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Abstract: Additives are sometimes used to address some of the most common critical issues concerning the composting process and final product quality, and ash generated by biomass combustion have been envisaged as a potential composting additive. Nonetheless, a deeper awareness for the effective feasibility of such ash reuse option should be pursued. In this work, all the ash types produced at different sections of a typical biomass combustion plant (namely bottom, boiler and fly ashes) were characterised with the scope of identifying the weaknesses and strengths of each residue in the light of their reuse as a composting additive. The results manifest that boiler and fly ashes were very enriched in nutrients such as calcium, potassium, magnesium and phosphorus. They also had high porosity and water holding capacity. Because of these properties, they could act as a mineral additive and a physical amendment in composting. The pH values for boiler and fly ashes were 12 and 13, respectively, so they could also act as a liming agent in composting of acidic substrates. The electrical conductivity was high (16 and 33 mS·cm⁻¹, respectively) and could be harmful for plant growth. On the other hand, bottom ash had low salinity and alkalinity, but the physical properties and nutrient content were not of interest for composting. Heavy metals content was not a concern in all the ash types.

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COVER LETTER

The present work relates to the residues generated by biomass combustion plants and the feasibility of their reuse as an additive in the organic waste composting. Biomass covers a prominent role among the renewable sources, whose diffusion worldwide is associated to energetic, economic and environmental advantages. Nonetheless, the environmental issues related to biomass are to be considered as well, of which the waste produced, consisting of the ashes, is of major concern. Actually, the reuse or recovery of biomass ash is becoming more important in the light of the circular economy approach, that is based on the reintroduction of waste materials in the production cycles in order to maximize their value. Defining suitable reuse options is complex because of the variations in the ash chemical composition and physical properties, depending on the fuel biomass, combustion technology and operating conditions. Moreover, several types of residues are produced in the same plant depending on the discharging point.

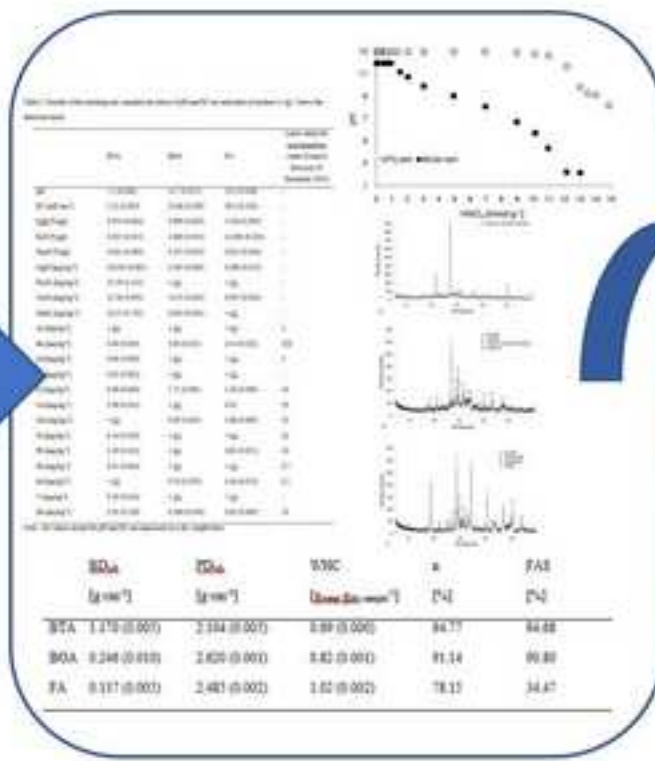
Some scientific works have already dealt with the reutilization of the biomass residues, but they consider only some of the ash types produced by biomass plants. In this proposal of article, all the ash types produced by biomass plants are evaluated. Moreover, the majority of the works published considers recovery options that evolved from the coal ash management but, due to biomass ash characteristics, their suitability is questionable and specific recovery options should be investigated.

In that regard, the present work considers the reuse of biomass ash as an additive in composting, with the aim to recycle the nutrients and micronutrients contained in this waste stream, that is one action that pursues the achievement of a more circular economy, improvement of the final product characteristics as a soil conditioner and the increase of the market value of compost.

For these reasons, Authors think the paper is original and should be considered for publishing.

In this work, different types of ash produced at different sections of a biomass combustion plant are characterized in terms of chemical composition and physical properties. For each of them, the characteristics that might have positive or negative effects on both the evolution of the composting process and the final product quality are identified and quantified. Such results provide the knowledge to evaluate the feasibility of using one or more ash types as a composting additive and define the related optimum dosages.

The article has been checked by a native tongue speaker with expertise in the field.



	SiO ₂	CaO	WBC	n	FAE
	[g wt ⁻¹]	[g wt ⁻¹]	[g wt ⁻¹]	[%]	[%]
FTA	1.175 (0.001)	2.114 (0.001)	0.89 (0.000)	84.77	84.88
BOA	0.248 (0.010)	2.620 (0.000)	0.82 (0.000)	81.14	80.80
FA	0.137 (0.000)	2.481 (0.000)	1.02 (0.000)	78.15	74.47

BIOMASS ASH CHARACTERISATION AS POTENTIAL ADDITIVE IN COMPOSTING

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HIGHLIGHTS

- The amount of biomass combustion ash produced worldwide is rapidly increasing.
- The lack of recovery option which are specific for biomass ash is acknowledged.
- Characterization is fundamental for evaluating any possible reuse option.
- Biomass ash could be used as an additive in the organic waste composting.
- Ash contains nutrients and micronutrients, has high pH, porosity and free airspace.

