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Plant optimisation and ash recycling in fluidised bed waste gasification

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ABSTRACT

We studied the gasification of two wastes in a fluidised-bed pilot plant aiming at finding sustainable methods for the utilisation of the ash produced. Two objectives were pursued: (1) optimisation of the operating conditions to achieve better ash quality while keeping reasonably high energy efficiency and (2) assessment of the ash quality in order to explore potential utilisation options for the ash. An extensive characterisation of the raw ash produced was carried out, finding that, in most cases, the existing fly ash utilisation methods are not applicable. The high concentrations of unburned carbon and harmful soluble compounds restrict ash utilisation or normal disposal, making pretreatment necessary prior to use in agriculture and construction. The only alternative that allows material recycling and energy recovery without the need of pretreatment is the use of the ash in cement kilns. However, competition with other fuels makes this option uncertain. Therefore, we further investigated more innovative utilisation concepts where pretreatment is not necessary, like the addition of ash in the manufacture of lightweight wall board and bricks with special properties. These utilisation options are based on low-cost preparation methods using ash in significant proportions, yielding a notably high-value product. We show that they are promising new applications with high market potential.

1. Introduction

Thermochemical treatment of biomass and waste is one of the current alternatives for future energy supplies and for limiting CO_2 emissions. Gasification offers a combination of flexibility, efficiency and environmental acceptability that is essential in meeting future energy requirements [1,2]. The gasification of biomass in large-scale applications is carried out in a fluidised-bed (FB). The basic technology exists today, but the technical and economic competitiveness of large-scale gasification units has to be improved to be comparable with the latest generation of fossil-fuelled power plants [3].

Besides the energy value and quality of the producer gas, one of the key factors limiting biomass gasification is fly ash quality. Fly ash from the gasification of biomass (FABG) differs considerably from conventional combustion ash. Unburned carbon is generally present in large amounts, typically 10–60% of the ash mass. This is a major issue because it has a direct impact on process efficiency and ash recycling. On the one hand, an increase in carbon conversion results in higher efficiency and has a direct positive influence on power production efficiency. On the other hand, the increase of carbon conversion makes it possible to recycle or make use of ashes as raw material in other processes. An essential part of the ash quality improvement and ash volume reduction is therefore the increase of carbon conversion, since it will facilitate the development of sustainable, economical methods for ash management. In addition to its high carbon content, FABG also contains polyaromatic hydrocarbons (PAHs) 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. Costs related to fly ash disposal can represent a significant share of the overall operating cost of gasification-based energy production. Consequently, improving the economics of biomass and waste gasification by developing sustainable and economical methods for ash utilisation and management is currently a subject of intense research [4].

Based on existing utilisation methods for fly ash from combustion and gasification, three main utilisation categories can be identified for gasification ashes derived from biomass and waste [4,5]: (1) *Use as fuel*: 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*: This can be divided into two categories depending on the strictness of specifications. Fine fly ash can be used as a cement replacement in concrete, an attractive option, but most biomass-derived fly ashes cannot fulfil the specifications. Other construction applications that require less stringent specifications include soil stabilisation, road base, structural fill (filler in asphalt or asphalt-like products), lightweight bricks and synthetic aggregate. (3) *Use in*

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Nomenclature

AR	air ratio (N m^3 ratio/kg air)
CC	carbon conversion (%)
DBMD	Dutch Building Material Decree
d.a.f.	dry and ash free
d.w.	dry basis
ER	equivalence ratio (fuel)
FABG	fly ash from biomass gasification
FB	fluidised bed
F_f	feed rate of biomass (kg/s)
LOI	loss-of-ignition
m_{c1}	ash production rate in cyclone one (kg/s)
m_{c2}	ash production rate in cyclone two (kg/s)
MBM	meat and bone meal
PAHs	polyaromatic hydrocarbons
PP	power plant
TOC	total organic carbon
w.b.	wet basis

Greek symbol

η_G	gasification efficiency (%)

agriculture: directly as fertiliser or soil improver. Landfill may also be considered a form of utilisation. However, it is expected that landfill costs will increase in the near future.

The main industrial utilisation of combustion ashes is in cement and concrete production [6]. Gasifier bottom ashes are similar to combustion ashes in composition and properties. Bottom ashes are typically well oxidised and contain only small amounts of unburned carbon, so they can be used in similar applications as the ashes of the same fuels from fluidised-bed combustion. Coal fly ash utilisation is well established with quality standards and commercial practices. In practice, the utilisation methods developed for ashes from combustion processes cannot be directly transferred to gasification fly ashes. As already stated, FABG differs considerably from conventional combustion ashes. FABG may contain high concentrations of unburned carbon and harmful soluble compounds, which restricts ash utilisation or normal disposal and makes it necessary to pretreat ash prior to use. For instance, utilisation in the cement and concrete industry without pretreatment is not possible for most FABG. The need for pretreatment has a direct impact on the final economics of the overall process [5].

In FB gasification the bed material and additives also have a major effect on the properties of fly ash. Bed material mixtures containing limestone or dolomite are commonly used in atmospheric gasification as they improve tar cracking and also act as sorbents in gas cleaning. In some applications lime or hydrated lime is used to bind impurities in gas cleaning. These materials make the fly ash strongly alkaline and increase the solidification properties of moistened fly ash.

The primary objective of this work was to search for sustainable methods for the utilisation of ashes from the gasification of two wastes: meat and bone meal (MBM) and orujillo, a by-product of the olive oil extraction industry. This was done by optimising the gasification process in order to reduce the volume of fly ash and improve ash quality while still maintaining the system at acceptably high thermal efficiency. In this paper we present a thorough study of the possible utilisation routes for these ashes. As already pointed out, FABG can represent a significant cost of gasification systems and thus pretreatment of ashes makes the economics problematic for their future utilisation. Therefore, economical methods for the management of this type of ash without pretreatment are the most attractive. For this reason, in this study we focused mainly on finding utilisation concepts that do not need any pretreatment and entail low-cost process preparation.

