

ADVANCED UTILISATION OPTIONS FOR BIOMASS GASIFICATION FLY ASH

A. Gómez-Barea; C. Fernández-Pereira; L.F. Vilches; C. Leiva; M. Campoy; P. Ollero
Chemical and Environmental Engineering Department. Escuela Superior de Ingenieros (University of Seville)
Camino de los Descubrimientos s/n E-41092, Seville, Spain

ABSTRACT: The objective of this work was to search sustainable methods for the direct utilisation of the fly ash generated in a 150 kW_{th} fluidised-bed pilot plant using Orujillo waste, a by-product from olive oil industry. An extensive characterization was made over raw ashes generated in the process. Existing (combustion) fly ash utilisation methods were found not to be directly applicable to these gasification ashes because of the high concentrations of unburned carbon and harmful soluble compounds. Further utilisation options for management of these ashes were identified. Two utilisation paths are investigated in detail in this work: the use of ash in the manufacture of gypsum wallboards and bricks with isolation properties. These utilisation options are based on low-cost preparation methods using ash in significant proportion, yielding a considerable high-value product. They represent promising new applications with high market potential. Dedicated tests to assess these two utilisation options are issued and from this the potential application of these routes is discussed.

Keywords: gasification; pilot plant; waste disposal

1 INTRODUCTION

Fluidised-bed gasification of biomass and waste fuels has been successfully demonstrated for a wide variety of feedstocks. Basic gasification technology exists today but the technical and financial competitiveness of large-scale gasification has to be improved to be comparable to the latest generation of fossil fuel-fired power plants.

Costs related to fly ash disposal represent a significant share of the overall operation costs for gasification-based energy production. Gasification fly ashes differ considerably from conventional combustion ashes. Unburned carbon is generally abundantly present, typically comprising 10–60% of the ash mass. Ashes also contain PAH compounds and in the case of waste gasification, chlorine and heavy metals as well. This makes the management of gasification fly ash a challenging task, especially for contaminated fuels.

In practice, the utilisation methods developed for ashes from combustion processes cannot be directly transferred to gasification ashes. For instance, the utilisation in cement and concrete industry without pre-treatment is not possible for most biomass gasification ashes. The need for pre-treatment has a direct impact on the final cost of the overall process. Consequently, lessening the cost of the biomass and waste gasification by developing sustainable and economical methods for ash utilisation and management is an imperative requirement.

Most of the coal combustion ashes are utilized in building industry applications, including the use as an addition to concrete and as a constituent and raw material for cement. In addition, coal combustion ashes are used as an aggregate or binder in road construction, as mineral fillers and as fertilisers. Waste materials as ash and slag, when properly processed, have shown themselves to be effective as construction materials and readily meet design specifications. The development of new composites made of waste combined with binders offers economic and environmental advantages. However, the amount of ashes added to blends is typically under 50% by weight.

Studies on utilisation routes for fly-ash from biomass gasification process are rather limited. Three main utilisation categories can be identified for the gasification ashes derived from biomass and wastes: (1) Use as fuel if the carbon content is high enough: co-firing in

coal/biomass-fired power plants; firing in a dedicated boiler; replacement fuel in smelters/incinerators and firing in cement kilns; (2) Use in construction: filler in asphalt or asphalt-like products; an additive in concrete manufacturing, bulk construction and raw building material, lightweight bricks, fire-resistant material, and stabilisation/solidification agent. (3) Use in agriculture: directly as fertilizer or as soil improver.

Investigation has been made in our group for searching utilization methods for the fly ashes generated in combustion and gasification processes [1, 2, 3, 4]. One of the most promising biomass in Spain is “Orujillo”, a by-product from the olive oil industry. Approximately 2 Mt/yr of orujillo are generated in Spain, concentrated in Andalusia, a region of southern Spain with a production of 1.2 Mt/yr. The extremely high production of this biomass residue and its heating value of 18.8 MJ/kg make it possible the use of orujillo as fuel for medium-size power plants (12 to 20 MW_e). Nowadays, there are several boilers fuelled with orujillo that generate steam for conventional steam turbines. However, a promising, more efficient alternative is the gasification of this olive residue to produce a gas for a gas engine or even for a gas turbine in a combined cycle [5]. Our group has been working on the utilization potential of the fly ash generated in a 150 kW_{th} FB gasification plant for the last few years [5, 6]. Main result up to now is that direct ash utilisation are not possible because of the high concentration in alkali elements (mainly potassium), chlorine and carbon. This makes some pre-treatment necessary including washing (for alkali metals and chlorine removal), low temperature combustion (for carbon, LOI, PAH reduction), and high temperature treatments (for more persistent contaminants). This treatment represents a significant share of the operating cost and makes the economics problematic for future utilisation of these ashes [7]. Economic methods for management of this type of ash without any pretreatment are more attractive and so two categories of methods have been identified according to the needed degree of pretreatment. First category needs easy-to-apply pretreatment whereas the second use the raw ash as received. The former includes the use of ashes as a soil amendment after leaching and/or low temperature oxidation while the latter includes the use as a secondary fuel in cement kilns and more advanced and innovative utilisation concepts like the use in the manufacture of

