promising candidates for the production of solid biofuels due to their potential for high yields, which may pose a more attractive alternative to farmers in the frame of the EU Agricultural Policy and the challenges of the agricultural sector [17,18]. On the other hand, herbaceous biomass has higher amounts of constituents that negatively impacts slagging, fouling, corrosion and by-product quality. The use of forest residues, herbaceous and fruit biomass is the greatest potential to increase the share of biomass in energy production. Up to now, herbaceous and fruit biomass make up only 7% of the total biomass utilization and mainly straw is used [19]. Currently the EU only exploits 48% of the biomass potential for bioenergy production, with herbaceous and fruit biomass having the highest potential followed by forest residues [20]. Thus, the potential for biomass use for energy production in the EU27, whether imported or indigenous, remains a viable option as another energy source than coal.

The growing use of biomass in the energy production sector will continue to influence the by-product quality, affecting its potential utilization routes. To ensure the sustainable use of biomass fuels in power plants for heat and electricity, one must maintain the quality of the fly ash, among other coal combustion by-products, for valuable end-use market applications.

Fly ash is a fine powder of mainly spherical, glassy particles, derived from burning of pulverized coal, with or without co-combustion materials, which has pozzolanic properties and consists essentially of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ; electrostatic or mechanical precipitation of dust-like particles from the flue gases of the power stations obtains the fly ash in bottom hoppers [21]. Coal

combustion products, to include fly ash, are mainly utilized in the building material industry, civil engineering, road construction, construction work in underground coal mining, and recultivation and restoration purposes in open cast mines, with the majority produced to meet requirements of standards or specifications for utilization in a certain area [22]. EU or EU member states' national standard regulations of fly ash utilizations in the EU27 are for various applications. EN 450-1 defines the use of fly ash in concrete, allowing co-firing shares of biomass up to 40% on a mass fraction percent for selected secondary streams, as well as up to 50% on a mass fraction percent for untreated clean wood [21]. EN 197-1 that defines the use of fly ash in producing common cements [23]. EN 12620 defines fly ash for use in aggregates for concrete [24]. EN 14227 [25] and EN 13282 [26] define fly ash use for road construction, and EN 13055-1 for use in lightweight aggregates [27]. National regulations by EU member states mainly consist of requirements for the environmental compatibility of fly ashes, which are regulated by EU member states national laws. National standards and regulations by the various EU member state are noted to be required to be followed for uses in concrete blocks, infill-filling of voids, mine shafts and subsurface mine workings-, production of bricks, earthworks and landscaping, production of mortar, floor screed and plasters, and mining mortars/civil engineering products [28]. A further fly ash use included in the national regulations is for soil ameliorant. Fly ash is noted to improve the texture of soils, improve soil aeration, percolation and water retention; it reduces crust formation and consumption of other soil amelioration agents such as fertilizers; it can decrease the mobility and availability of material in the soil [29,30]. Drawbacks are the reduction in bioavailability of some nutrients in soil due to alkaline fly ash and excess salinity and a high phytotoxic elements [30]. For example, in Germany those parameters and their limits are established in a document known as the LAGA Assessments – Guidelines from the German-Federal/State Working Group on Waste [31], in the Netherlands it is the Dutch Decree on Soil Quality [32].

Meanwhile, it is noted there are many applications where the fly ash meet performance requirements that are not regulated by EU standards or EU member states' national standards; thus, these utilization options are not widely practiced. Those include, among others, absorbents, metal recovery, ceramics and glass, geopolymers, cenospheres recovery, carbon recovery [30], stabilization, solidification, and encapsulation [33] and waste water treatment [34]. Reported in Ref. [35] is utilization of fly ash for metal recovery from waste to energy plant residues. While most fly ash utilization applications evolved from fly ash obtained from coal combustion, the increase use of biomass in thermal conversion technologies leads to a change in the constituents of fly ash due to biomass generally having higher amounts of alkalis, magnesium, phosphorous, and chlorine along with lower amounts of alumina, silica, and iron. Therefore, the requirements for the use of biomass ashes would likely need other assessment criteria to evaluate thoroughly its performance for a given application in order to identify the best utilization route from any changes in the fly ash chemical composition, morphology, physical properties, and mechanical properties, which affect its quality.

As biomass fly ashes are likely not to conform to chemical requirements in some standards, but may still be able to perform for a given end use application, a process to evaluate its performance for end use market applications appears to be a more valuable assessment. The non-conformity of biomass fly ashes is likely an expectation, as biomass ashes differ according to the following three groups: agricultural residues – high in silica and potassium, low in calcium; wood-based fuels – low in silica and potassium, high in calcium; and manure – high in calcium and phosphorus [9]. Furthermore, the inorganic matter in biomass is composed mostly



of minerals, most importantly silicates, oxides and hydroxides, phosphates, carbonates, chlorides and nitrates [36], and the potassium and trace elements, including plant nutrients, are not associated to the mineral matter but bound to the carbohydrate matrix in biomass [9]. In coals the mineral matter is mainly associated with clays consisting mainly of aluminosilicates. Thus, to address fly ash differences from biomass combustion that does not meet conformity requirements in a standard, one may seek a European Technical Approval (ETA). In the EU, utilization of fly ash that not conforming to any standard, but still has a market value, occurs after obtaining an ETA. The ETA permits using fly ash as a construction product verified by an Attestation of Conformity with CE marking, noted to be granted when certain conditions applies. Those conditions are no relevant harmonized standards for the product exists, no mandate for such a standard has been given by the European Commission, the European Commission considers that a standard cannot be developed (yet), and a product deviates significantly from the relevant harmonized product [37]. Thus, there exists an avenue for the use of non-conforming ashes with a proven value, which suggests performance-based evaluations along with an enhanced evaluation of mineral phases that qualitatively or quantitatively identify certain risks, is a valued approach to biomass ash assessments.

In certain circumstances, an ETA issued through a Common Understanding of Assessment Procedure (CUAP) requires agreement among the European Organization for Technical Approvals (EOTA) members (according to art. 9.2 of the Council Directive 89/106/EEC). Issuance of an ETA for a product to a manufacturer is based on assessment principals listed in an ETA Guideline for the relevant product sector. An ETA issued is valid in all European Economic Area (EEA) countries, valid for a period of five years, renewable thereafter [37].

Under the REACH Regulation (Registration, Evaluation, Authorization, and Restriction of Chemicals) enterprises that manufacture or import more than one tonne of a chemical substance per year are required to register it in a central database in the EU. The registration is required for by-products that are to be used commercially to meet the requirements of European and national standards. The registration is noted to require information on the properties and the potential risks, along with information about toxicology and ecotoxicology of the substances. Coal combustion products are listed in the European Inventory of Existing Commercial Chemical Substances and so are defined as phase-in substances under the REACH Regulation [22]. Therefore, an ETA can be considered as a means to have biomass fly ashes supplied on the EU market.

Listed below are chemical requirements of a major standard for fly ash utilization in concrete. The chemical requirements noted and defined by EN450-1 are summarized in Table 1.

The loss on ignition of fly ash primarily exists of unburned carbon, which can be contained in fly ash as coke particles. In case the amount of unburned coal in fly ash is large, the amount of the reactive components, which contributes to the fly ash quality, is usually smaller. The water demand of fly ash with an increased loss on ignition (LOI) can be higher due to the large surface area of these coke particles. This is contradictory to the commonly experienced liquefying effect of fly ash in concrete. In most of the European member states the LOI of fly ash for concrete is restricted to category A, i.e. a maximum mass fraction of 5%. In some countries, where concrete is not subjected to the effect of frost and de-icing salt a mass fraction of 7% (Belgium, Ireland, United Kingdom) or a mass fraction of 9% (Czech Republic, Portugal) are permitted based on national experience [38].