1 **BIOMASS ASH CHARACTERISATION AS POTENTIAL ADDITIVE IN COMPOSTING**

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16 **ABSTRACT:** Additives are sometimes used to address some of the most common critical issues
17 concerning the composting process and final product quality, and ash generated by biomass combustion
18 have been envisaged as a potential composting additive. Nonetheless, a deeper awareness for the effective
19 feasibility of such ash reuse option should be pursued. In this work, all the ash types produced at different
20 sections of a typical biomass combustion plant (namely bottom, boiler and fly ashes) were characterised
21 with the scope of identifying the weaknesses and strengths of each residue in the light of their reuse as a
22 composting additive. The results manifest that boiler and fly ashes were very enriched in nutrients such as
23 calcium, potassium, magnesium and phosphorus. They also had high porosity and water holding capacity.
24 Because of these properties, they could act as a mineral additive and a physical amendment in

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10 27 ¹, respectively) and could be harmful for plant growth. On the other hand, bottom ash had low salinity and
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18 31 Keywords: additive; ash; biomass; characterisation; composting; organic waste.
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21 22 33 **1. INTRODUCTION** ¹ 23

24 34 Circular economy (CE) is an approach for achieving a more sustainable economic growth that has risen to
25
26 35 the role of strategic objective in many countries during the last decade [1,2]. The circular economy
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28 36 strategy is based on the efficient use of resources, whereof waste management is a relevant part [1,3]. In
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30 37 particular, waste prevention and reuse are the main themes of most of the new national strategies based on
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32 38 CE [1].
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34 39 A recent move towards CE has been accomplished by the European Union with the framework document
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36 40 "A zero waste programme for Europe" and the related action plan [4,5], with the objective of obtaining
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38 41 improvements in the Member States' targets related to waste management. Though the current waste
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40 42 management is based on a hierarchy of management options where prevention, reuse, recycling and
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42 43 recovery of waste are to be pursued, in many cases suitable operations to replace or produce materials
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44 44 from waste are still to be studied and landfilling remains the most common management method.
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46 45 Another important issue in the circular economy strategy is the transition from fossil fuels to renewable
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50 ¹ ANC: acid neutralisation capacity; BAsh: biomass ash; BD: bulk density; BOA: boiler ash; BTA: bottom ash; CE:
51 circular economy; CHP: combined heat and power; EC: electrical conductivity; FA: fly ash; FAS: free airspace; Gm:
52 specific gravity; LOI: loss of ignition; n: total porosity; PD: particle density; TS: total solids; WHC: water holding
53 capacity; XRD: X-ray diffraction.
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46 sources [1,6].

47 The recourse to renewable energy reduces the environmental impact and attributes a strong degree of
48 sustainability to the economic system [7].

49 In this framework, biomass has a prominent role in the European energy scenario and its use as an energy
50 source is expected to grow up to 110.5 Mtoe (million tonnes of oil equivalent) by 2020, which
51 corresponds to an increase of about 22% comparing to the 2012 consumption [8]. At present, combustion
52 and combined heat and power (CHP) based on combustion are the most common biomass valorisation
53 approaches. According to James et al. [9], a future trend in the use of biomass for energy production could
54 potentially lead to a production of $15.5 * 10^7$ tonnes of ash in the EU-27 by 2020. Suitable recovery
55 options for the reuse of biomass combustion ash (BAsh) are to be pursued in order to divert it from
56 landfilling and maximise the potential of this waste product [9].

57 The use of BAsh as an additive for the organic waste composting could be an adequate option.
58 Composting is a biochemical process that degrades and stabilises organic substrates under special
59 conditions of moisture, aeration and heat-insulation [10,11]. Some conditions, such as excessively low or
60 high moisture, temperature and pH, the scarcity of free airspace, the shortage of nutrients can negatively
61 affect the composting process and the quality of final compost. Additives to the composting admixtures
62 may be used to correct such unfavorable conditions, enhance the process and final product quality [11],
63 and BAsh could be one of them.

64 One favorable aspect in using BAsh as a composting additive is the enrichment of final product with
65 minerals essential for plant growth [12-14], which improve the compost quality and marketability. Also,
66 BAsh has very low moisture and bulk density, while porosity is high, and these physical properties could
67 help maintaining air diffusion in the composting admixtures [11,15,16]. If ash is used as a composting
68 additive, higher pH values are expected during the overall process, that could contribute to controlling the
69 pH decrease at the early stage of the composting process [17].

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70 On the other side, excessively high pH values could affect the process itself and the final product quality.
71 Disadvantageous effects of ash could be linked to the heavy metals content and the lacking or low
72 concentration of nitrogen, that could affect the final compost quality [13,14,17]. Moreover, BAsh salinity
73 could be harmful for plant growth [18,19].
74 As far as we know, there are few studies focused on the use of BAsh in composting [13,14,17,18], and
75 none of them investigates the reutilisation opportunities related to all the ash types generated by a thermal
76 power plant. While, since extremely large variations in composition are reported, according to the feed
77 characteristics, combustion technology, operating conditions applied and the discharging point where ash
78 is produced [20-22], the chemical composition and physical characteristics of all the ash types should be
79 the basis for evaluating such application.

80 Based on these assumptions, the objective of the present work was the characterisation of the ash samples
81 collected at three different sections of an industrial biomass thermal-power plant for evaluating the
82 perspectives of using one or more BAsh as an additive in composting. To this aim, the chemical
83 composition and main physical properties of ash were determined and discussed, showing that selected
84 ash types could be the most adequate for improving the composting process and the final compost quality,
85 though possible drawbacks were observed as well.

87 **2. MATERIALS AND METHODS**

88 Representative samples of approximately 60 kg each of biomass and combustion residues were sampled
89 from an industrial thermal power plant (13 MWe) located in Sardinia, Italy. The plant is equipped with a
90 reciprocating grate and exclusively fueled with biomass. The temperature in the combustion chamber is
91 1040°C.

92 The combustion residues are discharged from three different sections as shown in Figure 1.
93 (Figure 1 here)

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95 The first is set at the bottom end of the combustion grate, the second is located at the bottom of the boiler,
96 and the third is situated in correspondence to the collection plate of the electrostatic precipitators.

97 Depending on the discharging point, the residues were named bottom (BTA), boiler (BOA) and fly ashes
98 (FA), respectively (Figure 2).

99 (Figure 2 here)

100 A representative sample of the feeding biomass was collected and characterised too. The fuel biomass
101 consisted in a mixture of pine and eucalyptus wood chips, representing 75% of the daily feed, and agro-
102 industrial residues, covering the remaining 25% of the daily supply. The fuel sample was collected from
103 different points of the feed stockpile. The collected samples were prepared for the successive analyses
104 according to EN ISO 14780 [23].