construction products such as lightweight wall boards or bricks with special properties. These two last utilisation methods provide attractive ways to valorise difficult fly ashes yielding relatively high-quality products which can compete favourably in the market. This article aims at increasing the knowledge about these two utilisation options.

2 EXPERIMENTAL

2.1 Materials

Ashes: Biomass gasification ashes generated at the DIQA pilot plant (University of Seville, Spain) were used for the present study. Pilot plant gasification tests were carried out at atmospheric pressure and temperatures of 700-850°C in order to assess the technical viability of Orujillo and MBM. General results and conclusions with regard to these technical parameters are fully discussed elsewhere [5, 6]. Besides the hydrodynamic role of the bed material in fluidised bed processes, there is also a major impact caused by the physico-chemical bed material properties on the resulting fly ashes. The bed material used in the pilot plant tests was ofite, a subvolcanic rock having an average particle size of 380 µm and an apparent particle density of 2620 kg/m³. The main characteristics of the solid materials used in the gasification tests are shown in Table I showing the main chemical characterisation of the orujillo, bed material ofite and ash. As seen in the table the potassium content of the ash is very high (6.83% as K₂O). Also, the high amount of unburned matter content (LOI: 18.24) is noteworthy.

Table I: Chemical compositions of fuel, bed material and ash

Parameter	Fuel (Orujillo) (wt%)	Parameter	Ofite (wt%)	Ash (wt%)
LHV (MJ/kg)	14.09	Moisture	0.47	1.31
HHV (MJ/kg)	15.02	Loss on ignition	0.64	18.24
C	36.57	CaO	11.15	23.23
H	3.71	MgO	7.90	8.10
N	1.00	Fe ₂ O ₃	9.15	5.53
O	27.32	Al ₂ O ₃	13.61	8.53
Moisture	10.82	SiO ₂	53.93	43.48
Ashes	20.41	K ₂ O	0.48	6.83
Volatile Matter	53.34	Na ₂ O	3.49	1.51
Fixed carbon	15.44			

Additives for lightweight wall boards: Gypsum (G) was used as binder and vermiculite (V) as an additive for the pastes prepared for manufacturing the plates. Vermiculite is a hydrated silicate comprising magnesium, aluminium and iron which has a flaky structure. Vermiculite is added to the pastes to provide the blends with fire protection properties. The vermiculite used in the present study is a commercial vermiculite with 84.9% of particles less than 1.41 mm in size. Glass fibres (G-F) 2-4 cm long and 20-50 microns in diameter were used to increase the mechanical resistance to bending and fissuring of the plates. To assess the resulting fire resistant properties of the new ash-based boards, they were compared with two commercial products (Com-1 and Com-2). Com-1 is made up of calcium silicate

whereas Com-2 is mainly composed of gypsum and vermiculite.

Clays for the bricks: Three kinds of clay bodies prepared by the addition of orujillo ash to clay compositions were tested. The selected clay compositions are representative of the products in a facing brick manufacturing company. Table II presents the three types of bricks manufactures tested.

Table II: Tested clay bodies

Ceramic composition	Clay (% by mass)	Gasification Ash (% by mass)
1	85 % F_A	15
2	80 % F_B	20
3	85 % F_C	15

2.2 Preparation

Lightweight wall boards shaped as plates: Our main goal was to develop a product with a high amount of fly ash. The composition of the plate was optimised in order to fulfil the requirements that follows: (1) fly ash must be the major component (>50% wt); (2) satisfactory mechanical properties (specified by the requirements demanded for the final product); and (3) acceptable fire resistance behaviour. The composition selected is shown in Table III.