The chemical requirements for chloride, sulfuric anhydrite, free lime and reactive calcium oxide, among others, are regulated in standards for various widely known reasons. The chlorine threshold limit prevents corrosion in concrete reinforced with steel. The

**Table 1**  
Chemical requirements for fly ash use in concrete by EN 450-1 (year 2012).

Parameter	Requirement (unless noted otherwise) [mass fraction percent]
Loss on ignition	Category A: 0 – 5 Category B: 2 – 7 Category C: 4 – 9
Chloride	≤0.1
Sulfuric anhydrite (SO <sub>3</sub> )	≤3.0
Free calcium oxide	≤2.5 <sup>a</sup>
Reactive calcium oxide	≤10
Reactive silicon dioxide	≥25 <sup>b</sup>
Silicon dioxide, aluminum and iron oxide	Sum of SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> ≥ 70 <sup>b</sup>
Alkalis (Na <sub>2</sub> O equivalent)	≤5.0 (as Na <sub>2</sub> O <sub>eq</sub> ) <sup>b</sup>
Magnesium oxide	≤4.0
Soluble phosphate	≤100 mg/kg <sup>2</sup>

<sup>a</sup> Expansion below 10 mm should be proven in case free calcium oxide amount exceeds 1.5 by mass %.

<sup>b</sup> For fly ash obtained from co-combustion.

presence of an increased sulfate content influences the setting time of cement and can also lead to destruction of concrete through adverse reactions. Increased free lime concentration can cause uncontrolled formation of calcium hydroxide, and as such fractures.

Additional chemical requirements involve the minimum amount of reactive SiO<sub>2</sub> to ensure sufficient pozzolanic activity of co-firing derived fly ashes. Increased alkali content can lead to increased alkali–silica reactions, and as such excess expansion. An increased MgO concentration can also lead to expansion, as a result of the formation of free MgO crystals that subsequently hydrate during cement hydration. This phenomenon typically occurs at a much slower rate and it may only be observed after several months or even years. Increased phosphate concentrations in fly ashes obtained from co-firing of sewage sludge or manure, typically delay the setting of cement.

The physical parameters, from EN450-1, for fly ash use in concrete are summarized in Table 2. Categories for the particle size exist, although Category S is only used in the United Kingdom.

A revised version of EN 450-1 was released in the course of 2013. This standard is applicable after publication in the Official Journal of the European Commission. An important improvement in the revised version, FprEN 450-1 (2012), compared with the previous version is that the ratio of coal firing is reduced to at least a mass fraction of 60%, while the fly ash content that is derived from co-fired material constitutes can amount up to a mass fraction of 30%. In case of green wood, only a mass fraction of 50% coal firing is

**Table 2**  
Physical requirements for fly ash use in concrete by EN 450-1 (year 2012).

Parameter	Requirement (unless noted otherwise) [mass fraction percent]
Fineness (residue on 45 μm mesh sieve)	Category N: ≤ 40 Category S: ≤ 12
Fineness variations (deviation from declared value)	Category N: ≤ ± 10 percentage points Category S: N/A
Density variation	±200 kg/m <sup>3</sup>
Expansion <sup>a</sup>	≤ 10 mm <sup>b</sup>
Activity index after 28 days	≥ 75%
Activity index after 90 days	≥ 85%
Initial setting time <sup>c</sup>	≤ 120 min more than paste with reference cement
Water demand	Category N: N/A Category S: ≤ 95% for test cement alone

<sup>a</sup> Expansion test is required when free calcium oxide amount lies between (1.0 and 2.5) mass fraction.

<sup>b</sup> For a mixture 30/70 mixture of pulverized fly ash and CEM I cement.

<sup>c</sup> For a mixture 25/75 by mass % mixture of pulverized fly ash and CEM I cement.

allowed [21]. These improvements are the result of the use of a European Technical Approval (ETA) for fly ashes that did not comply with the previous current EN 450-1, even though those fly ashes appeared qualitatively suitable for use in concrete.

The use of coal-based fly ash as a clay substitute during the production of Portland clinker is not subjected to standards or regulations. The ash requirements are typically established in bilateral contracts as a result of the specific needs of each individual cement plant. These needs are governed by the composition of lime stone and/or marl as well as the plant configuration. The use of siliceous and calcareous fly ash as a constituent of blended cements is defined by EN 197-1 (2011), for which the most important requirements are provided in Table 3. The use of ashes that were obtained from elevated co-firing ratios can be used as raw material in cement production, since a cement producer eventually chooses the fly ash ratio in the raw meal mix.

Further specific thresholds in EN 450-1 are provided for the loss on ignition, as well as the sulfur and chlorine content. The latter are intended to inhibit undesired expansion or reactions in concrete constructions. The use of fly ash with a LOI of up to a mass fraction of 7.0% or 9.0% is permitted provided that particular requirements for durability – especially frost resistance – and compatibility with admixtures are met, in accordance with the appropriate local standards and regulations for concrete and mortar. The requirement for LOI is prescribed by national application documents [38].

This work presents the fly ash quality evaluations from wood dust co-firing with a hard coal and wood dust mono-combustion in an industrial pulverized fuel power plant, along with evaluations of the energy crop *Cynara Cardunculus* (cardo) in various co-firing shares with a Greek lignite, ranging from (0 to 100) % in a pulverized fuel pilot-scale test facility. Cardo is a perennial, herbaceous crop of Mediterranean origin well adapted to the xerothermic conditions of Southern Europe [39,40] with reported high yield potentials [40,41]. Hard coal and lignite is available in most European countries, most notably in Eastern Europe, while most of Southern Europe and Western Europe will continue to import sources or switch to other sources in the future [2]. Thus, the fly ash assessments for wood dust firing are likely more applicable to power plant operations in Western and most of Southern Europe, whereas the co-firing cases with cardo are more applicable to Eastern Europe and some of Southern Europe. The present paper

presents scarce work done on investigating biomass fly ashes utilization, which is obtained from combustion of high thermal shares in pulverized fuel boilers.

## 2. Materials and methods

### 2.1. Pilot-scale test facility

Fig. 1 shows a diagram of the pilot-scale test facility. The facility consists of a cylindrical combustion chamber with a top-fired swirl burner, a SCR catalyst, an ESP, and a fabric filter. In the inner annulus of a swirl burner the coal is injected with primary air and a center pipe allows injecting of secondary fuels. The computer aided monitoring system for the mass flow of the secondary fuel dosing system allows for a precise tuning of the desired biomass mass fraction in the fuel feed. The maximum thermal load of the facility is 0.5 MW. A more detailed description is provided in Ref. [42].

### 2.2. Large-scale industrial power plant facility

The large scale demonstration of pure wood dust firing was at Rodenhuize power plant, Unit 4, owned by GDF Suez (Belgium) located in Gent, Belgium. The unit started up on 100% biomass firing in May 2011, and it has been routinely operated in this way since September 2011, with a capacity of about 180 MW<sub>el</sub> pure wood dust firing, approximately 560 MW<sub>th</sub>. It is a pulverized fuel dry bottom boiler with low NO<sub>x</sub> burners, a high-dust SCR, and an ESP for air pollution control devices. Fig. 2 shows a schematic of the boiler.

The co-firing rate sequence of the unit was in 2009 increased biomass thermal share fraction from (25 to 50) %, known as “Advance Green”, and in 2012 a demonstration for increased biomass share to 100% thermal share, known as “Max Green”, took place. The Rodenhuize power plant also serves as a back-up for a new, dedicated Blast Furnace Gas (BFG) unit located on the Arcecor–Mittal site, within the industrial area in the vicinity of the power plant. A pneumatic conveying system is used to transport the milled wood dust from the 12 hammer mills to the 24 burners of the boiler. The wood dust is transported in dense phase independently from the primary air and is injected in a concentric way inside the primary pipe about one meter upstream of the inlet to the burner.