105 The moisture (M) and the total solids (TS) content were determined by using a thermostatic oven at
106 105°C. The pH and the electrical conductivity (EC) levels were determined using a pH-meter (Orion4
107 Star, Thermo Fisher Scientific, MA, USA) and a conductivity meter (HQ30d, Hach Company, CO, USA),
108 respectively [24].

109 The total carbon (C_{total}) and nitrogen (N_{total}) contents were measured using an elemental analyser (CHN-
110 1000, LECO Corporation, MI, USA). The sulfur content was analyzed using an Inductively Coupled
111 Plasma - Optical Emission Spectrometer (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA) after acid
112 digestion on hot plates of 0.5 g of biomass and ash samples with 1.35 ml of hydrogen peroxide, 1 ml of
113 nitric acid 65% and 1 ml of hydrochloric acid 37%. The chlorides content was determined using an Ion
114 Chromatography System (ICS-90, Dionex, CA, USA) according to EN 16995 [25].

115 The minor and major elements content was determined by microwave-assisted acid digestion, according
116 to EPA Method 3052 and by alkaline fusion with lithium metaborate in platinum melting pots at 1050°C
117 [26], followed by ICP Spectrometry (ICP-OES, Optima 7000DV, PerkinElmer, MA, USA). Batch, one-

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118 stage leaching tests were conducted on BAsh at a liquid to solid ratio of 10 L·kg⁻¹ according to EN 12457-
119 2 [27] for materials with particle size below 4 mm (BOA and FA), and according to EN 12457-4 [28] for
120 materials with particle size below 10 mm (BTA). The eluates were analyzed for the water-soluble
121 fractions of major and minor elements by ICP Spectrometry (ICP-OES, Optima 7000DV, PerkinElmer,
122 MA, USA). The pH and EC values of the eluates were determined according to EN 15933 [24].
123 Loss of ignition (LOI) was determined by drying the samples in a furnace at 550°C, according to EN
124 15169 [29].
125 The BOA and FA buffering capacity was evaluated by means of the acid neutralisation capacity (ANC)
126 tests by the addition of increasing amounts of nitric acid according to CEN/TS 15364 [30]. The ash
127 mineralogy was determined using a Rigaku Geigerflex X-ray diffractometer (XRD), with application of
128 Cu-K α radiation at 30 kV/30 mA and scan speed equal to 2° of (2 θ)/min between 4 and 60°.
129 As for other physical properties, water holding capacity, bulk density and particle density were
130 determined. Water holding capacity was determined by soaking the samples in water for 24 h and draining
131 the excess water overnight, according to Ahn et al. [31]. Bulk density was measured according to UNI EN
132 15103. Particle density was determined using a gas pycnometer (Accupyc II 1340, Micromeritics
133 Instruments Corporation, GA, USA) in accordance to ASTM B 923 [32].
134 Total porosity, (n, Eq. 1), and the share of pores filled with air, named free airspace (FAS, Eq. 2), were
135 obtained by means of the equations proposed by Haug [11].

136

$$137 \quad n = 1 - [(BD_m * TS_m)/(G_m * \rho_{water})] \quad (1)$$

$$138 \quad FAS = n - BD_m * [(1 - TS_m)/\rho_{water}] \quad (2)$$

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140 where

141 n is the total porosity [%],

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142 FAS is the free airspace [%],

143 BD_m is the wet bulk density of the material [$g \cdot cm^{-3}$],

144 TS_m is the total solids content of the material [%],

145 G_m is the specific gravity (unitless), that corresponds to the ratio between particle density of the sample
146 [$kg \cdot m^{-3}$] and density of water,

147 ρ_{water} is the density of water [$kg \cdot m^{-3}$].

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149 **3. RESULTS AND DISCUSSION**

150 **3.1 Chemical characterisation**

151 The biomass and ash chemical characterisation is reported in Table 1.
152 (Table 1 here)

153 The biomass showed chemical composition, total solids content and LOI at 550°C, that were aligned with
154 what found by recent literature [22, 33-35]. The most abundant major elements were calcium, silicon and
155 potassium (0.76, 0.59 and 0.33%wt, respectively), while the most significant heavy metals were Zn, Cu
156 and Cr (14.7, 6.6 and 4.2 $mg \cdot kg^{-1}$, respectively). Boiler and fly ashes had a negligible water content, while
157 BTA showed a significant moisture. It is worth to mention that the collecting method affected BTA
158 moisture significantly. The thermal power plant is equipped with a BTA quenching tank in order to
159 prevent possible fires and avoid external air from entering the combustion chamber [36].

160 Bottom ash had a high carbon content (14.8% wt) and a notable LOI value at 550°C (28.1% wt), that is
161 consistent with what reported by Hinojosa et al. [37] for bottom ash generated by a fixed bed combustor
162 and could be ascribed to the unburned organic matter. Boiler and fly ashes had a carbon content lower
163 than BTA. Consistently, loss of ignition in BOA was lower than in BTA, while it could not be determined
164 in FA because of the interferences related to the high sulfur content. It can be assumed that FA was
165 mainly composed by inorganic matter, as reported in a recent study by Yeboah et al. [38].

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166 Nitrogen content in all the ash types was below the detection limit (< 0.006%). Biomass ash usually has a
167 very low nitrogen content because during combustion N contained in the fuel forms gaseous compounds
168 that are emitted in the atmosphere [39].

169 Bottom ash was the most enriched in silicon, that was also abundant in BOA (38.0 and 33.9% wt,
170 respectively). In addition, BTA and BOA had similar amounts of aluminum and iron (approximately 7.5
171 and 3.4% wt, respectively). On the counterpart, FA had the most abundant levels of calcium (41.4% wt)
172 and potassium (13.1% wt), followed by BOA (24.7% wt of CaO and 8.1% wt of K₂O). Boiler and fly ashes
173 had similar amounts of sodium (1.2% wt), while BOA was the most enriched in magnesium (5.5% wt) and
174 phosphorus (3.1% wt). In particular, the difference in terms of phosphorous content between BOA and the
175 other residues was evident (0.8% wt in BTA and FA).