Table III: Composition (wt%) of the plates

Material	BGA	G	V	G-F	Water/solids Ratio
Composition (wt%, dry basis)	60	30	9.5	0.5	0.7

The solid components shown in Table III were placed in a planetary mixer and were mixed until a homogeneous mixture was achieved. Water was gradually added and mechanically blended until a homogeneous paste was obtained. The paste was placed in 2 cm thick, 28 cm high and 18 cm wide moulds. After 24 hours the paste was removed from the moulds and left to cure at ambient temperature for more than 28 days (average temperature: 20°C; average relative humidity: 45%). This paste was also used to make test pieces of different shapes and sizes which were employed in the mechanical tests. Compared to other residues of similar characteristics, the water/solids ratio used in the blend was high [2, 3, 4]. This enabled us to obtain a relatively easy-to-mould product.

Bricks: Clay bricks are usually manufactured from clay, sand and small amount of suitable organic material like sawdust that burns off at the sintering process and gives the bricks the desired porosity. Often some inert material like crushed and milled recycled bricks or coal ash is also added to the mix to control the properties of the mass and finished product. In our investigation we used ash as potential suitable organic material. Carbon containing ash like our gasification ashes would bring inert material to the brick mass and produce porosity at the sintering phase. The high carbon gasification ash is expected to behave like organic material in the sintering leaving small cavities in the brick matrix. We tested three kinds

of clay bodies prepared by the addition of orujillo ash to clay compositions. The selected clay compositions are representative of the products in a facing brick manufacturing company. The ash content in the clay bodies was 15% and 20% by mass. These high ash contents were used to consume a considerable amount of ash in the mix. To the best of our knowledge this percentage is rather high compared with figures tested on brick manufacture trials using fly ash from FB gasification (7). After the mixer was prepared the solid mixture was introduced in an electrical furnace. The firing temperatures tested were 1000°C, 1025°C, 1050°C and 1075°C for 4 h, in a firing time of 24 h approx (cold/cold). Fig. 1 shows various bricks manufactured in the course of the present investigation.



Figure 1: Bricks manufactured during this investigation

2.3 Characterisation

To characterise the physical and mechanical properties of plates under study, some tests were carried out. In addition fire resistance and environmental (leaching tests) properties were also undertaken.

Lightweight plasterboard was characterised by the compressive strength (before and after the fire test), surface hardness based on the plate resistance to penetration of a Shore C durometer, pH, water content obtained by measuring the mass of the sample during the curing process, and accordingly the water absorption capacity. Details of the procedures and results can be found in [8]. The fire resistance properties were calculated using standard fire-resistance tests as described in European regulations [9]. In order to analyse the fire resistance of the plates in a similar way to that recommended by the European standards, the time necessary for the non-exposed surface of the plates to reach 180°C was taken as reference (t_{180}). The environmental study involved subjecting the ash to two well-known leaching tests, the DIN 38414-S4 test [10] and the CEN/TS 14405 column test [11], as well as subjecting the product to one of the most commonly used leaching tests for monolith samples in the waste management field, the NEN 7345 diffusion test [12]. Atomic Absorption Spectrophotometry and Inductively Coupled Plasma techniques were used for metal analysis of DIN 38414-S4, CEN/TS 14405 and NEN 7345 leachates.

Conventional parameters in the brick manufacturing industry were used for characterizing the ash-containing bricks.

3 RESULTS AND DISCUSSION

3.1 Lightweight wall boards

Table IV shows the mechanical properties of the product. It shows the density (ρ), pH, water absorption capacity (A), compressive strength (R_c) and surface hardness (S_H) of the plates. From the density's point of view, the plates (652 kg/m³) maybe classified as low-density gypsum boards [13] (between 600 and 800 kg/m³). From the pH value, the material can also be classified as normal plasterboard (pH between 8.5 and 10) [13]. The high water absorption capacity (67.4%) is probably due to the low density of the plates as well as the high porosity (caused by the addition of vermiculite) and the relatively high particle size of the ash. As can be seen in Table IV the mechanical quality of the material is rather poor. This is concluded by comparing the results shown in Table IV to those shown by mortars manufactured with coal combustion fly ash and fly ash derived from the combustion of the same biomass [1, 2, 3, 4]. Both the high carbon content (high LOI) and a relatively high average ash particle size makes this material less cohesive. It is also worth noting that the surface hardness value, S_H , in Table IV (28 Shore C) is below the minimum requirement of the EU Standards (40 Shore C) [13].