### 2.3. Analyses

The characterization of the biomass fuels was performed according to the European standards drawn up by the Technical Committee CEN/TC 335 for biomass solid fuels. Tables 4–6 show the fuels proximate and ultimate analyses. As expected, there were noticeable differences in the moisture and ash contents of the lignite and hard coal versus the volatile content of the biomass fuels.

Fuel ashes were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) to determine concentrations of the major and minor elements in accordance with DIN 51729. Figs. 3–5 show the fuel ash components.

Fig. 3 shows the contents of alkalis and sulfur is higher for the cardo, while the silica, iron and alumina contents are lower. The silica, alumina, and iron are known to contribute to the pozzolanic reactivity of fly ashes. The higher contents of alkali, sulfur and phosphorous oxide warrant caution in regards to fly ash quality.

Fig. 4 shows that the wood dust I, the quality for the Advanced Green case, hereafter referred to as wood or wood dust, had also a decrease in silica and alumina, while having increases in alkalis, sulfur, phosphorous oxide, and calcium oxide. The increase in calcium oxide could be positive if it leads to more amorphous calcium with cementitious properties.

**Table 3**  
Requirements for fly ash use in cement by EN 197-1.

Parameter	Siliceous fly ash [mass fraction percent]	Calcareous fly ash [mass fraction percent]	
	V	W1	W2
Loss on ignition <sup>a</sup>	Category A: 0 – 5 Category B: 2 – 7 Category C: 4 – 9		
Reactive calcium oxide <sup>b</sup>	≤10	10–15	≥15
Free calcium oxide <sup>c</sup>	≤1		
Reactive silicon dioxide <sup>d</sup>	≥25		–
Compressive strength after 28 days <sup>e</sup>	–	–	≥10 MPa
Expansion <sup>f</sup>	–	–	≤10 mm

<sup>a</sup> LOI of up to (7 or 9) mass % accepted in case durability requirements at end-use site are met.

<sup>b</sup> Fraction that under normal hardening conditions can form calcium silicate hydrates or calcium aluminate hydrates.

<sup>c</sup> Up to 2.5 mass % accepted provided that expansion threshold of 10 mm or lower is met.

<sup>d</sup> Fraction that is soluble after treatment with hydrochloric acid (HCl) and with boiling potassium hydroxide (KOH) solution.

<sup>e</sup> For a mortar with pulverized fly ash (<40 μm) as binder at concentrations between (10 and 30) mass %.

<sup>f</sup> For a mixture 30/70 w/w mixture of pulverized fly ash and CEM I cement.

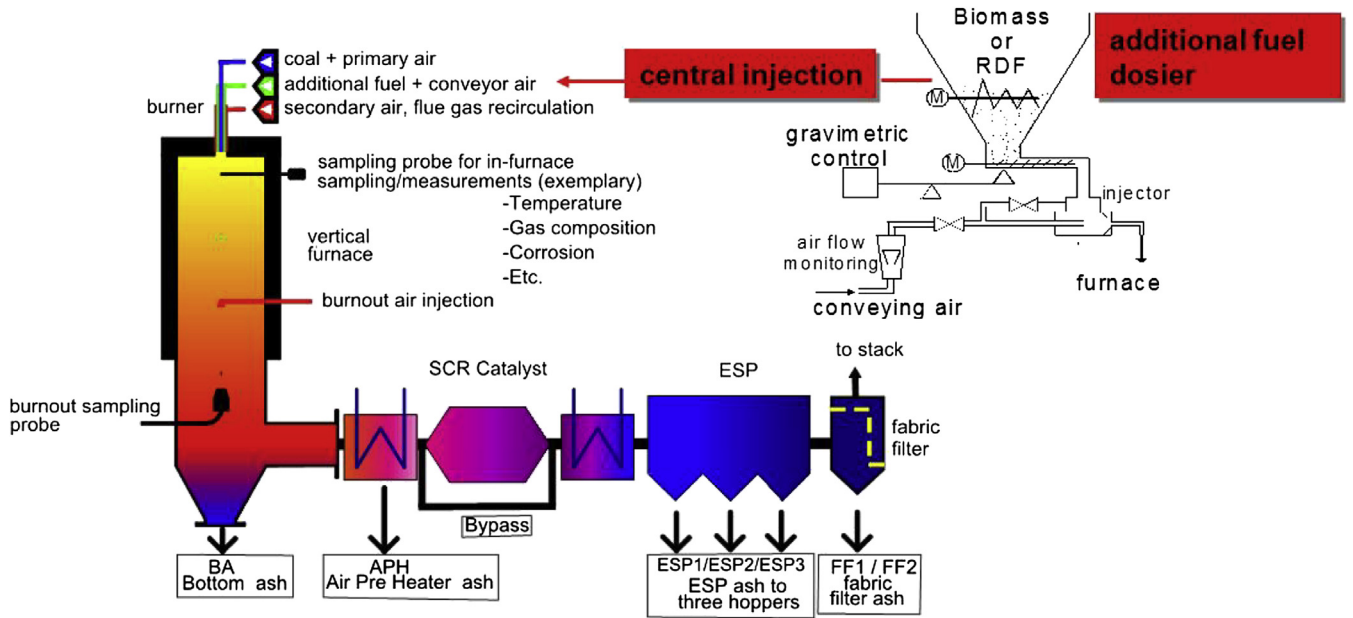


Fig. 1. Institute of combustion and power plant technology (IFK) 0.5 MW<sub>th</sub> pulverized fuel pilot-scale test facility.

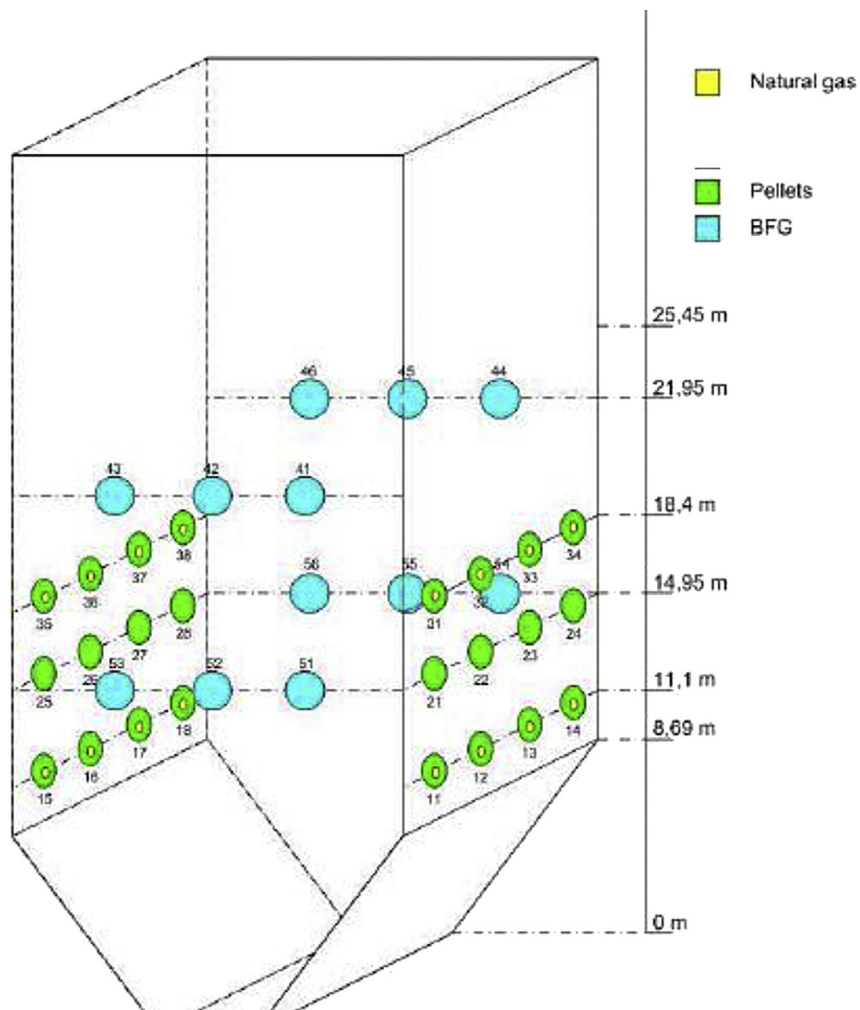


Fig. 2. Rodenhuijze power plant, current configuration (Max Green), wood dust firing at rows 1, 2, and 3; BFG burners at level 5 to level 2.