176 The most abundant minor metals in biomass ash were Zn, Cr and Cu, which reflected the original biomass
177 composition. FA was enriched with the most volatile metals (Pb, Zn and Cu), while the least volatile ones
178 (Cr, Ni and V) were abundant in BTA. The analytical results obtained were in accordance to literature
179 studies [35,37,38 40-42].

180 As Steenari et al. [39] suggested, most of the elements present in BASH were taken up by the plants during
181 their lives and retained in the combustion residues. The occurrence and distribution of the elements in the
182 different ash types were due to volatilisation during combustion and the particles formation mechanism
183 [42,43].

184 The mineralogical composition, as described by the X-ray diffraction (Figure 3), confirmed the high Si
185 content in BTA and high Ca level in FA, and also identified different calcium-bearing minerals contained
186 in the three ash types.
187 (Figure 3 here)

188 Calcium was present as a silicate in all the ash types, as a carbonate and sulfate hydrate in BOA, and as a
189 hydroxide in FA. Beyond deriving from the calcium content in the original biomass, calcium hydroxide in

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190 FA could also derive from the lime added to abate the acid gases from the flue gas before the collection
191 and removal of fly ash. In BOA, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was also present. Quartz (SiO_2) was the most
192 intense peak in both BTA and BOA, while sylvite (KCl) was one of the most significant mineral in FA.
193 These results were coherent with the above described chemical composition and consistent with literature
194 studies [34,42-44].
195 All the ash types characterised had high pH values; in particular, BOA and FA showed the highest pH
196 values (12.0 and 13.0, respectively) due to the presence of alkali compounds, such as calcium hydroxides
197 in fly ash. Both the pH values and chemical composition agreed with what was reported in recent
198 literature [34,37,38,42].
199 The presence of Ca, Mg and K hydroxides and carbonates caused a high neutralisation potential in BASH
200 [17,44]. The results of the ANC test conducted on BOA and FA are shown in Figure 4.
201 (Figure 4 here)
202 Fly ash had a very high capacity of maintaining high pH values under acid attack. This trend confirmed
203 the high FA buffering capacity, and was aligned with the results from the chemical and mineralogical
204 analyses.
205 The water extractable fraction of metals is a fundamental information to evaluate the potential
206 environmental risk entailed with the reuse or disposal of residues [44]. Also, it underlines the easily
207 leachable and available fraction of macro and micronutrients [45]. Table 2 shows the water-soluble
208 concentration of metal constituents in bottom, boiler and fly ashes in the leaching tests eluates, as well as
209 the pH and EC values.
210 (Table 2 here)
211 Calcium and potassium were the most abundant macro-elements in the FA and BOA eluates; sodium also
212 was present in a significant amount as water extractable fraction from FA.
213 By comparing the results with the limit values set by the European Union legislation for the acceptance of

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214 waste at landfills [46], all the BAsh types fulfilled the criteria established for granular non-hazardous
215 waste. In particular, As, Ba, Cu, Ni and Zn complied with the requirements for the acceptance of waste as
216 an inert material in all the ash types analyzed. The limit values for inert materials were also fulfilled for
217 Cr and Se in BTA, Pb in BOA, and Cd and Sb in BOA and FA.
218 The electrical conductivity in BOA and FA was very high (15.6 and 33.4 mS·cm⁻¹, respectively). Such
219 results were due to the presence of ionic species deriving from water-soluble compounds, such as
220 portlandite, potassium chloride, gypsum [39].

221

222 **3.2 Physical properties**

223 The main physical properties of the different BAsh were assessed too and the results are displayed in
224 Table 3.
225 (Table 3 here)

226 It can be noticed that, while bulk density varied significantly according to the considered BAsh, the
227 particle density did not. According to Eq. (1) and (2), low BD and high PD and total solids content were
228 connected to high porosity and free airspace [11,15,16]. The values of bulk and particle densities
229 determined for the BAsh considered in our work were consistent with recent literature [47-49]. Boiler and
230 fly ashes showed low moisture content and BD, and high PD, thus they exhibited high porosity and FAS
231 values.

232 Bodì et al. [47] observed that low BD leads to high water storing capacity. The water holding capacity in
233 BOA and FA was higher than the BTA one, and similar to the values reported by Ahn et al. [31] for soil
234 compost blends, and by Karhu et al. [50] for soils.

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236 **3.3 Perspectives of ash utilisation in the composting process**

237 In their composting experiments with ash addition, Fernández-Delgado Juárez et al. [17] and Koivula et

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238 al. [18] reported that the final composts benefitted from increasing BAsh addition in terms of nutrient
239 content. The results presented in this work showed that not all the ash types were enriched in nutrients.
240 Among the samples analyzed, FA was the most enriched in calcium and potassium, and contained high
241 magnesium level, while BOA had also a notable level of calcium and potassium as well as the highest
242 magnesium and phosphorous content. Bottom ash was highly enriched in Si, while nutrients were found in
243 smaller amounts. Thus, FA and BOA could be considered the ash types that would improve the compost
244 nutrient content the most. This is an important result because high nutrient content could provide compost
245 with a wider market due to the increased agronomic value [51-53]. Of particular relevance are
246 phosphorus, that is an essential nutrient and often constitutes the limiting factor for plant growth, and
247 potassium, whose content in the composts produced from organic waste is usually low [51]. Moreover, in
248 BOA and FA the water-soluble fraction of nutrients, such as Ca and K, was high, which was interesting
249 because related to the nutrients availability for plant growth [45].
250 Another distinctive feature of BAsh was the high pH which could make them act as a liming agent
251 [14,17]. In the perspective of producing a high quality compost, pH values at 12-13 were considered
252 worth the interest by other authors. Fernández-Delgado Juárez et al. [17], Kuba et al. [13] and Kurola et
253 al. [14] used for their composting experiments wood ash characterised by pH values of 12.5, 12.3 and
254 12.8, respectively. According to these authors, the addition of ash with such high pH values constitutes a
255 base supply, and results in a pH increase during the process and in the final product. In this respect,
256 similar results could be expected from the use of BOA and FA, the latter having the highest buffering
257 capacity, according to the ANC curves obtained. The addition of a liming agent is advantageous in order
258 to limit eventual excessive pH decrease, that is observed at the early stage of composting when acid
259 producing substrates (such as food waste) are used and could inhibit the microbial activity during
260 composting [54,55]. It also represents a benefit after the composting process, in particular if the amended
261 compost has to be applied to acidic soils, as reported by Bougnom et al. [56]. On the other hand, an

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262 excessive pH rise has an inhibitory effect on the thermophilic microorganisms growth [55,57] therefore,
263 in case of reusing BOA and FA, the amount of ash to add has to be evaluated for any case taking into
264 account this aspect.