2. Experimental

2.1. Materials

2.1.1. Orujillo

Orujillo is a residue of the olive oil extraction industry available in large quantities in various EU countries, especially Spain, Greece and Italy. Despite this, there is not much pilot plant experience as compared to other residues [7–9]. This fuel has a high heating value but contains large amounts of alkali metals (primarily potassium), which can cause serious deposit formation and agglomeration in high-temperature processes like fluidised-bed gasification or combustion [10]. Several studies have been published on the gasification of leached orujillo [11,12]. Leaching especially obviates measures to deal with ash slagging, deposition and bed agglomeration.

2.1.2. MBM

MBM is a waste difficult to dispose of. We found no studies on FB gasification of MBM in the specialised literature. Only a few co-gasification experiments have been reported from the IGCC plant in Puertollano [13], where a maximum MBM content of 5% in the feed blends was tested. On the other hand, there is relatively widespread experience with MBM combustion [14,15]. In this work, due to problems related to feeding as-received MBM into the reactor [8], the MBM was pelletised. The pellets had a constant diameter of 4 mm and a variable length ranging between 5 and 20 mm. Table 1 contains a typical analysis of the orujillo and MBM used in the tests described in this study.

2.1.3. Bed material and additives

Bed materials used included silica sand, ofite and limestone. Ofite is a complex subvolcanic rock with the mineralogical formula of $(Ca{\cdot}Mg{\cdot}Fe{\cdot}Ti{\cdot}Al)_2{\cdot}(Si{\cdot}Al)_2O_6$. The ofite used in this work had an average particle size of 380 μm and a particle density of 2620 kg/m^3. The limestone used in the MBM gasification tests had an average particle size of 750 μm and a particle density of 2580 kg/m^3. Approximately 12 kg of inert bed material were used during each test. In the tests using blends of ofite and limestone as additives, the ratio of ofite to limestone was 65/35 by weight, which gave an approximate ofite-to-lime ratio of 80/20 by weight after the calcination of the limestone. Table 2 shows the ultimate and proximate analysis and the particle-size distribution of the inert bed material and dolomite. The gasification tests using sand as bed material were not technically successful because of defluidisation

Table 1
Chemical characterisation of the fuels

	Orujillo		MBM	
	% (w.b.)	% (d.b.)	% (w.b.)	% (d.b.)
LHV (MJ/kg)	14.09	15.80	19.75	20.57
HHV (MJ/kg)	15.02	16.84	21.27	22.05
C	–	41.01	–	45.04
H	–	4.16	–	6.4
N	–	1.13	–	7.47
S	–	–	–	0.64
O	–	30.64	–	21.58
Moisture	10.82	–	6.91	–
Ashes	20.41	22.88	17.57	18.87
Volatile matter	53.34	59.81	67.05	72.03
Fixed carbon	15.44	17.31	8.47	9.1

Table 2
Chemical and physical characterisation of ofite and limestone

	Ofite	Limestone
Main analysis (wt%)		
Si as SiO_2	53.93	0.30
Al as Al_2O_3	13.61	0.10
Fe as Fe_2O_3	9.15	–
Ca as CaO	11.15	55.40
Mg as MgO	7.90	0.20
Na as Na_2O	3.49	–
K as K_2O	0.48	–
Sulphates as SO_3	–	0.10
Moisture at 105 °C	0.47	0.80
Weight loss at 750 °C	0.64	43.50

Size distribution (Accumulated) (wt%)									
Size (μm)	2500	1900	1410	1000	500	250	125	100	62
Ofite	100	98	74.3	45.6	17.9	8.54	5.9	5.47	3.8
Limestone	–	–	100	99.9	1.14	0.13	0.10	0.07	0.01

problems caused by rapid sintering. Hence sand characterisation is not reported here.

Other materials were used to study some products (vermiculite, clay, additives, etc.) but these are specific to each application and are presented in the context of the application in which the material is used.

2.2. *Test facility*

The experiments were carried out in an experimental rig described in previous publications [7,8], which discuss the pilot-plant experience with these two fuels in detail. Only the most noteworthy conclusions dealing with the impact on ash quality and quantity are given here. This includes the study of the effect of operating conditions and bed material on gas and ashes produced. Fig. 1 and Table 3 presents a schematic diagram and some relevant operating and design data for the pilot plant, respectively.

2.3. *Test procedure and sampling*

The reactor design was flexible, which enabled setting various modes of thermal operation. The tests with orujillo were carried out with the oven off. This form of operation simulated the usual setup found in most gasification pilot plants, insulated with blankets. With this operational setup, the heat losses are high owing to the small scale of the plant. The tests with MBM were performed by adjusting the oven to provide the heat necessary to compensate for wall heat losses. Therefore, the tests carried out with MBM can be considered adiabatic. This operational procedure has revealed itself to be ideal for simulating full-scale systems where the area-to-volume ratio is much smaller (and hence also useful for simulating relative heat losses based on the thermal biomass input).

Table 3
Technical and operating data for the pilot plant facility

Inside bed diameter	0.15 m
Bed height	1.40 m
Inside freeboard diameter	0.25 m
Freeboard height	2.15 m
Fluidisation velocity	0.8–1.4 m/s
Bed material	Ofite, limestone
Fuel	Orujillo, MBM
Fuel feed rate	6–35 kg/h
Gasification agent	Air
Operating temperature	700–850 °C
Operating pressure	Atmospheric
Fluidisation regime	Bubbling

At the beginning of each run, the bed material was heated up with the preheated air. After about an hour of heating, the bed temperature exceeded 400 °C, and a small amount of biomass was fed in. In this oxidising atmosphere, the biomass was combusted and the reactor rapidly heated up to the desired process temperature. The computer-based data acquisition system monitored and recorded the temperature, the pressure drop and the feed rate values during the whole test. The transition from combustion to gasification was accomplished by increasing the biomass feed and thus decreasing the ratio between the air and biomass flowrates.

In every test an initial transition period of around 4–7 h was followed by a steady-state period of 5–10 h, which ended with the shutdown of the gasifier. The initial transition period was shorter in tests with MBM because the heating rate was higher, thanks to the heating support provided by the oven. After each test the two cyclone bins, the extraction ash bin and the overflow bin were sampled. The four locations were sampled twice and analysed for each run. Finally, a temperature probe was placed after the cyclones and another just before the blast entered the scrubber. This sampling protocol enabled us to correlate the ash volume and quality to the operating conditions.