**Table 4**  
Fuel proximate, ultimate analyses, and calorific values, lignite and cardoon.

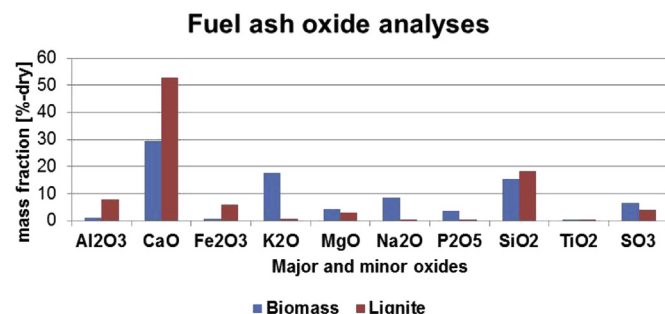
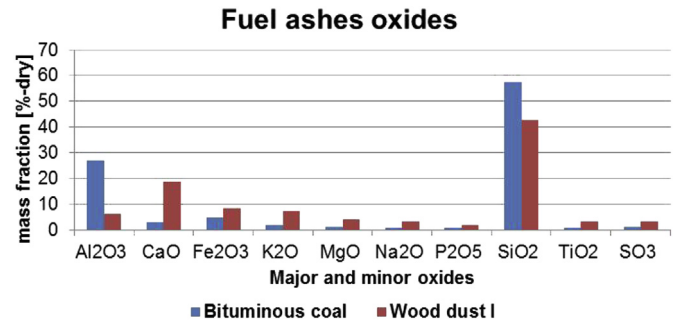
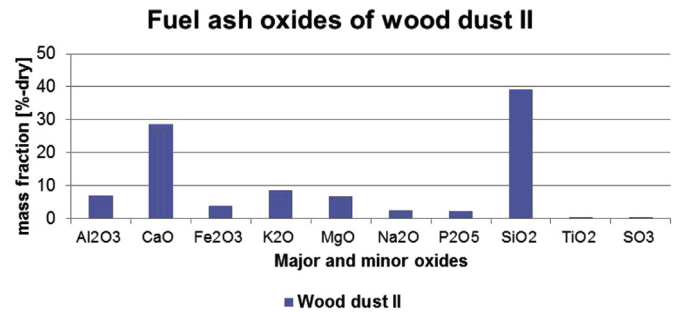
	Lignite	Cardoon
Moisture [mass fraction percent-as received]	53.3	11.4
<i>Proximate analysis [mass fraction percent]</i>		
Volatiles (dry-ash-free)	68.75	83.63
Ash (dry)	31.4	7.73
Fixed carbon (dry-ash-free)	31.25	16.35
<i>Ultimate analysis [mass fraction percent (dry-ash-free)]</i>		
Carbon	58.44	50.71
Hydrogen <sub>(fuel)</sub>	4.9	6.41
Nitrogen	1.44	0.77
Sulfur	0.34	0.2
Oxygen <sub>(by diff.)</sub>	34.88	41.88
Chlorine	<0.01	0.19
<i>Heating values</i>		
LHV [kJ/kg, as received]	4776	15,621
LHV [kJ/kg, dry]	13,014	17,632

**Table 5**  
Fuel proximate, ultimate analyses, and calorific values, “Advanced Green”, Russian hard coal and wood.

	Coal	Wood dust
Moisture [mass fraction percent (%)-as received]	10.4	6.67
<i>Proximate analysis [mass fraction percent]</i>		
Volatiles (dry-ash-free)	39.36	79.70
Ash (dry)	9.0	2.13
Fixed carbon (dry-ash-free)	60.65	20.36
<i>Ultimate analysis [mass fraction percent (dry-ash-free)]</i>		
Carbon	80.68	51.68
Hydrogen <sub>(fuel)</sub>	5.64	5.74
Nitrogen	2.35	0.42
Sulfur	0.39	<0.3
Oxygen <sub>(by diff.)</sub>	12.37	38.22
Chlorine	<0.01	<0.3
<i>Heating values</i>		
LHV [kJ/kg, as received]	26,068	17,396
LHV [kJ/kg, dry]	29,114	18,917

**Table 6**  
Fuel proximate, ultimate analyses, and calorific values, “Max Green”, mono-wood dust combustion.

	Wood dust
Moisture [mass fraction percent (%)-as received]	4.9
<i>Proximate analysis [mass fraction percent]</i>	
Volatiles (dry-ash-free)	81.50
Ash (dry)	0.66
Fixed carbon (dry-ash-free)	18.52
<i>Ultimate analysis [mass fraction percent (dry-ash-free)]</i>	
Carbon	50.80
Hydrogen <sub>(fuel)</sub>	6.44
Nitrogen	<0.3
Sulfur	0.032
Oxygen <sub>(by diff.)</sub>	42.02
Chlorine	<0.01
<i>Heating value</i>	
LHV [kJ/kg, as received]	17,459
LHV [kJ/kg, dry]	18,484

**Fig. 3.** Cardoon (biomass) and Greek lignite, pilot-scale experiments.**Fig. 4.** Hard coal and wood dust, Rodenhuize power plant, “Advance Green”.**Fig. 5.** Wood dust fuel ash oxides, Rodenhuize power plant “Max Green”.

In Fig. 5 the wood dust II, the quality for the Max Green case, hereafter referred to as wood or wood dust, is again shown to have high amounts of silica and calcium oxide, which contributes significantly to pozzolanic behavior and cementitious behavior of fly ashes, respectively. The wood dust qualities are similar and comparable.

The morphology of samples was observed using Zeiss LEO 1455VP scanning electron microscope (SEM). The SEM was operated with a typical accelerating voltage of 20 keV. The microscope had an Oxford Instruments INCA system for energy dispersive X-ray fluorescence analysis (EDX). The elements present in a scanned area were determined from the analysis of energy dispersive spectra (EDX) that are produced by X-ray excitation from the particles under the electron beam. Each sample was prepared by coating with a gold layer of approximately 10 nm. The analyses involved backscattered electron and secondary electron images.

#### 2.4. Fuel preparation and characterization

The cardoon pellets was provided by the Greek Centre for Research and Technology Hellas Chemical Process and Energy Resources Institute (CERTH/CPERI), and the Public Power Corporation, currently the owner and operator of all lignite-fired power plants in Greece, provided the lignite used. The cardoon pellets were prepared by milling at the biomass milling facility at IFK. The lignite was prepared through using a fan beater mill that is part of the pulverized fuel pilot-scale test facility. Due to the low heating value and high moisture content of the lignite, natural gas was used in order to support the flame in the near burner region. The  $d_{10}$ ,  $d_{50}$ ,  $d_{90}$  of the cardoon was 33.72  $\mu\text{m}$ , 244.01  $\mu\text{m}$ , and 838.34  $\mu\text{m}$ , respectively. The lignite had a  $d_{50}$  of about 105  $\mu\text{m}$  and  $d_{90}$  of about 475  $\mu\text{m}$ . The larger particle size for cardoon is indicative of the need for a longer residence time in order to achieve a good burnout.