Table IV: Physical and chemical properties of the plates

ρ (kg/m ³)	pH	A(%)	R_c (MPa)	S_H (Shore C)
652	9.95	67.4	0.43	28

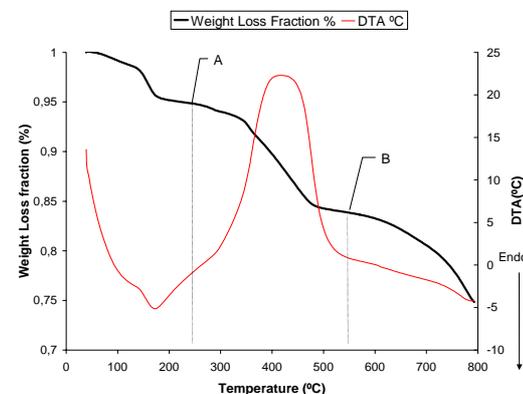


Figure 2: TG and SDTA curves

The presence of water in the tested products is a key parameter related to fire resistance capacity. A high water content has a positive impact on heat propagation resistance. TG and DTA results for the tested material are plotted in Fig. 2, where the change in mass of the product up to approximately 250°C (point A) is due to the evaporation of water. This is supported by observing the endothermic response of the DTA curve from room temperature to 250°C. Between 250 and 550°C (points A and B in the figure) an exothermic process takes place. This can be attributed to the combustion of unburned carbon. As can be observed, the increments are below 20°C for the whole range of temperatures.

The fly ash under research presents high concentrations of unburned carbon (LOI around 18%). This differs considerably from conventional ash

combustion where LOI values of 2-5% are typical. Consequently, a thorough study of the fire resistance behaviour of plates containing gasification ash was undertaken. The fire resistance of the product developed and two commercial plates used for comparison purposes was calculated based on the time necessary for the unexposed side to reach 180°C (t_{180}) when the exposed side was subjected to the standard fire-resistance temperature-time curve. Fig. 3 shows the results obtained in the fire test for 20 mm-thick plates. The t_{180} of the developed product was over 24 min. By comparing the three curves in Fig.3, you can see that the behaviour of the plate tested in this study is similar to that of commercial plates of the same dimensions. In all the cases an evaporation plateau can be observed at approximately 90°C on the unexposed surface, caused by the water present in the plate [1]. As Fig.3 illustrates, the change in temperature of the unexposed surface of the plate (T_{in}) was not significant. This is remarkable because of the relatively high LOI of the ash used in the plate. Moreover, no smoke was emitted from the plate at any time during the test.

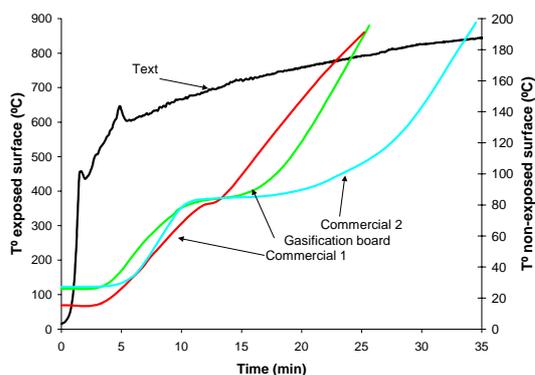


Figure 3: Fire resistance test curves

Table V shows the mechanical properties of the board after the fire test. After the fire test, the compressive strength resistance of the plate dropped dramatically (roughly 95%). This is due to the mass loss that occurred in the mortar after heating (25 % w/w according to the data shown in the TG-SDTA test). The loss of mass in the plate during the fire tests turned out to be lower than in the TG-SDTA test (19.6% w/w vs. 25%). This is probably due to the lack of homogeneity of the temperatures which take place throughout the surface of the plate during the fire-test. The surface hardness also decreased considerably (85% and 67% on the exposed and unexposed surfaces, respectively). The differences between the two S_H values are explained by the low thermal level of the unexposed surface as compared to that of the exposed surface (200 °C vs. 900 °C). Clearly, the higher the temperature, the higher the rate of physico-chemical transformations.