265 Carbonation reactions are expected to occur when admixtures amended with ash having high buffering
266 capacity are exposed to water and aerobic conditions, somehow limiting the emissions of the CO₂
267 produced during the process. Several authors suggest that the abiotic heat production deriving from
268 carbonation exothermic reactions could be the prevailing cause of the higher temperature observed in ash-
269 amended admixtures [13,17,18], the other causes being the enhanced microbial activity and heat capacity
270 of the material deriving from the ash addition [13,18,58]. Carbonation reactions and an enhanced
271 temperature trend can be expected if FA is used as a composting additive, while boiler ash is predicted to
272 be less reactive than FA and, according to its composition and mineralogy, BTA is not expected to be
273 subject to such reactions. The high temperature values that could be observed in the composting
274 admixtures when ash is used could arise controversial effects on the overall composting process. Miyatake
275 and Iwabuchi [59] observed that at 70°C the thermophilic bacteria diversity increased, but the organic
276 matter degradation decreased. Thus, the need for external control in order to limit the temperature rise
277 could be enforced when ash is used.

278 The increase of temperature and process pH may enhance ammonia evaporation from the composting
279 admixtures and influence the final product characteristics [13,14,17,18,55]. To this regard, BOA and FA,
280 being the most reactive ash types among the ones considered in this work, could result in increased
281 ammonia losses when added to the mixtures.

282 In addition, nitrogen is usually very poor or lacking in BASH [13]. This is confirmed by the results
283 presented in this study; indeed nitrogen was not detected in the samples characterised. If biomass ash is
284 added to a composting admixture, the final compost is expected to be poorer in N because of the dilution
285 of nitrogen-containing compounds present in the original substrate. In such cases, the recourse to a

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286 supplementary N source could be recommended, as sometimes also suggested by literature [60]. On the
287 other hand, nitrogen leaching seems to be limited by ash addition [13,18]. Therefore, the ash overall
288 impact on nitrogen content in the final compost has to be evaluated carefully and well balanced.
289 Biomass ash has high electrical conductivity [13,17,18]. As a result, ash addition increases the salinity of
290 the final product [17,18]. An excessively high EC in compost is harmful for the plant growth, since it
291 causes osmotic problems and affects water intake ability [17,18]. High EC values were found in FA and
292 BOA, thus their use as an additive might increase the final composts electrical conductivity too.
293 Conversely, BTA had low salinity level.
294 Ash metal content is reported to be the most relevant disadvantage that may negatively affect the final
295 compost quality [13,14,17,18]. According to the results from the leaching test, the ash considered in the
296 present study did not represent a possible harm for the environment, and the heavy metal total content was
297 consistent with the levels reported in recent experimental works [13,14,17,18]. The ash-amended
298 composts obtained in these studies had metal content lower than the limits set by the respective reference
299 laws [61,62]. Thus, the ash-amended composts obtained did not represent a detriment for plant growth
300 with regards to the metal content. In addition, some authors observed that alkaline additives may reduce
301 heavy metals mobility in amended composts, further reducing harmfulness [57,63,64].
302 Nonetheless, the reuse in composting should be conditioned by the assessment of the contamination risk
303 for any specific case. The reuse of ash in composting should not affect the final compost quality, and the
304 national standards should always be fulfilled. In some countries there are quality requirements for each of
305 the materials involved in the compost production, besides of the final product [13,14], and the extensive
306 adoption of such approach could be suggested.
307 With regard to the LOI content, BTA had the highest organic matter content and BOA also contained
308 small amounts of unburned carbon. Since other authors reported that ash with high carbon content has a
309 potential in limiting odor emissions [65], these two ash types may be effective in odor control.

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310 As for the ash physical properties, low moisture content and BD, and high PD characterised both BOA
311 and FA. Therefore, these ash types are expected to be beneficial for the air diffusion in the admixtures and
312 the overall composting degradation process.

313 High values of water holding capacity may be beneficial in case of high moisture content in the materials
314 involved in the compost production [31,66] because it facilitates air circulation and diffusion. However,
315 care must be taken so that the presence of ash does not excessively reduce the moisture of the admixture
316 impairing the evolution of the composting process.

317 As a conclusion, advantages for the composting process (such as an improved air diffusion and liming
318 effect) and final product (like higher nutrients content) could be attained when ash is used as a composting
319 additive. In order to obtain such advantages, the knowledge of each BASH type physical-chemical
320 characteristics is fundamental. Firstly, some of the ash types produced at a power plant could facilitate
321 achieving such beneficial effects, while others might not. Secondly, attention should be paid to the overall
322 effect of BASH presence on either the composting process (for instance, in relation to pH, temperature and
323 moisture content) or the compost final quality (in terms, for instance, of final pH or heavy metal content).
324 Such effects may be either advantageous or adverse depending on the circumstances, such as the
325 properties of substrate undergoing composting, soils and crops where the ash-amended composts are to be
326 employed, and the ash amounts used.

327 Analytical results such those obtained in the present study constitute the basis for discerning the paths to
328 convert biomass combustion residues into valuable materials.