For the large scale industrial campaign with co-firing Russian hard coal and wood dust (Advance Green), the wood pellet suppliers were from Canada, Scandinavia, and Baltic States. After



**Table 7**  
Comparison of fly ash oxides with SIP, Rodenhuize power plant.

Mass fraction percent of each equivalent oxide	Limit range [mass fraction percent]	Rodenhuize Advance Green		Rodenhuize Max Green
		50% wood/50% coal	100% wood	100% wood
CaO	0.1–45	8.72	23.14	31.54
SiO <sub>2</sub>	20–76	52.20	41.60	38.35
K <sub>2</sub> O	0.01–8	4.19	6.82	10.5
SO <sub>3</sub>	0.01–15	0.90	3.64	0.61
P <sub>2</sub> O <sub>5</sub>	0.01–10	1.05	2.17	2.11
MgO	0.01–15	2.49	6.26	5.4
Fe <sub>2</sub> O <sub>3</sub>	0.01–27	5.61	3.85	3.8
Al <sub>2</sub> O <sub>3</sub>	5–40	23.03	10.31	6.23
Na <sub>2</sub> O	0.01–8	0.94	1.15	1.04
TiO <sub>2</sub>	0.01–8	0.86	1.00	0.37
LOI	0.1–20	–	–	14.2
Free CaO	0.01–9	–	–	–

arriving at a terminal in the neighborhood of the Rodenhuize power plant (Sea Invest), the pellets were stored there and due to the way of discharging different cargos next to or on top of each other it was possible that they were blended before being sent to the plant via a conveyor belt. Thus, the result is that the origin of the pellets fired during the large-scale demonstration campaign may have been a slight blend. The  $d_{10}$ ,  $d_{50}$ ,  $d_{90}$  of the wood dust fired during the Advanced Green large-scale tests were about 105  $\mu\text{m}$ , 485  $\mu\text{m}$ , and 920  $\mu\text{m}$ , respectively. The company Enviva, with origins in the southern part of the United States of America in the state of Georgia produced the wood pellets for the Max Green case. The  $d_{10}$ ,  $d_{50}$ ,  $d_{90}$  of the wood dust fired during this case were nearly the same values as for the Advanced Green case. All the wood pellet characteristics had to be within the ranges of the Initiative of Wood Pellets Buyers (IWPB) specifications [13], which is a basis for the procurement of wood pellets and is followed at the Rodenhuize power plant.

### 2.5. Investigated cases

The scenario for the large scale demonstration consisted of pure wood dust combustion and a co-combustion share of 50% on a

thermal share basis. The fuel mixtures on a thermal share basis for the pilot-scale fly ash cases tested were as follows:

- Case 1: 100% lignite, 0% cardoon;
- Case 2: 90% lignite, 10% cardoon;
- Case 3: 50% lignite 50% cardoon; and
- Case 4: 0% lignite 100% cardoon.

## 3. Results and discussion

### 3.1. Large-scale industrial power plant facility

In assessing the fly ashes with the requirements according to the REACH Regulation in order for fly ashes to be registered, the fly ashes oxides amounts were compared with those ranges listed in the Substance Identity Profile (SIP) for ashes (residues), and coal for substance sameness checking [43]. Table 7 shows results for comparing fly ashes obtained from industrial scale demonstration short-term trials with SIP chemical oxide requirements.

Table 7 shows that the fly ashes generated meet the main oxide constituents in accordance with the REACH Regulation. Thus, such ashes could be registered in the database and continue with procedures to ensure they are marketable in the EU. This would entail evaluating certain mineral phases as required by the SIP, assessing other chemical constituents, evaluating physical parameters, and continuing with conducting performance based evaluations that identify the best utilization option for the generated ashes. Therefore, once the ashes have been associated with a good sustainable utilization practice, their marketability would be guaranteed by registration through the REACH Regulation database and the issuing of an ETA, if necessary.

Results of the fly ash monitoring from the industrial power plant short-term tests according to some EN450-1 parameters are displayed in Table 8.

These results in Table 8 demonstrate that none of the sampled fly ashes comply with the standard, but the 50% thermal share will meet the upcoming revised standard, issued in 2013. As such the use of the ash in concrete is subject to a European Technical Approval (ETA).

**Table 8**  
Compliance results of fly ash with EN 450-1, short-term tests, (red color indicates non-compliance).

Developments phase of concrete	Parameter	Limit [by mass]	Rodenhuize Adv. green		Rodenhuize Max Green
			50% wood/50% coal	100% wood	100% wood
Durability	SO <sub>3</sub>	≤ 3%	3.1	1.9	0.4
	Cl	≤ 0.10%	0.0	0.0	0.0
	Na <sub>2</sub> O <sub>eq</sub>	≤ 5.0%	5.5	7.6	2.2
	MgO	≤ 4.0%	3.2	3.9	5.5
Strength development	SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	≥ 70%	74.8	67.0	40.3
Other parameters					
Fly ash category	-		A	C	A
Initial strength gain	≤ P <sub>2</sub> O <sub>5</sub>	≤ 5.0% <sup>12</sup>	1.5	1.5	1.8
Co-firing	EN 450	≤ 20.0%	No	No	No
Co-firing	EN 450 (revised)	≤ 50.0%	Yes	No	No

<sup>12</sup>Will only apply in revised EN 450-1



**Table 9**  
Compliance results of fly ash with EN 450-, long-term monitoring, (red color indicates non-compliance).

Developments phase of concrete	Parameter	Limit [by mass]	Rodenhuize Adv. green		Rodenhuize Max Green
			50% wood/ 50% coal	100% wood	100% wood
Durability	SO <sub>3</sub>	≤ 3%	1.0	3.4	0.5
	Cl	≤ 0.10%	0.1	0.6	0.7
	Na <sub>2</sub> O <sub>eq</sub>	≤ 5.0%	4.0	5.3	7.0
	MgO	≤ 4.0%	2.7	5.8	4.8
Strength development	SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	≥ 70%	88.1	52.1	42.6
Other parameters					
Initial strength gain	≤ P <sub>2</sub> O <sub>5</sub>	≤ 5.0% <sup>13</sup>	1.1	2.0	1.9
Co-firing	EN 450-1	≤ 20.0%	No	No	No
Co-firing	EN 450-1 (revised)	≤ 50.0%	Yes	No	No

<sup>13</sup>Will only apply in revised EN 450-1

Furthermore, the fluctuations in silica content can be significant as a result of less silica from clay minerals in the fuel blend; these fluctuations are an important hurdle for use of ash in the construction industry. The results in Table 8 were obtained from short-term parameter tests; any variation in fuel quality can have a large impact on the ash quality, and subsequently compliance with standards. Therefore, long-term monitoring campaigns were conducted at the power plants, for which the results are displayed in Table 9.

Results in Table 9 indicate that in case of 50% co-firing of clean wood in Rodenhuize, the ashes are fully compliant with nearly all requirements of the current EN 450-1. Currently this would require an ETA, although co-firing ratios up to 50% thermal share will be compliant with the newly revised EN 450-1, issued in 2013. The definition of fly ash according to EN 450-1 is similar in EN 197-1; compliance in accordance with EN 450-1 usually also results in compliance with EN 197-1. Even non-compliance with EN 450-1 can lead to the use as raw material during cement production, since a cement producer eventually chooses the fly ash ratio in the raw meal mix.

The fly ashes that were sampled during the short-term parameter tests in the Advanced Green scenario at the Rodenhuize power plant were not compliant with the chemical requirements posed in EN 450-1. For this purpose a number of additional experiments were conducted to determine whether the fly ashes during this scenario could be suitable for use in alternate applications, such as

low-grade concrete products. These experiments were not repeated for the fly ashes obtained during the Max Green scenario, as it is thought to have similarities with 100% wood firing in the Advanced Green scenario. Fig. 6 shows the results of the reactive silicon dioxide test.