3. Results and discussion

We briefly discuss the main results in the gasification trials and analyse the characteristics of the ash generated. An extensive characterisation of the ashes is then described in order to screen for potential utilisation routes. Selected uses are further discussed on the basis of this characterisation. Finally, advanced uses are explored and market potential is discussed.

3.1. *Analysis of performance of gasification tests*

A detailed analysis of the gasification tests is given in [7,8]. Only the most relevant aspects related to the impact of operating conditions on the ashes are discussed in detail in the present paper.

Initial trials with orujillo were done with common silica sand as bed material. No valid data using silica sand as bed material were obtained. The sintering and agglomeration processes were problematic, even at low temperatures (750–800 °C), but the difficulties were overcome by using ofite as bed material, which prevented ash from melting and hence established stable operating conditions. The first column in Table 4 gives a summary of the most relevant parameters obtained from gasifying orujillo. In the tests described here the effect of ER was analysed using two air flowrates

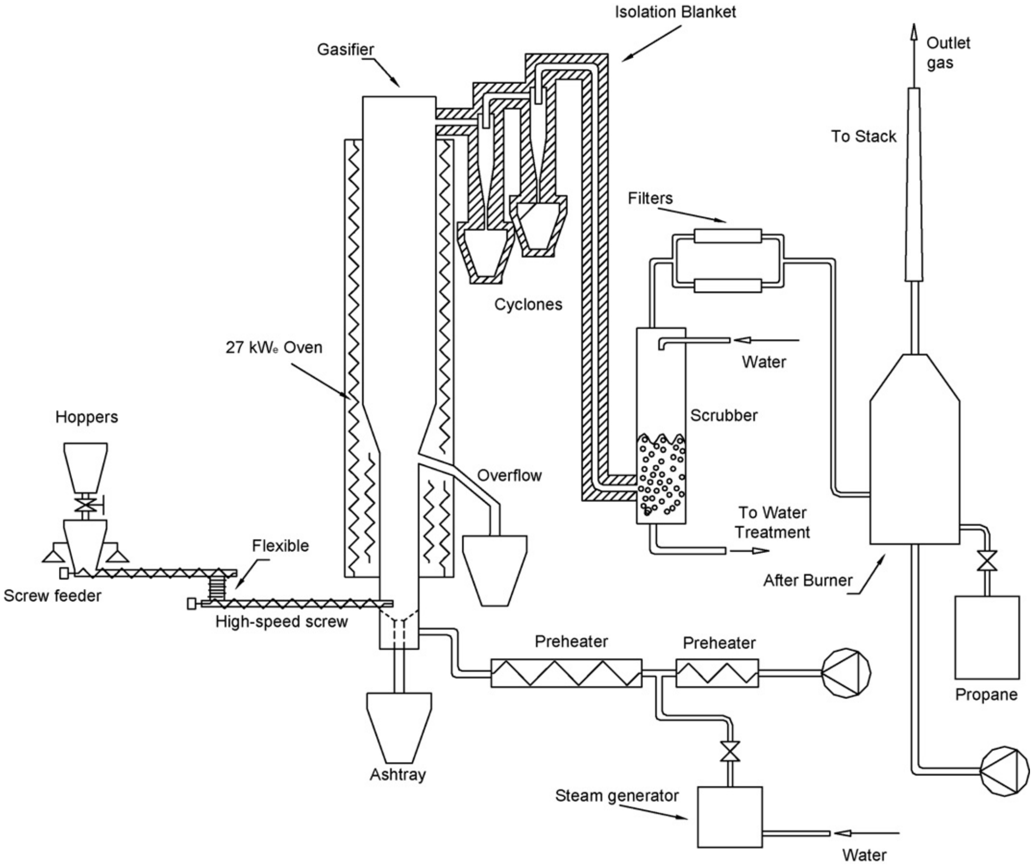

Fig. 1. BFB pilot plant facility.

(18 and 20 N m^3/h) and several orujillo feed rates ranging from 15 to 30 kg/h. These conditions established an air/orujillo mass ratio within the range of 0.8–1.5 (N m^3 air/kg orujillo d.a.f.) and an equivalence ratio (ER) ranging from 0.17 to 0.31. The carbon conversion varied between 73.4% and 86.1%. Fig. 2 shows how the carbon conversion, defined as the degree to which the carbon in the fuel is converted into gaseous products, can be properly optimised by demonstrating that there is an optimum of gasification efficiency within the range shown in Fig. 2. By way of summary, the use of ofite allowed us to optimise gasification by operating at higher temperature. However, more than 90% conversion was not possible because of the agglomeration problems caused by sintering. Therefore, we identified as optimum an ER that makes it possible to obtain relatively acceptable carbon conversion with maximum efficiency.

A complete set of successful MBM tests was carried out using ofite, limestone and a mixture of the two as bed material. As with orujillo, two independent variables were used. Three levels of air-to-fuel ratio were set by modifying the air and MBM flowrates. A summary of the typical results obtained is given in the second column of Table 4. The experimental results indicate that MBM is not a good “gasifiable” feedstock since the final gas composition has low CO and H_2 concentrations due to the high dilution by nitrogen.