Since the plates studied here were obtained from waste material, an environmental study was carried out to characterize the tested product more completely and be able to better evaluate its possible uses. The study involved subjecting the gasification ash and the plate to three of the most commonly used leaching tests in the waste management field, and a chemical analysis of the leachates obtained. In Spanish legislation there is no

legal requirement for the re-use of waste materials in this type of product. Only the Autonomous Government of Catalonia has established regional regulations for waste management, including limited recycling for some wastes considered as by-products [14]. The recycling procedure requires determining the standard DIN 38414-S4 leachate; after that, the concentration of certain heavy metals in the leachate must be determined. Table VI gives the limits that apply to the assessment of different slags (metallurgical and MSWI slags) in the construction sector, according to Catalan regulations. Taking into account the metal concentrations in the DIN leachate shown in Table VI, the gasification ash could be used in this application, as its chemical parameters are practically below the limits established by the standards. Nevertheless, although the Order on Slag Valorisation mentioned above does not set any limits for PAH in the slags, it does fix a limit for unburned matter (LOI) in MSWI slags at 5 wt%, a value clearly under the 18% wt% measured in orujillo ash. Thus, though the heavy metal leachability of the ash is low, it would require a pre-treatment stage, probably through combustion, prior to its use in this kind of application.

Table V: Mechanical properties of the plates after the fire test

ρ (kg/m ³)	R_c (MPa)	S_H (Shore C)	
524	0.02	Unexposed side	9
		Exposed side	4

Table VI: Metals Limits for DIN leachates according to the Order on Slag Valorisation ($\mu\text{g/L}$)

Component	Limit	Orujillo gasification ash
Cd	100	<30
Cr(VI)	100	---
Cr_{total}	500	<50
Ni	500	50
Cu	2000	55
Zn	2000	20
As	100	<1
Hg	20	<50
Pb	500	100

The recycling or reuse of secondary materials in the Netherlands in the building industry is commonplace; more than 10 percent of all granular materials used in the building industry are recycled materials. The Dutch Building Materials Decree (DBMD) [15] contains rules related to the use of stony and earth building materials in construction and other works. The aim of the DBMD is to prevent pollution of the soil and surface water. The decree prescribes a standardized column leaching test for granular building materials (NEN 7343) and a tank leaching test (NEN 7345), for bound or shaped materials.

Table VII shows the figures for the concentrations of different metals analyzed in the ash column test leachates obtained using the CEN/TS 14405 test, which is similar to the NEN 7343. In general, it can be seen that the concentrations of the metals are low and are, in all cases, at the part per billion level (ultratracés). A comparison is

made with the limits stated in the DBMD for Categories 1 (unrestricted use) and 2 (restricted use, if isolation measures are taken). As can be seen, Cat. 2 limits are not exceeded for any metal, although in the cases of Hg and Se no conclusions can be drawn, because as occurs with Cd, Sb and Sn, measured concentrations are always under their detection limits. Cat. 1 limits are exceeded for Cu, Ba, Mo, Ni and V. Table VIII shows the NEN 7345 leachate concentrations of test pieces taken from the plate.

Table VII: Category 1 and Category 2 limit values for column test leachate concentrations according to the DBMD at a layer thickness of 0.7 m

Element	DBMD		Orujillo gasification Ash
	Cat. 1 mg/kg	Cat. 2 mg/kg	
As	0.88	7	0.49
Ba	5.5	58	6.05
Cd	0.032	0.066	<0.05
Co	0.42	2.5	0.28
Cr	1.3	12	0.05
Cu	0.72	3.5	1.61
Hg	0.018	0.076	<0.49
Mo	0.28	0.91	0.81
Ni	1.1	3.7	1.34
Pb	1.9	8.7	0.49
Sb	0.045	0.43	<0.10
Se	0.044	0.1	<0.49
Sn	0.27	2.4	<0.49
V	1.6	32	0.10
Zn	3.8	15	3.52

We can see that all the metals are under detection limits except Ba. After 64 days the accumulated Ba concentration was 18 mg/m². Nevertheless, this value is still well below the limit set by the Dutch Building Materials Decree for Category 1 (600 mg Ba/m²). Therefore, no environmental problems are expected for the plates developed in this study, at least from the heavy metals point of view.

3.2 Bricks

The fired test probes, after a firing similar to the tunnel kiln firing, do not present defects. Table IX and X show the main results of the test. The more significant effects of the ash addition were: (a) High reduction of the ceramic body strength; (b) High decrease in the net density of the ceramic bodies. (c) Notable increase in the water absorption joined to a higher porosity. The high increase in the mixing water cause the reduction of the ceramic body strength whereas the increase in the water absorption joined to a higher porosity was mainly due to the pore-forming properties of the ashes tested.