The reactive silicon dioxide (SiO<sub>2</sub>) was evaluated to ensure the fly ash will be able to have enough pozzolanic qualities. The standard, EN 450-1, requirement states the value should exceed a mass fraction of 25%. The analyses of the fly ash samples collected during the Advanced Green short-term campaign at Rodenhuize indicate that sufficient reactive silicon dioxide is present during 50% thermal share of co-firing of wood, as well as 100% wood firing. Furthermore, this indicates there potential suitability as use in the production as cement as the reactive silicon dioxide meet the limit according to EN 197-1.

Samples of cement type CEM I 42.5 was replaced with fly ash (as it is) at a mass fraction of 25% and tested with respect to the mechanical properties. Mechanical strength development and the activity index were evaluated for 28 and 90 days. Fig. 7 display results of compressive strength.

Fig. 7 demonstrates that the compressive strength development for the fly ashes is comparable to the reference cement, with the improvement over 90 days being known in the industry. The pure biomass fly ash performance during the 90 day time frame, which was also an improvement to the reference cement, is a different occurrence one would expect when considering the relatively low

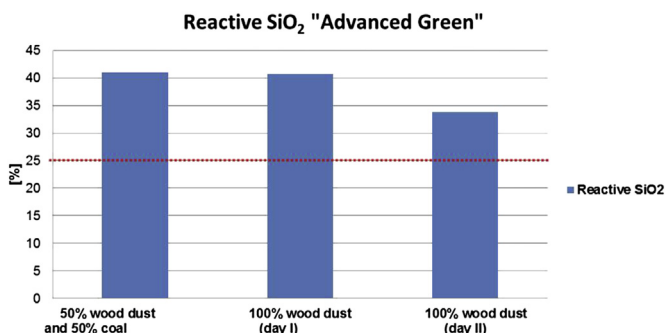


Fig. 6. Reactive silicon dioxide content of fly ashes, "Advanced Green".

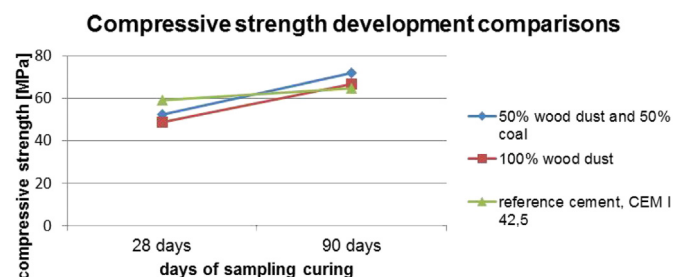


Fig. 7. Compressive strength development of fly ashes, "Advanced Green".

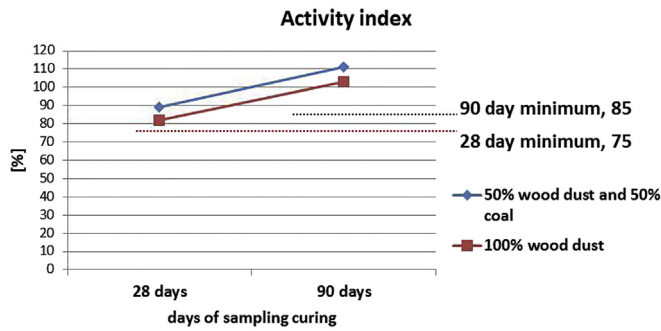


Fig. 8. Activity index of fly ashes, Advanced Green.

amount of summed oxides in case of 100% wood firing. Therefore, it appears that there is either a certain form of silica in the biomass fly ash present rendering it more suitable for strength gain applications than initially expected, or it is a phenomenon of an amorphous calcium content giving rise to a higher cementitious property. Further work is needed to detail this finding. Fig. 8 shows results of the activity index tests.

The activity index is defined as the ratio in percentages of the compressive strength of standard mortar bars –prepared with a mass fraction of 75% test cement and a mass fraction of 25% fly ash– over the compressive strength of standard mortar bars prepared with 100% test cement, when tested during the same duration. The requirement for the activity index is that at 28 days and 90 days it should not be lower than 75% and 85%, respectively. Fig. 8 illustrates that both criteria are met in case of 50% thermal share of co-firing of wood and 100% wood dust firing. It should be noted that the results of the activity index experiments give no direct information on the strength contribution of fly ash in concrete. However, these do imply that the fly ashes have good pozzolanic activities in alternative end use applications, such as making of bricks, low grade road repairs, etc.

The fly ash samples that were collected during short-term parameter tests (Advanced Green) have also been investigated for use as fertilizer, of which the results are displayed in Table 10. The results of these fly ash analyses have been compared with a number

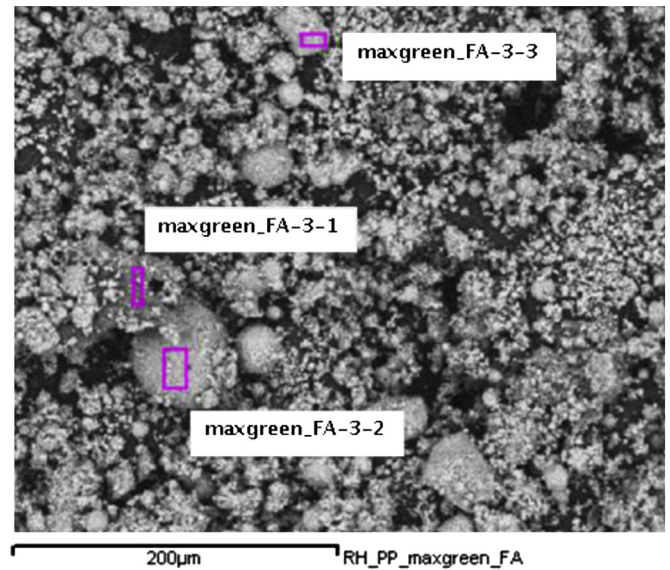


Fig. 9. SEM micrograph of fly ash particles.

of current member state regulations. These regulations mostly define maximum metal thresholds, and in some occasions also minimum nutrient content.

The results in Table 10 indicate that both fly ashes from Rodenhuize’s “Advanced Green” scenario could actually be used as fertilizer in forestry in Finland, while the ashes of 50% thermal share co-firing could also be used in Austria. The limits for other member states tend to be more stringent which leads to non-compliance with respect to requirements for cadmium, copper, lead, chromium and zinc content. Assessing long-term monitoring leaching results for the “Max Green” scenario, not shown, according to the local Flemish legislation for utilization of by-products as a construction material and for soil improvements, revealed that only one parameter was outside the requirements, namely the leaching of Cr<sup>6+</sup>. The origin of Cr is not clear. Although that parameter is only explicitly mentioned for use as construction material, interested

Table 10  
Compliance results of fly ash as fertilizer in accordance with member state regulations, Rodenhuize.

Country	Austria <sup>a</sup>	Denmark <sup>b</sup>	Finland <sup>b</sup>		Germany <sup>c</sup>	Sweden <sup>b</sup>	Rodenhuize 50% wood	Rodenhuize 100% wood
Use	Fertilizer	Fertilizer	Forestry	Agriculture	Fertilizer	Forestry		
<i>Minimum nutrient content [g/kg]</i>								
Ca			60	80			87	165
K							43	59
Mg							19	33
P							7	8
Zn							0.4	0.8
K + P			10	20			49	66
<i>Maximum metal content [mg/kg]</i>								
Cd	5/8	5/15 <sup>d</sup>	17.5	1.5	1.5	30	3.0	8.8
Cu	200/250		700	600		400	120	320
Pb	100/200	120	150	100	150	300	82	250
Cr	150/250	100	300	300		100	145	160
Zn	1200/1500		4500	1500		7000	350	810
As	20/20		30	25	40	30	15	14
Ni	150/200	30/60	150	100	80	70	67	59
Hg		0.8	1.0	1.0	1.0	3.0	0.4	0.4
Se								
B						500		

<sup>a</sup> BMLFUW (2011); values below lower limit requires no chemical analysis of the soil; values up to the upper limit do require chemical analysis of the soil.