Table 4
Comparison of main MBM and orujillo gasification parameters

	Orujillo	MBM
Bed material	Ofite	Ofite, $CaCO_3$, Ofite + 20%$CaCO_3$
Air ratio (N m^3 air/kg fuel d.a.f.)	0.8–1.5	1.2–2.8
Equivalent ratio	0.17–0.31	0.20–0.42
Gasification temperature (°C)	700–820	710–860
Freeboard temperature (°C)	530–650	500–600
Gas yield (N m^3 gas dry/kg fuel d.a.f.)	1.9–2.5	2.1–3.7
LHV (MJ/N m^3)	4.5–5.5	1.0–3.0
Gasification efficiency (cold)	0.50–0.70	0.25–0.40
Carbon conversion	0.7–0.85	0.80–0.97
Gas composition (%v/v, dry)		
H_2	8.0–12.0	1.0–8.0
CO	9.0–14.0	3.0–12.0
CH_4	2.5–3.5	2.0–5.0
CO_2	16.0–20.0	10.0–16.0

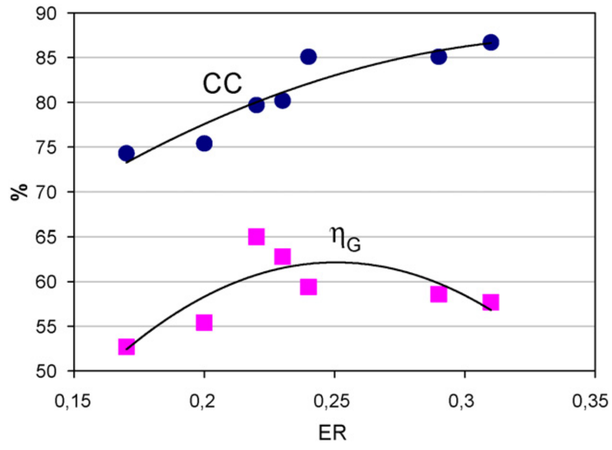

Fig. 2. Carbon conversion (CC) and gasification efficiency (η_G) as a function of equivalence ratio.

Table 5
Effect of additive on gas produced and analysis of volume and quality of ash generated by MBM gasification (100% ofite and ofite/CaO = 80/20)

	Without $CaCO_3$	With 20% $CaCO_3$
Tar content (g/N m^3, dry)	17–21	8–13
Particle concentration (mg/N m^3, dry)	200–900	2000–4000
Carbon cyclone one (wt%)	4	8
Carbon cyclone two (wt%)	12	9
W/F (kg inert/kg fuel h^{-1})	1.25	1.3
m_{C1}/F_f (kg ash/kg fuel)	0.07	0.13
m_{C2}/F_f (kg ash/kg fuel)	1.52×10^{-3}	1.16×10^{-3}

Table 7
Total carbon content (%) of orujillo ashes for the different sample locations

Test	T bed (°C)	ER	%C overflow	%C cyclone one	%C cyclone two
1	700	0.17	37.54	20.18	22.08
2	740	0.20	20.77	12.00	15.24
3	750	0.22	37.44	15.78	18.08
4	760	0.23	29.85	14.51	19.51
5	785	0.24	19.85	14.03	15.86
6	780	0.29	8.24	11.58	9.66
7	820	0.31	5.33	9.09	12.04

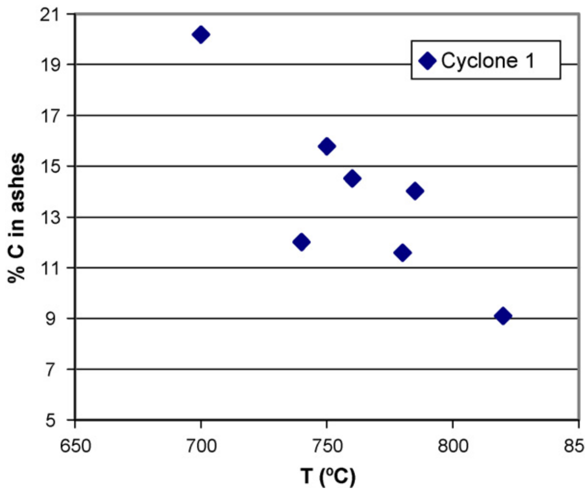

Fig. 3. Carbon content of ashes in cyclone one as a function of bed temperature.

A general comparison between MBM and orujillo gasification performance is given in Table 4. As shown in the table, MBM gasification ashes have a lower carbon content (typically 4% for MBM vs. 7–18% for orujillo). In spite of this, the gas obtained from MBM gasification is rather poor (low LHV and gasification efficiency). The reason is the severe dilution of the producer gas obtained from MBM gasification. This is due to the lower oxygen content of MBM as compared to orujillo, which makes the air-to-fuel ratio higher for MBM gasification. The tests carried out with lime stone as bed material (or blends of this with ofite) showed a reduction up to 50% in tar content. However, no major differences were found in gas composition. The effect of using limestone as an additive is shown in Table 5.

3.2. Basic characterisation of ashes

Tables 6 and 7 show the basic characterisation of the ashes sampled. In particular, Table 6(a) shows the elemental and ultimate analysis of the ashes from the cyclones, ash bin and overflow for a typical orujillo test. For comparison, the first two columns of Table 6 include the analysis of the orujillo. In Table 6(b) the main size-distribution analysis for representative ash samples is presented. Also, it is included in this table some reference values for comparison, including the size-distribution of a sample taken from a power plant (PP) burning orujillo and another from coal combustion. Table 7 displays the carbon content of the ash sampled at various locations where it was generated in the gasification of orujillo in different tests, i.e., at different temperatures. Fig. 3 illustrates how the carbon content of ashes from cyclone one decreased as temperature increased (or, equivalently, when ER decreased). As already discussed, increasing the carbon conversion is a key point in this work because, apart from the positive impact on efficiency, it also makes it possible to utilise the gasification ash produced. This is mainly because the high carbon content of gasification fly ash limits its field of application. In the case of biomass gasification, the relatively high chlorine and alkali content of ashes (and heavy metals if wastes are gasified) makes its potential utilisation even

Table 6
Typical ash chemical (a) and physical (b) analysis of orujillo ashes for the different sample locations

	Fuel (orujillo)		Cyclone one		Cyclone two		Overflow		Bottom ash	
	% (w.b.)	% (d.b.)	% (w.b.)	% (d.b.)	% (w.b.)	% (d.b.)	% (w.b.)	% (d.b.)	% (w.b.)	% (d.b.)
(a) Chemical analysis										
C	–	41.01	–	8.61	–	11.81	–	9.45	–	0.44
H	–	4.16	–	<0.05	–	0.14	–	0.48	–	<0.05
N	–	1.13	–	0.29	–	0.5	–	0.22	–	0.08
O	–	30.64	–	5.08	–	6.96	–	6.23	–	0.27
Moisture	10.82	–	0.98	–	2.81	–	1.13	–	0.15	–
Ash	20.41	22.88	85.17	86.02	78.32	80.59	82.68	83.62	99.06	99.21
Volatile matter	53.34	59.81	7.79	7.86	11.05	11.37	10.99	11.12	0.96	0.97
Fixed carbon	15.44	17.31	6.06	6.12	7.81	8.04	5.2	5.26	0	0