The results obtained show that the three clay bodies tested do not meet the requirements for high density (HD) clay masonry units. Low density (LD) clay masonry units, according to UNE-EN 771-1, with high thermal insulating capacity, can be probably

manufactured with orujillo ash, provided that the ceramic body strength is improved.

Table VIII: NEN 7345 [Accumulated leaching test results after 64 days (mg/m²)]

Component	Cumulative (mg/m ²)	Limits DBMD (mg/m ²)
Sn	<20	29
As	<20	41
Hg	<20.5	0.4
Se	<20.5	1.4
Mo	<4	14
Sb	<4	3.7
Zn	<1	200
Pb	<20	120
Cd	<2.1	1.1
Co	<2	29
Ni	<4	50
V	<4	230
Cu	<12	51
Ba	18	600
Cr	<2	140

Table IX: Characterization tests

Ceramic test	Nomenclature	Typical values	Units
Water (mixing water)	AAM	20-22	%
Moisture	H		%
Dry bending strength	RFS	5-8	N/mm ²
Water absorption	AA	3-24	%
Net Density	D	1650-2350	kg/m ³
Fired bending strength	RFCs	20-40	N/mm ²
Drying linear shrinkage	CLS	4-5	%
Firing linear shrinkage	CLC	0-6	%

Despite further investigation is needed, preliminary conclusions allow us to be quite optimistic. The results obtained up to now have showed that the three clay bodies tested are very near (but slightly under) the requirements for facing bricks, i.e. HD clay masonry units. However, the percentage of ashes was very high. For instance, according to [7], red and white bricks were manufactured using ash proportions up to 6.3 ww%. A possible solution is the optimisation of the type of clay and/or the use of a lower ash proportion. These two measures are under current investigation. In addition, LD clay masonry units, with high thermal insulating capacity, can be probably manufactured with orujillo ashes.

Table X: Extrusion, drying and firing results

Ceramic comp.	Firing temp. (°C)	Ceramic test							
		AA M	H	AA	D	RFS	RFC _s	CL _S	CL _C
1	1050	35.7	21.7	32.1	1340	4.4	11.5	0.2	2.0
1	1075		-	29.8	1370		11.4	0.3	2.6
2	1050	36.4	31.2	37.1	1280	2.9	4.6	1.3	1.2
2	1075		32.1	35.6	1290		4.3	1.7	1.9
3	1000	27.3	18.9	13.4	1680	2.6	10.5	0.4	2.3
3	1025		19.2	12.6	1710		10.3	0.3	2.5
Typical values		20 - 22		3 - 24	1650- 2350	5 - 8	20 - 40	4 - 5	0 - 6

4 CONCLUSIONS

This work demonstrates that fly ash from fluidised bed gasification of biomass has potential as the main constituent in lightweight wallboards and bricks. We have manufactured lightweight plasterboard plates by a low-cost moulding and curing method with 60%w/w fly ash and bricks by adding 20%w/w fly ash to clay mixtures. The lightweight plates showed low density and acceptable physical-chemical and environmental properties, in accordance with European Standards. Although the mechanical properties were poor, the plates satisfied the minimum EU requirements for gypsum plasterboards. Results over the bricks showed that the three clay bodies tested were just slightly under the requirements for facing bricks, i.e. HD clay masonry units. These results are considered promising because the high percentage of the ashes used in the tested bricks.

The results obtained here are quite satisfactory for both utilization options. Further studies, however are needed. Optimising the blend composition for the lightweight plates to expand the applicability of these attractive utilisation methods are under study. Regarding the bricks, we are investigating various alternatives: optimisation of the type of clay, the addition of a lower ash proportion and searching for new material to be used as low density clay masonry units. These utilisation options provide attractive ways to valorise difficult fly ashes yielding high-quality products using relatively high ash volumes.

Nomenclature

A	water absorption capacity
BGA	biomass gasification ash
Cat	Category
DBMD	Dutch Building Materials Decree
DTA	Differential thermal analysis
FB	fluidised bed
HD	high density
LD	low density
LOI	loss of ignition
MSWI	municipal solid waste incineration
P	density
R _c	compressive strength
SDTA	Standardized differential thermal analysis
S _H	surface hardness

TG termogravimetry
ρ density

Acknowledgements

The authors acknowledge the financial support for this research by the Commission of Science and Technology, European Commission and Junta de Andalucía. We also acknowledge Cerámicas Malpesa (Bailén, Spain) for its help in preparing the brick samples.

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