<sup>b</sup> Nordic Innovation Centre (2008), for Denmark and Finland the figures are regulated; for Sweden the figures are recommendations.

<sup>c</sup> LAGA (1998).

<sup>d</sup> Straw ash/wood ash.

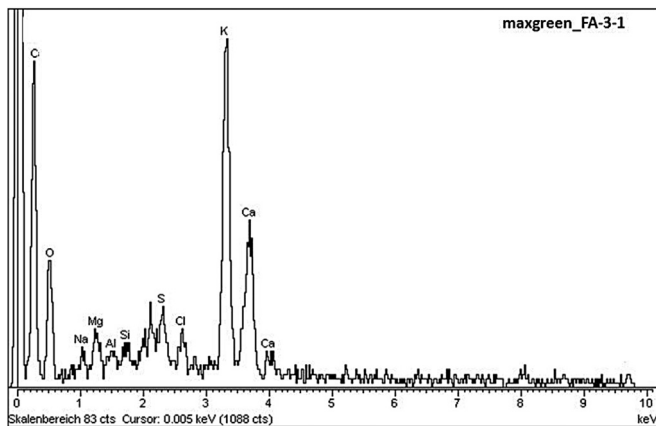


Fig. 10. EDX spectrum of fly ash particle, FA 3-1, Rodenhuize power plant.

parties for utilization as soil improver or fertilizer fear that it can also lead to problems. The question of what parameters are really important and what is the limit value of other parameters in case of reusing ashes from 100% biomass combustion as fertilizer or soil improver is an actual issue. Further work is required to address the issue. The following Figs. 9–12 show SEM pictures and EDX diagrams of fly ash for the Max Green case, the new configuration of the power plant.

From the SEM picture of the fly ash one can see spherical particles of many size ranges, non-spherical particles, and particles with holes representing hollow particles. The varying sizes in the

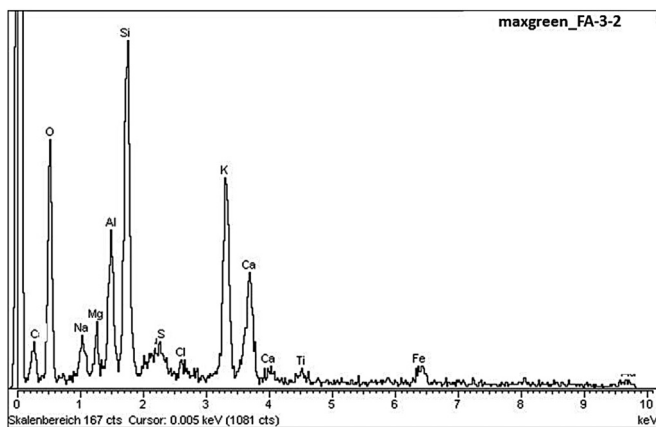


Fig. 11. EDX spectrum of fly ash particle, FA 3-2, Rodenhuize power plant.

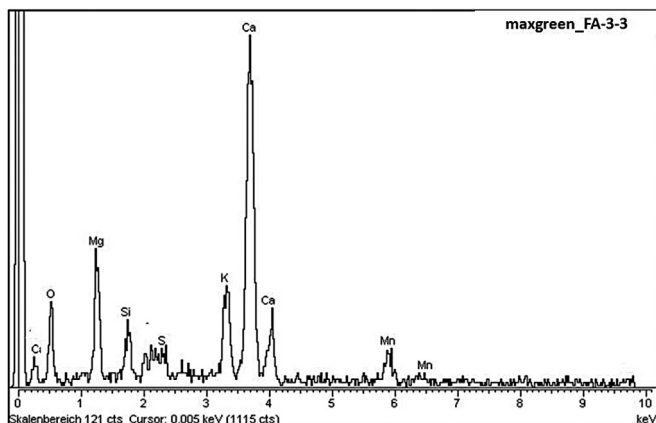


Fig. 12. EDX spectrum of fly ash particle, FA 3-3, Rodenhuize power plant.

particle spheres suggest a possible application as cenospheres recovery, recovering the smaller particles and hollow particles. The EDX diagrams show that Ca, Si, C, Mg, and Al had high intensity peaks in some diagrams compared to other identified elements. The carbon and calcium contents suggest possible use in emission abatement processes. The aluminum content may suggest a possibility to recover the metal, which would support reducing the dependency upon extraction of these metals from primary products and better sustainable practices in the industry. Alternative cements and geopolymers are options, as the fly ash appears to exhibit a good quality as an alumina–silica source material for those processes. Also, utilizing the fly ash in the production of cement clinker is an option, which will reduce the CO<sub>2</sub> emissions associated with the cement clinker production process, which is estimated at about 7% of all anthropogenic CO<sub>2</sub> emissions. These applications would require further studies and all associated cost factors must be addressed that could lead to issuing an ETA for such uses. However, these have been shown to be promising routes that warrant a stronger focus towards creating possible EU standards or regulations to guide their applications in those market value end-uses, among others.

### 3.2. Pilot-scale pulverized fuel test facility

In assessing the fly ashes with the composition of main constituents requirement according to the REACH Regulation in order for fly ashes to be registered, the fly ashes oxides amounts were compared with those ranges listed in the SIP for ashes (residues), and coal for substance sameness checking. Table 11 shows results for comparing fly ashes obtained from pilot-scale experiments with SIP chemical oxide requirements.

Table 11 shows that generally the fly ashes generated meet the main oxide constituents in accordance with the REACH Regulation, except the thermal shares of 10% and 50%. That discrepancy is minor, which could be due to how the calcium oxide is bound, and could easily be mitigated by ash post processing, if necessary. Thus, such ashes could be registered in the database and continue with procedures to ensure they are marketable in the EU. Again, this would entail evaluating certain mineral phases as required by the SIP, assessing other chemical constituents, evaluating physical parameters, and continuing with conducting performance based evaluations that identify the best utilization option for the generated ashes, leading to issuing an ETA for such ashes. Tables 12 and 13 show the fly ashes compared to fertilizer use requirements from some EU member states national standards.

From the comparison in Tables 12 and 13 one observes that the limits in the solid bulk ash compositions are out of specification for Ni and As for fertilizer consideration. The fly ashes may likely still

Table 11  
Comparison of fly ash oxides with SIP, pilot-scale tests.

Mass fraction percent of each oxide	Limit range	100% lignite	10% cardoon	50% cardoon	100% cardoon
CaO	0.1–45	43.54	48.03	46.27	43.93
SiO <sub>2</sub>	20–76	31.34	28.47	28.25	26.93
K <sub>2</sub> O	0.01–8	0.87	1.06	1.86	4.22
SO <sub>3</sub>	0.01–15	5.52	6.43	7.16	8.05
P <sub>2</sub> O <sub>5</sub>	0.01–10	0.33	0.31	0.42	0.68
MgO	0.01–15	3.67	3.67	3.83	3.78
Fe <sub>2</sub> O <sub>3</sub>	0.01–27	5.11	4.48	4.31	4.21
Al <sub>2</sub> O <sub>3</sub>	5–40	8.92	6.87	6.92	6.52
Na <sub>2</sub> O	0.01–8	0.18	0.29	0.58	1.31
TiO <sub>2</sub>	0.01–8	0.52	0.41	0.40	0.38
LOI	0.1–20	–	–	–	–
Free CaO	0.01–9	–	–	–	–

**Table 12**

Compliance results of fly ash as fertilizer in accordance with member state regulations, pilot-scale tests, I.