	Granulometry % (w.b.)							
	>300 (μm)	300–150 (μm)	150–75 (μm)	<75 (μm)	>90 (μm)	90–75 (μm)	75–45 (μm)	<45 (μm)
(b) Physical analysis								
Orujillo								
Overflow	85.9	7.5	3.4	3.2				
Cyclone one					18	9	16	57
Cyclone two					1	7	22	70
Orujillo					43	33	23	1
Ofite	96.5	1	0.5	2				
PP combustion orujillo	4	22	40	34				
Coal combustion ash	1	4	14.2	34	30.8			

Table 8
Main elements in different ashes, ofite and orujillo (fuel)

Sample	wt%											
	Moisture	LOI	Fe_2O_3	CaO	MgO	SiO_2	Al_2O_3	Na_2O	K_2O	P_2O_5	Cl	S
Orujillo ash	1.75	20.26	5.32	26.08	8.64	41.02	8.03	1.29	8.26	1.50	0.64	0.11
MBM ash	2.12	16.64	2.89	44.49	3.62	12.48	3.45	4.13	1.48	17.95	–	0.20
Ofite	0.47	0.64	9.15	11.12	7.9	53.93	13.61	3.49	0.48	0.09	0.62	–
Orujillo (fuel)	10.82	77.12	3.4	27.0	6.3	50.4	5.5	0.6	10.5	1.47	0.21	–

Table 9
Metal concentrations in different samples

Sample	Metals in mg/kg													
	As	Hg	Se	Mo	Zn	Pb	Cd	Co	Ni	Cr	V	Cu	Ba	Sb
Orujillo ashes	<160	<100	<100	<100	210.5	<160	<16	<10	<100	761.5	83	145.75	288.75	<200
MBM ashes	<100	<100	<100	<20	398	100	<10	<10	864	636	<20	212	134	<20
Orujillo fuel	<160	<100	<100	<100	182	<160	<16	<10	<100	646	60	182	270	<200

more difficult. This is very important from the economic point of view in future large-scale applications.

3.3. *Further characterisation of ashes*

An extensive characterisation was made of the ashes generated in the foregoing tests, which facilitated the assessment of utilisation and management methods for the ashes. Up to now, characterisation work has included physical characterisation and elemental analysis: C, H, N (ASTM D-5373) and S (ASTM D-4239). However, further characterisation is necessary for the assessment and screening of existing and/or new utilisation options. Basically, this comprises trace elements (ASTM D-3683), ash leachability (DIN 38414, TCLP (USEPA 1311), column test and up-flow percolation test EN 14405), analysis of eluates (metals) and thermal analysis (TGA, DSC, DTA). In this article we present the basic results for the understanding of the selective screening given in the section below. Except where specifically indicated, the characterisation results are given for average values of the fly ashes, that is, cyclones one and two for all the tests. As a result, the values are indicative for each biomass and conclusions about the effect of operating conditions cannot be drawn from the results. A detailed characterisation of ashes obtained in the different gasification trials carried out with orujillo and MBM, together with other residues such as demolition wood and sewage sludge, can be found elsewhere [4]. In addition, due to the strong effect of bed material on the resulting fly ashes collected in the cyclones in an FB system, the characterisation of ofite is also reported in most of the tables that follow.

Main elements: The average values of the main elements found in orujillo and MBM ashes are displayed in Table 8 (average of the two cyclones in different operating conditions). The chemical composition of the fly ashes was determined by atomic absorption spectrophotometry after the digestion of the samples. The table also includes the content of the main elements in ofite and the original orujillo (fuel).

Table 10
PAH values in some ashes

Samples	Test	Location	PAH (mg/kg)
Orujillo ash	1	Cyclone (one + two)	67.5
Orujillo ash	7	Overflow	<1,4
Orujillo ash	7	Cyclone (one + two)	10
Orujillo ash	–	Cyclone 1 (average tests 1–7)	18.8
Orujillo ash	–	Cyclone two (average tests 1–7)	86.8
MBM	6	Cyclone one	165

Metals: The metal concentrations in the ashes are reported in Table 9. Metal analysis in the fly ash was carried out using atomic absorption spectrophotometry and inductively coupled plasma techniques after the digestion of the samples. The values of orujillo and MBM ashes displayed in Table 9 are the average of the two cyclones for the different operating conditions tested.

PAH: The PAH concentration values for some ash samples are shown in Table 10. Average orujillo values are included for all the tests as well as values in cyclones one and two and averages. The PAH value for the ashes collected from the overflow are also reported. As expected, the PAH is much lower than the value found in the fly ashes (cyclones one and two). These values agree with the carbon content of different ashes in Table 7.

LHV of ash: In general, the carbon content of gasification fly ash is much higher than that of combustion fly ash, which is disadvantageous for most applications. However, this carbon content is very important for the possible use of the fly ashes as fuel. The calorific value of full-scale FB gasification ash can in fact be very high. For instance, the values for fly ash from the FB gasifiers at Lahti (60 MWth) and Amer (85 MWth) range from 14 to 25 MJ/kg [4], which is comparable to the heating values of peat and wood, despite the high ash content. The loss-on-ignition (LOI) for these ashes ranges from 7 to 60 wt%. The average LHV for orujillo and MBM ashes were 5075 and 1000 MJ/kg, respectively. While the heating value of orujillo ashes is acceptable, MBM has very little energy content. However, in both cases the heating values were much lower that those shown for industrial scale ashes as reported above.

3.3.1. *Leaching properties*

DIN 38414: Average DIN 38414 leaching data from orujillo and MBM ashes are shown in Table 11. The table also contains the DIN leaching results of orujillo (fuel) and ofite. This could be of help for tracking key components.

TCLP: The same information shown above in Table 11 for the DIN leaching test is now given for the USEPA TCLP test in Table 12.