329
330 **4. CONCLUSIONS**

331 Biomass fuel and the combustion residues (bottom, boiler and fly ashes) were collected from a thermal
332 power plant and analyzed. The physical-chemical characterisation of the initial biomass and the related
333 ash was presented, showing that the ash properties were greatly affected by the section of the thermal

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334 plant where the ash was discharged. In the light of pursuing the reuse of ash to maintain its nutrient value
335 in the natural cycle, the perspectives of using ash as an additive in composting were evaluated. Among
336 the biomass combustion ash considered in the present work, boiler and fly ashes were particularly
337 enriched in calcium, potassium, magnesium and phosphorus, thus they could represent a suitable mineral
338 addition. They also had high porosity, thus could provide optimal aeration conditions in the composting
339 admixtures. The pH values for boiler and fly ashes were 12.0 and 13.0, respectively, so they could act as a
340 liming agent in composting of acid producing substrates, though there are possibilities of obtaining an
341 alkaline compost whose use could be restricted to selected types of soils or crops only. In addition, high
342 salinity values characterised boiler and fly ashes, which could be harmful for plant growth. Conversely,
343 bottom ash had low salinity and alkalinity, and contained unburned organic matter, which offers a
344 possibility of odor control, but was poor in nutrients and had scarce porosity. Low nitrogen content was
345 common to all biomass ash. This could be detrimental for compost quality for any ash type used;
346 moreover, boiler and fly ashes, being very reactive, could provoke an improved temperature and pH
347 growth in the early stage of composting and a consequent increase in ammonia evaporation. As for the
348 main environmental concern, heavy metals content did not constrain the potential reuse of ash in
349 composting.
350 That being said, attention should be paid to the ash type considered for the reuse as an additive, since the
351 beneficial effects are strictly linked to its properties, which vary with the discharging point. The feasibility
352 and the ash amounts to be used must be carefully assessed on the basis of an in depth and specific
353 chemical-physical characterisation, and the adoption of standards for the additives to be used in
354 composting may be suggested. Moreover, some conditions, such as the properties of substrates
355 undergoing composting, and soils and crops where the ash-amended composts are to be employed, should
356 be taken into account.

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Table 1: Characteristics of biomass and bottom (BTA), boiler (BOA), and fly ash (FA) samples; standard deviation is indicated in brackets (n.d.: not determined; < d.l.: below the detection limit).

	Biomass	BTA	BOA	FA
Moisture [%]	46.60 (0.428)	37.33 (1.345)	1.41 (0.001)	0.66 (0.041)
LOI 550°C [%]	97.34 (0.096)	28.12 (0.541)	4.25 (0.036)	n.d.
pH	4.5 (0.073)	7.5 (0.049)	12.0 (0.028)	13.0 (0.007)
EC [$\text{mS}\cdot\text{cm}^{-1}$]	8.67 (0.382)	0.88 (0.020)	15.58 (0.325)	33.40 (1.131)
C [% wt]	49.82 (0.503)	14.80 (0.212)	5.55 (0.021)	2.44 (0.026)
H [% wt]	5.80 (0.178)	1.48 (0.148)	0.24 (0.068)	1.23 (0.035)
N [% wt]	0.20 (0.046)	< d.l.	< d.l.	< d.l.
S [% wt]	0.02 (0.003)	0.04 (0.002)	0.63 (0.004)	3.67 (0.023)
Cl ⁻ [% wt]	0.20 (0.039)	0.31 (0.095)	0.56 (0.002)	3.41 (0.305)
SiO ₂ [% wt]	0.59 (0.065)	38.02 (0.156)	33.94 (0.392)	2.17 (0.110)
CaO [% wt]	0.76 (0.042)	10.79 (0.121)	24.65 (0.115)	41.37 (0.123)
K ₂ O [% wt]	0.33 (0.015)	4.29 (0.057)	8.14 (0.163)	13.08 (0.083)
Na ₂ O [% wt]	< d.l.	0.75 (0.027)	1.17 (0.013)	1.20 (0.018)
MgO [% wt]	0.11 (0.007)	3.07 (0.025)	5.50 (0.073)	4.28 (0.078)
Al ₂ O ₃ [% wt]	0.15 (0.008)	7.54 (0.001)	7.80 (0.182)	0.91 (0.032)
Fe ₂ O ₃ [% wt]	0.05 (0.006)	3.39 (0.044)	3.35 (0.108)	0.53 (0.005)
MnO ₂ [% wt]	0.01 (0.001)	0.13 (0.001)	0.28 (0.006)	0.09 (0.003)
TiO ₂ [% wt]	0.01 (0.001)	0.36 (0.002)	0.41 (0.006)	0.04 (0.003)
P ₂ O ₅ [% wt]	< d.l.	0.84 (0.019)	3.10 (0.059)	0.78 (0.008)
As [$\text{mg}\cdot\text{kg}^{-1}$]	3.05 (1.344)	2.69 (0.275)	4.18 (0.551)	19.46 (0.326)
Cd [$\text{mg}\cdot\text{kg}^{-1}$]	0.23 (0.054)	0.60 (0.002)	2.09 (0.096)	4.82 (0.057)
Co [$\text{mg}\cdot\text{kg}^{-1}$]	0.35 (0.071)	11.17 (0.386)	12.50 (0.460)	2.26 (0.059)
Cr [$\text{mg}\cdot\text{kg}^{-1}$]	4.20 (0.566)	278.06 (0.942)	45.42 (0.714)	21.25 (0.744)
Cu [$\text{mg}\cdot\text{kg}^{-1}$]	6.62 (0.038)	68.34 (0.128)	190.96 (0.052)	192.92 (1.186)
Mo [$\text{mg}\cdot\text{kg}^{-1}$]	0.25 (0.067)	1.05 (0.211)	0.73 (0.416)	2.56 (0.155)
Ni [$\text{mg}\cdot\text{kg}^{-1}$]	2.20 (0.000)	42.58 (2.995)	32.82 (0.264)	12.24 (2.938)
Pb [$\text{mg}\cdot\text{kg}^{-1}$]	2.70 (0.141)	7.93 (0.332)	33.44 (0.715)	76.48 (0.741)
Sb [$\text{mg}\cdot\text{kg}^{-1}$]	0.69 (0.010)	1.03 (0.152)	0.50 (0.139)	2.56 (0.155)
Se [$\text{mg}\cdot\text{kg}^{-1}$]	0.95 (0.071)	0.15 (0.070)	1.00 (0.102)	2.20 (0.136)
Tl [$\text{mg}\cdot\text{kg}^{-1}$]	< d.l.	0.75 (0.072)	1.65 (0.212)	1.73 (0.254)
V [$\text{mg}\cdot\text{kg}^{-1}$]	1.49 (0.101)	53.87 (0.443)	54.85 (0.515)	8.44 (0.234)
Zn [$\text{mg}\cdot\text{kg}^{-1}$]	14.65 (0.355)	142.77 (7.359)	218.05 (1.529)	804.59 (8.381)

Note. All values except for moisture, pH and EC are expressed on a dry weight basis

Table 2. Results of the leaching test; standard deviation of pH and EC are indicated in brackets (< d.l.: below the detection limit).