Country	Austria <sup>a</sup>	Finland <sup>b</sup>		Germany <sup>c</sup>		
Use	Fertilizer	Forestry	Agriculture	Fertilizer	100% lignite	10% cardoon
<i>Maximum metal content [mg/kg]</i>						
CD	5/8	17.5	1.5	1.5	0.97	0.84
CU	200/250	700	600		66.4	31.9
PB	100/200	150	100	150	23.2	14.4
CR	150/250	300	300		209	196
CR (VI)				2		
ZN	1200/1500	4500	1500		87.9	79.1
AS	20/20	30	25	40	66.6	71.2
NI	150/200	150	100	80	212	214
HG		1.0	1.0	1.0	<0.1	<0.1

<sup>a</sup> BMLFUW (2011) values below lower limit requires no chemical analysis of the soil; values up to the upper limit do require chemical analysis of the soil.

<sup>b</sup> Nordic Innovation Centre (2008), for Denmark (values not shown) and Finland the figures are regulated; for Sweden (values not shown) the figures are recommendations.

<sup>c</sup> LAGA (1998).

**Table 13**

Compliance results of fly ash as fertilizer in accordance with member state regulations, pilot-scale tests, II.

Country	Austria <sup>a</sup>	Finland <sup>b</sup>		Germany <sup>c</sup>		
Use	Fertilizer	Forestry	Agriculture	Fertilizer	50% cardoon	100% cardoon
<i>Maximum metal content [mg/kg]</i>						
CD	5/8	17.5	1.5	1.5	0.90	0.99
CU	200/250	700	600		38	63.4
PB	100/200	150	100	150	13.6	16.9
CR	150/250	300	300		196	200
CR (VI)				2		
ZN	1200/1500	4500	1500		84.7	125
AS	20/20	30	25	40	81.3	76.2
NI	150/200	150	100	80	182	154
HG		1.0	1.0	1.0	<0.1	<0.1

<sup>a</sup> BMLFUW (2011) values below lower limit requires no chemical analysis of the soil; values up to the upper limit do require chemical analysis of the soil.

<sup>b</sup> Nordic Innovation Centre (2008), for Denmark (values not shown) and Finland the figures are regulated; for Sweden (values not shown) the figures are recommendations.

<sup>c</sup> LAGA (1998).

be utilized for, among others, low grade strength applications, low grade in-fill applications, or other construction applications if an ETA can be obtained. It has been shown that metals can be captured from filter ashes as a metal recovery option from fly ashes [35]. Thus, applying a metal recovery process to the ashes before other utilization options would lead to a higher value residual ash for the market. The cost of the recovery would likely be paid by selling the recovered metals on the applicable market.

**Table 14**

Compliance of fly ash for mine backfilling with Germany regulations, pilot-scale tests.

Country	Germany <sup>a</sup>				
Use	Mine backfilling	100% lignite	10% cardoon	50% cardoon	100% cardoon
<i>Maximum metal content [mg/kg]</i>					
CD	10	0.97	0.84	0.90	0.99
CU	600	66.4	31.9	38	63.4
PB	1000	23.2	14.4	13.6	16.9
CR	600	209	196	196	200
CR (VI)					
ZN	1500	87.9	79.1	84.7	125
AS	150	66.6	71.2	81.3	76.2
NI	600	212	214	182	154
HG	10	<0.1	<0.1	<0.1	<0.1

<sup>a</sup> LAGA (1998).

Table 14 shows results for comparison with mine backfilling limits in Germany. In Table 14 it is shown that all fly ashes meet the requirements for mine backfilling according to the Germany standard. This is a known practice with lignite ashes in many EU member states with significant lignite mines deposits, and the practice can be maintained even with high thermal shares up to pure combustion of a herbaceous biomass. Therefore, it appears that high thermal shares of a herbaceous biomass with a lignite fuel would not result in a fly ash that would negatively impact a main current practiced utilization option.

#### 4. Conclusions

It can be stated that using biomass fly ashes is more straightforward when assessing compliance with standards where their impact on the chemical and physical parameters is minimal or negligible, in order to deploy established fly ash utilization options. Elevated co-firing shares tend to hamper this, since biomass typically displays a broad variation in composition, ash content, and ash quality also over time.

Two types of fly ash qualities scenarios were considered. Pure wood dust combustion fly ash is likely more applicable for Western and some parts of Southern Europe. Those regions tend to import more hard coal and a clean green wood could be a substitute for the hard coal. The consideration of a high thermal share of a herbaceous biomass with a lignite is likely more applicable to Eastern Europe and a small part of Southern Europe, since the climate is more favorable for growing herbaceous biomass and lignite mines are in large numbers in those regions. Moreover, herbaceous biomass and forest residues are among the highest biomass potentials for bioenergy in the EU. It is believed that all fly ashes generated will be able to meet registration requirements according to the REACH Regulation, rendering them marketable in the EU.

A fair number of European standards are available for ash utilization options of coal combustion derived fly ash. Some of these standards may currently be under revision, as was the case with the revised EN 450-1 that defines the use of fly ash in concrete. The revised version allows co-firing shares up to 40% on weight basis for selected secondary streams, as well as up to 50% on weight basis for untreated clean wood. At those co-firing rates the fly ash characteristics will still be largely governed by the ash content of the coal, which is beneficial for compliance with the EN 450-1. Simultaneously, it will become easier for power plant operators to trade fly ash from elevated co-firing shares, since a European Technical Agreement (ETA) will not be required anymore for such a fly ash.

Higher co-firing shares than the maximum in EN 450-1 could still lead to the use as raw material during cement production, since a cement producer eventually chooses the fly ash ratio in the raw meal mix. This project illustrated that the ash obtained from elevated clean wood co-firing shares in the Rodenhuize power plant may be suitable for use in low-grade concrete products. While the fly ash obtained during 50% co-firing of clean wood would comply with the updated version of EN450-1. Furthermore, fly ash obtained during 50% co-firing of clean wood as well as 100% clean wood firing, could be used as forestry fertilizer in Finland. The fly ashes from the herbaceous and lignite co-firing up to pure herbaceous biomass combustion still would meet mine backfilling limits, which gives a boost to higher thermal share of the more problematic biomass types in regards to fly ash utilization.

SEM-EDX analyses showed that from the structure and varying particle sizes of the fly ashes from the pure wood dust firing in the demonstration activity at Rodenhuize power plant suggest possible applications as cenospheres recovery, recovering the smaller particles and hollow particles. The carbon and calcium contents



suggest possible use in emission abatement processes. The aluminum content may suggest a possibility to recover the metal, which would support reducing the dependency upon extraction of these metals from primary products and better sustainable practices in the industry. Alternative cements and geopolymers are options, as the fly ash appears to exhibit a good quality as an alumina–silica source material for those processes. Also, utilizing the fly ash in the production of cement clinker is an option, as the reactive silica limit was met. This will reduce the CO<sub>2</sub> emissions associated with the cement clinker production process, which is estimated at about 7% of all anthropogenic CO<sub>2</sub> emissions.

Further work include evaluations of bioavailability of nutrients, studies of uses not regulated for biomass fly ash that have a high sustainable potential of utilization, evaluating other parameters that should be included to evaluate biomass fly ashes (such as powder X-ray diffraction), and identifying parameters that could support the issuing of standards for biomass ashes in the EU. Furthermore, a multi-component or multi-system utilization approach to the fly ashes would create further utilization options, while providing other alternatives to generate revenue from the use of fly ashes. Such considerations have been the subject of various recent research reported in literature, involving various separation techniques of the different fly ash sizes that have varying morphologies, etc. Further work is required to evaluate the fly ashes in such a manner.

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