Column tests: In some applications, the information provided by the EN 14405 column test is one of the references for the assessment of plausible ash utilisation according to the Dutch Building Material Decree (DBMD). Thus, some of the ashes were analysed under this approach. Table 13 includes this information for the orujillo fly ash used to make bricks (discussed in the section below).

Metal analysis in leachates was carried out using atomic absorption spectrophotometry and inductively coupled plasma techniques.

Table 11
DIN 38414 leaching test results of some samples

Sample	Leachate DIN (mg/L)											
	pH	As (ppb)	Zn	Pb	Cd	Ni	Cr	V	Cu	Ba	K	P
Orujillo ash	12.59	<1	0.1	0.1	<0.03	0.1	<0.05	<1.9	0.09	1.83	27.35	0.02
MBM ash	10.25		0.07	<0.1	<0.02	<0.05	<0.05	<1.9	<0.05		100.0	0.01
Ofite ash	8.51		0.03	<0.1	<0.03	<0.05	<0.05	<1.9	0.05	<0.3	0.2	1.26
Orujillo (fuel)	6.35	35	0.18	0.13	<0.03	0.57	<0.05	<1.9	0.23	1.7	189.19	55.04

Table 12
TCLP leaching test results of some samples

Sample	TCLP leachates (mg/L)											
	pH	As (ppb)	Zn	Pb	Cd	Ni	Cr	V	Cu	Ba	K	P
Orujillo ash	10.29	5.00	0.03	0.20	0.04	0.28	<0.05	<1.9	<0.05	3.45	38.39	0.04
MBM ash	5.07		0.67	0.21	0.03	4.4	<0.05	<1.9	0.05			21.56
Ofite	4.83	<1	0.08	<0.1	<0.03	0.05	<0.05	<1.9	<0.05	0.7	1.3	0.32
Orujillo (fuel)	4.96	25	0.3	0.16	0.03	0.43	<0.05	<1.9	0.15	3.2	100.0	100.00

3.4. *Preliminary screening of utilisation options*

3.4.1. *Use in agriculture*

The ashes from biomass combustion can be utilised as fertilisers and soil conditioners. These applications are regulated by national standards which specify the admissible contents of impurities and minimum nutritional properties for agricultural uses. Fly ashes from biofuel gasification do not fulfil typical national requirements because of high heavy metal content, PAH content and low nutrient values in most cases [4]. Fly ashes from waste material gasification did not meet the requirements for fertilisers in any of the tested cases. The use of gasification ashes for current applications is very challenging because there are large amounts of better combustion ashes available for these applications.

We checked the following potential utilisation options: (1) soil conditioner, soil rehabilitation and plant growing medium, (2) soil nutrient and fertiliser and (3) neutralising agent and liming agent. The main parameters to take into account are trace elements (As, B, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn), the main nutrients for agriculture use (Ca, Mg, K, P) and the PAH content. The utilisation standards checked were: Metals Limit in Compost (Spain), Heavy Metal Limit in Sewage Sludge for Agricultural Applications (Spain), Metal Limit Values for Ash Utilisation in Cultivation (Finland) and Recommended Minimum and Maximum Values for Components in Ash Products in Sweden. Tables with the limits of these regulations can be found in [16].

Table 13
Column test results of some ashes

	Leachate column test (mg/kg)	
	Orujillo ash	Ash for bricks[a]
pH	12.17	10.73
As	0.49	0.54
Ba	6.05	1.1
Cd	0.05	0.05
Co	0.28	0.06
Cr	0.05	0.26
Cu	1.61	1.17
Hg	0.49	0.49
Mo	0.81	0.4
Ni	1.34	0.1
Pb	0.49	0.49
Sb	0.1	0.1
Se	0.49	0.49
Sn	0.49	0.49
V	0.1	3.13
Zn	3.52	8.16

[a] see Section 3.5.2.

In general, high concentrations of P and Ca (typical of bones) were found in MBM ashes (Table 8). In orujillo ashes, on the other hand, high values of K were measured (Table 8). The solubility of these components, in contrast, was very low. The solubility of P in MBM ashes showed especially low values – under 1% in DIN leaching tests (Table 11) – whereas the results of TCLP leaching tests turned out to be much higher, roughly 60% (Table 12). In addition, high Cr content was measured in orujillo and MBM ashes (Table 9), but it is thought that the main reason is the decomposition of steel in the reactor due to the severe abrasion in the fluidised-bed process. The chlorine content of orujillo ashes was 0.5–1.5 wt% (Table 8), which is probably the main handicap of this ash. In both ashes the PAH were found to be very high (typically 100 mg/kg) (Table 10). The low solubility of P and Ca make the attractiveness of this route doubtful, at least in common soils. Therefore, the use of both ashes in agriculture as soil amendments could be a reasonable route if previous treatments such as combustion and washing are applied.

3.4.2. *Use as fuel*

Two options were considered: use in cement kilns and use in existing boilers [16]. The manufacture of cement is an energy-intensive process and energy demand can account for between 30% and 40% of the production cost. Substitute fuels have been explored by the cement industry, including tyres, waste paper, waste oils, waste wood, paper sludge, sewage sludge, plastics and spent solvents. Therefore, biomass gasification ash would naturally be competing with other low-grade fuels [4]. This option is very interesting because it makes recycling and energy recovery possible. On the other hand, there are often some restrictions with respect to the maximum amounts that can be used, which are closely related to the type of biomass/waste. In cement kilns the key ash parameters are total organic carbon (TOC), and chlorine and sulphur content.

Three feed locations are possible, in principle: (1) entry into the combustion chamber in the rotary kiln (where pieces of tyres are added). This option is limited by the fine content of the fly ashes. (2) Feeding with the raw material in the preheating section. Here, TOC and chlorine limits are the limiting factors. (3) Mixed with the fuel (in the burners). This alternative is limited by chlorine. Therefore, all options are limited. However, the most promising option is (3) because some cement plants have a “chlorine by-pass” which allows them to operate with higher chlorine content in the feed. The specific quantity that can be fed in depends on the particular ash. For instance, in a plant processing 1,100.000 t/y of raw material for clinker manufacturing, and taking as reference a limit value of chlorine in the clinker of 100 g/t clinker, using orujillo ashes as a feed (taking 0.1% Cl as a basis) means that approximately 90,000 t/y could be added to the process if these ashes were the only Cl-containing biofuel introduced to the plant. Usually, in existing plants there are other Cl-containing biofuels and this value can be reduced significantly [4]. This is a technically possible route. The key point is, of course, cost negotiation (other fuels can compete favourably).