	BTA	BOA	FA	Limit values for non hazardous waste (Council Decision 19 December 2002)
pH	7.1 (0.049)	12.7 (0.055)	13.2 (0.026)	-
EC [mS·cm ⁻¹]	1.22 (0.003)	23.80 (0.100)	39.4 (0.120)	-
CaO [% wt]	0.054 (0.004)	0.899 (0.003)	1.018 (0.095)	-
K ₂ O [% wt]	0.205 (0.015)	1.800 (0.013)	12.062 (0.201)	-
Na ₂ O [% wt]	0.032 (0.000)	0.107 (0.005)	0.812 (0.004)	-
MgO [mg·kg ⁻¹]	320.63 (0.061)	0.305 (0.000)	0.489 (0.053)	-
Fe ₂ O ₃ [mg·kg ⁻¹]	15.39 (1.123)	< d.l.	< d.l.	-
Al ₂ O ₃ [mg·kg ⁻¹]	13.58 (0.991)	14.25 (2.043)	0.855 (0.001)	-
MnO ₂ [mg·kg ⁻¹]	10.15 (0.741)	0.045 (0.001)	< d.l.	-
As [mg·kg ⁻¹]	< d.l.	< d.l.	< d.l.	2
Ba [mg·kg ⁻¹]	0.40 (0.010)	3.00 (0.025)	4.14 (0.232)	100
Cd [mg·kg ⁻¹]	0.06 (0.004)	< d.l.	< d.l.	1
Co [mg·kg ⁻¹]	0.03 (0.002)	< d.l.	< d.l.	-
Cr [mg·kg ⁻¹]	0.06 (0.004)	1.71 (0.081)	1.29 (0.009)	10
Cu [mg·kg ⁻¹]	1.06 (0.011)	< d.l.	0.05	50
Mo [mg·kg ⁻¹]	< d.l.	0.60 (0.005)	2.88 (0.000)	10
Ni [mg·kg ⁻¹]	0.14 (0.010)	< d.l.	< d.l.	10
Pb [mg·kg ⁻¹]	1.39 (0.101)	< d.l.	0.83 (0.051)	10
Sb [mg·kg ⁻¹]	0.07 (0.004)	< d.l.	< d.l.	0.7
Se [mg·kg ⁻¹]	< d.l.	0.32 (0.010)	0.40 (0.051)	0.5
V [mg·kg ⁻¹]	0.19 (0.014)	< d.l.	< d.l.	-
Zn [mg·kg ⁻¹]	1.91 (0.139)	0.166 (0.100)	0.82 (0.000)	50

Note. All values except for pH and EC are expressed on a dry weight basis

Table 3. Physical properties of biomass ashes; standard deviation is indicated in brackets.

	BD _{wb} [g·cm ⁻³]	PD _{wb} [g·cm ⁻³]	WHC [g _{water} ·g _{dry sample} ⁻¹]	n [%]	FAS [%]
BTA	1.170 (0.005)	2.104 (0.005)	0.69 (0.000)	94.77	94.68
BOA	0.246 (0.010)	2.620 (0.001)	0.82 (0.001)	91.14	90.80
FA	0.137 (0.005)	2.485 (0.002)	1.02 (0.002)	78.15	34.47

Note. BD: bulk density; PD: particle density; WHC: water holding capacity; n: total porosity; FAS: free airspace.

Figure 1
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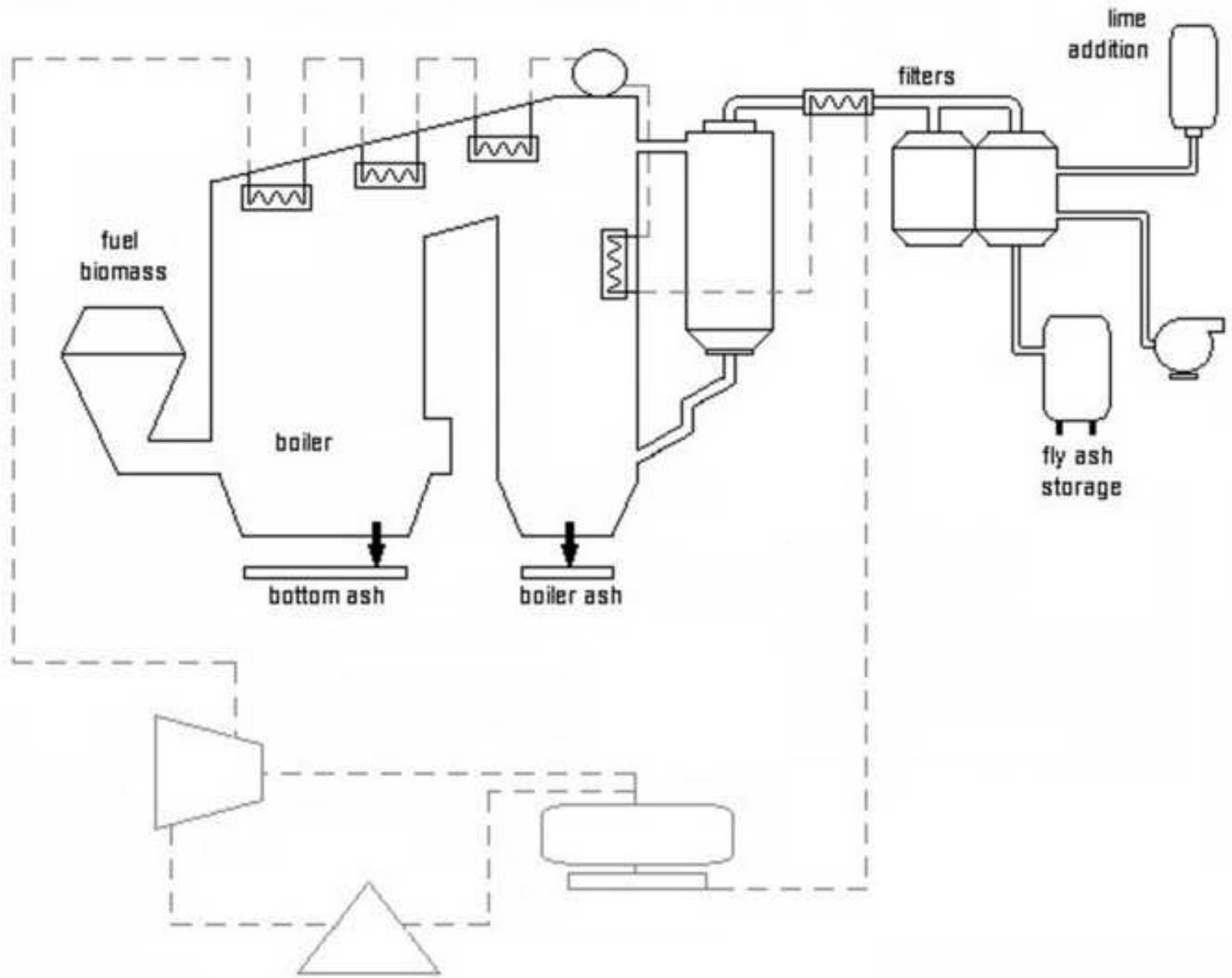