The use of existing boilers and power plants was also checked for the ashes under study. Various power plants burning biomass were visited in Spain, some burning orujillo as the main fuel. Although FABG from orujillo is a rational option in these plants, heavy metals, Cl and K severely limit the mixing of these ashes with the orujillo before feeding the boiler. Corrosion-derived problems caused by K_2O and ClH in baghouse filters, heaters, etc. are the main cause of rejection by industrial owners. So, in principle, we consider this route not technically possible.

3.4.3. *Use in construction*

As discussed in Section 1, this route is usually the natural option for coal combustion ashes [6,17,18]. However, FABG differs considerably from conventional combustion ashes in that it may contain high concentrations of unburned carbon and harmful soluble compounds. This greatly restricts ash utilisation in construction for most fine applications. We based our evaluation of cement, concrete and other construction applications on the following standards and/or regulations: (1) fly ash for concrete (EN 450) ASTM C618 chemical requirements (EN 450-1: 2001); (2) fly ash for cement (EN 197); (3) EN 12859 for construction board. From Tables 8 and 9 the following can be concluded: (a) none of the ashes fulfil the LOI limit given in EN 450-1: 2001. (b) Chlorine concentration is also over the Cl limit for orujillo ashes. This is mostly soluble in water, so washing previously could reduce its concentration. (c) All samples are within the limits of SO_3 but none of them fulfil the CaO limits. (d) $SiO_2 + Al_2O_3 + Fe_2O_3$ is lower than the required limit. The orujillo ashes do not fulfil the total alkali content requirement.

Among the metals in ashes, we see that Cr is the only heavy metal that violates the limits (Table 9). However, it is thought that this is because of steel decomposition and not because of the gasified material itself. Orujillo ashes surpass the Cu limit (and possibly the Mo limit) for Category 1 of the Dutch Building Material Decree (DBMD) [19], but not the limit for Category 2. However, in many cases the metal concentrations measured (only 14 metals were measured) were under detection limits and no conclusions can be drawn.

In principle, the direct use in well-known construction applications as an additive in cement and for concrete manufacture is ruled out. Pretreatment such as washing and/or combustion is necessary. The results suggest investigating less “fine” applications, such as road stabilisation, asphalt fillers or bulk fill. However, we investigated further applications aiming at coming up with new products, satisfying three basic requirements: (1) the product contains a considerable percentage of fly ash; (2) ash can be used in the product without any pretreatment; (3) the manufacturing method is low in cost.

3.4.4. *Preliminary conclusions of screening*

In summary, the high carbon content of both ashes (especially orujillo) is a general handicap difficult to overcome in terms of the economics of future ash utilisation. MBM ash from other thermochemical processes is often considered attractive for fertiliser manufacture, but the high PAH content found in this work makes this application difficult. In addition, the low solubility of P and Ca make the attractiveness of this route doubtful, at least in common soils. In acid soils, however, the solubility of some key agriculture components could improve to a great extent. This is supported by the results of TCLP tests. Therefore, the use of both ashes in agriculture as soil amendments could be a reasonable route if previous treatments such as combustion and washing are applied. Obviously, the economics of these options needs further evaluation. In the following section we investigate additional routes where no pretreatment of the ashes is needed.

3.5. *Identification of further utilisation routes*

Three routes were tested further for the orujillo ash; each of these is an in-depth study and details are published elsewhere [5,20,21,22,23]. However, the general appraisal of the three routes is briefly examined and the capacity of each route as a plausible utilisation option is discussed.

3.5.1. *Stabilisation/solidification (S/S)*

The principle of stabilising hazardous wastes rests on the concept that the alkaline components in fly ashes reduce the leachability of metals in a high-pH matrix. There is a pH window that gives the lowest metal concentration in the leachate. This window depends on the metal element, but for a given fly ash, an optimum can be found for minimising the end product’s leachability [20]. We ran tests trying to stabilise arc furnace dust (AFD) waste with orujillo ashes. AFD is a dust that results from the collecting systems of particulate material in a carbon–steel electric arc furnace (electric arc furnace for carbon steel production). The hazardous metals normally found in EAF dust are lead, cadmium and chromium [20]. Blends containing 45 wt% AFD dust, 45 wt% ash and 10 wt% Portland cement were tested. After 28 days of curing, mechanical (compression strength) and leaching properties (DIN 38414 and TCLP) were measured in the resulting solids. Orujillo ashes gave very good mechanical properties to the final S/S solid, but the blends need to be optimised to improve the metal immobilisation. This route needs further research and is still under investigation. Preliminary results are published in [4]. In principle, though further studies are still needed, this is a possible ash reutilisation route.

3.5.2. *Use in lightweight construction board*

In this study we investigated a new lightweight construction board made of orujillo ashes [5,21,22]. Our goal was to come up with a product which satisfies two basic requirements: (1) the product is mostly made of fly ash and (2) ash can be used in the product without any pretreatment. We manufactured sheets by means of low-cost moulding and curing methods, using ash percentages up to 60 wt%. Gypsum and additives (vermiculite and fibre) were added to provide the sheets with acceptable mechanical and thermal properties.

The sheets showed acceptable physical–chemical properties (low density, humidity and pH) according to European standards. Although mechanical properties were poor, the sheets satisfied the minimum EU requirements for wall board. Mechanical properties were influenced by the high LOI of the ash used. The fly ash under research had high concentrations of unburned carbon (LOI around 18%), which differs considerably from conventional ash combustion where LOI values of 2–5% are typical. Contrary to what was expected, the high LOI of the ash did not affect the fire-resistance behaviour of the boards [4,5]. A thorough study of the fire-resistance behaviour of sheets containing gasification ash was undertaken [5]. The fire resistance of the product developed and two commercial sheets 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. 4 shows the

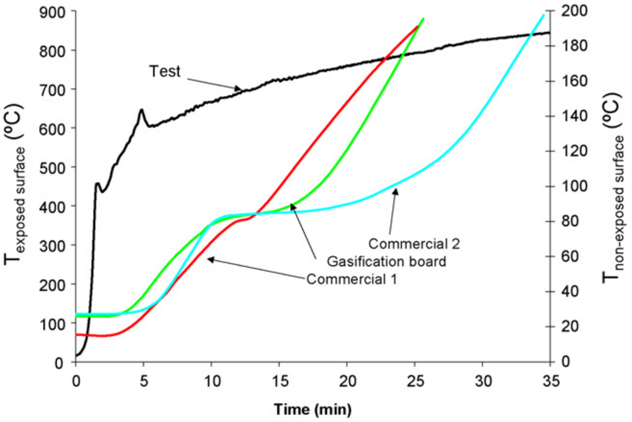

Fig. 4. Fire-resistance test curves.

results obtained in the fire test for 20 mm-thick sheets. The *t*180 of the developed product was over 24 min. By comparing the three curves in Fig. 4, we can see that the behaviour of the sheet tested in this study was similar to that of commercial sheets of the same dimensions. Details of experiments can be found in [5].

The recycling of ash is not expected to lead to environmental problems because leaching of heavy metals was shown to be slight. In conclusion, the results obtained here are quite satisfactory, although further studies focused on optimising the mortar composition would be most welcome in order to expand this attractive utilisation option. A detailed discussion of this study has been published elsewhere [5]. The results lead us to conclude that the sheets could be used commercially as lightweight construction board and, therefore, the potential for commercial development is quite promising.

3.5.3. *Use in brick manufacture*

Clay bricks are manufactured from clay, sand and small amounts of suitable organic matter like sawdust that burns off in 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 the finished product. Carbon-containing ash could be used in clay brick manufacturing as an additive raw material, which would incorporate an inert material into the brick mass and produce porosity in the sintering phase. High-carbon gasification ash is expected to behave like organic matter in sintering, leaving small cavities in the brick matrix.

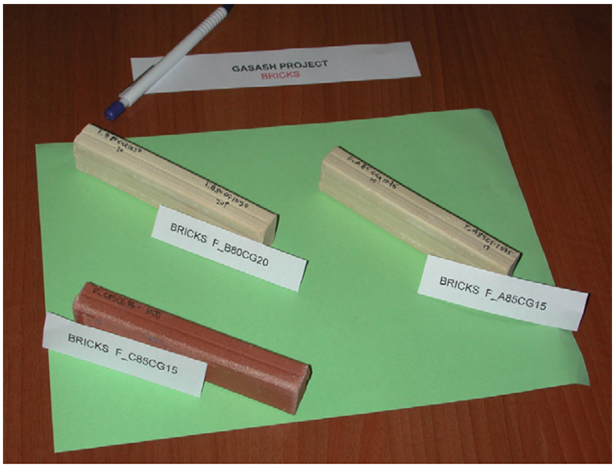

Fig. 5. Bricks manufactured during this investigation.

We tested three kinds of clay bodies prepared by the addition of orujillo ash to clay compositions. Fig. 5 shows various bricks manufactured in the course of the investigation. The selected clay compositions are representative of the products from 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 clay body. The firing temperatures tested were 1000, 1025, 1050 and 1075 °C for 4 h, with a firing time of approximately 24 h. The fired test probes, after a firing similar to that of a tunnel kiln, did not show defects. The most significant effects of the ash addition were a high reduction of the ceramic body strength, a high decrease in the net density of the ceramic bodies and a notable increase in water absorption, together with higher porosity. The causes of these effects are the high increase in the mixing water and the pore-forming properties of the ashes.

Although further investigation is needed, preliminary conclusions allow us to be quite optimistic. The results obtained up to now have shown that the three clay bodies tested are very near (but slightly under) the requirements for facing bricks, i.e., high density (HD) clay masonry units. However, the percentage of ashes was very high. For instance, in [24] red and white bricks were manufactured using ash proportions up to 6.3 wt%.

A possible solution is the optimisation of the type of clay and/or the addition of a lower proportion of ashes. These two measures are under current investigation. In addition, low-density (LD) clay masonry units, according to UNE-EN 771-1, with high thermal insulating capacity can probably be manufactured with orujillo ashes, provided that the ceramic body strength is slightly improved or the proportion of ash is lowered.

4. Summary and conclusions

We studied the gasification process of two wastes (meat and bone meal and orujillo) in a fluidised-bed pilot plant. A primary objective was the optimisation of gasification conditions to achieve better ash quality and acceptable gasification efficiency in the process. The effect of operating conditions, bed material and additives on gas and ash produced were studied. For orujillo testing, an optimum air-to-biomass ratio was established to obtain relatively acceptable carbon conversion (90%) with maximum efficiency. For MBM testing, up to 97% carbon conversion was achieved but the heating value of the gas was low due to excessive nitrogen dilution. The second objective was to find sustainable methods for the utilisation of the ashes produced in the pilot unit, for which we carried out an extensive characterisation of the raw ashes produced. In the light of this characterisation we found that, in most cases, these ashes are not suitable for existing fly ash utilisation methods, mainly because the high carbon, chlorine and alkali content (and some cases heavy metals) strongly limit the field of application of the ashes. Therefore, physical or thermal treatments are necessary prior to ash utilisation. These treatments include washing (for alkali and chlorine removal), low temperature combustion (for carbon, LOI, PAH reduction) and high temperature treatments (for more persistent contaminants). In general, the high carbon and PAH content of both ashes and the chlorine content of orujillo make the economics problematic for future utilisation of these ashes. For this reason, methods that do not need treatment are preferable. Two categories of methods were identified. The first one needs easy-to-apply pretreatment. It includes the use of ashes as a soil amendment after leaching and/or oxidation. Category 2 comprises methods using raw ashes, including traditional use as fuel in cement kilns but also some more innovative utilisation concepts like the manufacture of lightweight wall board and bricks with special properties. These two utilisation options, in addition, are based on low-cost preparation methods, using ash in considerable proportions. Therefore, they seem to be the most promising applications studied in this work.

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