Figure 2
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Figure 3

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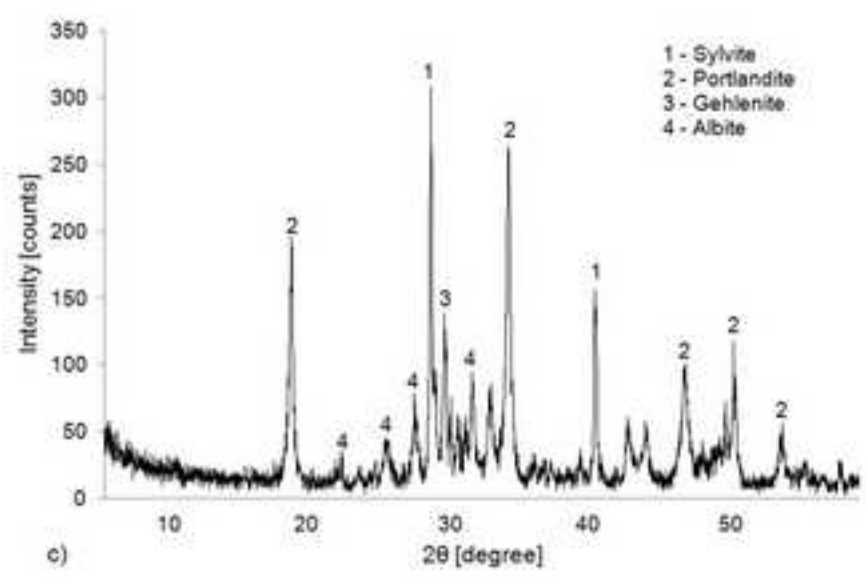
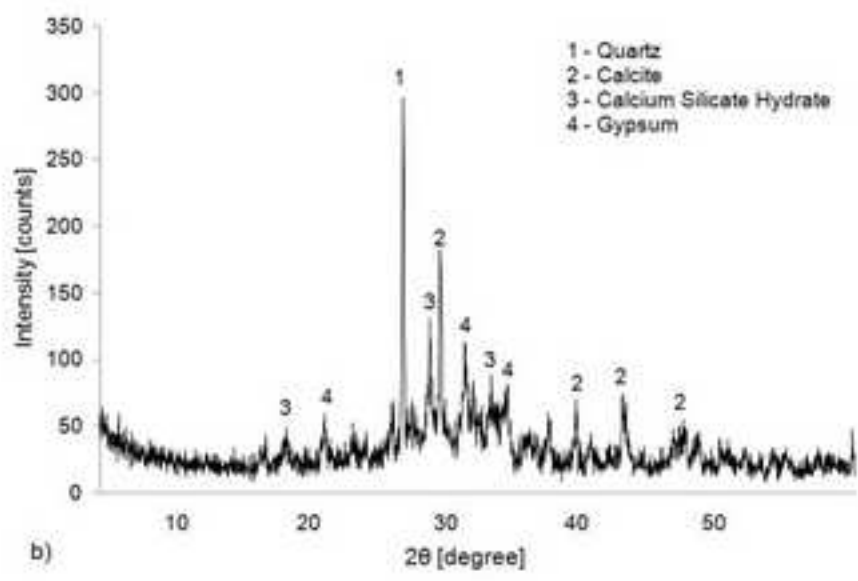
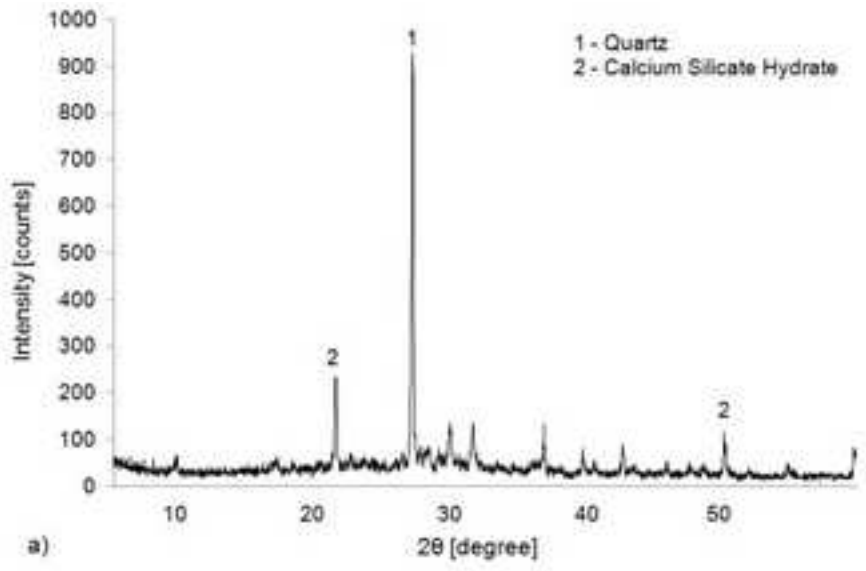
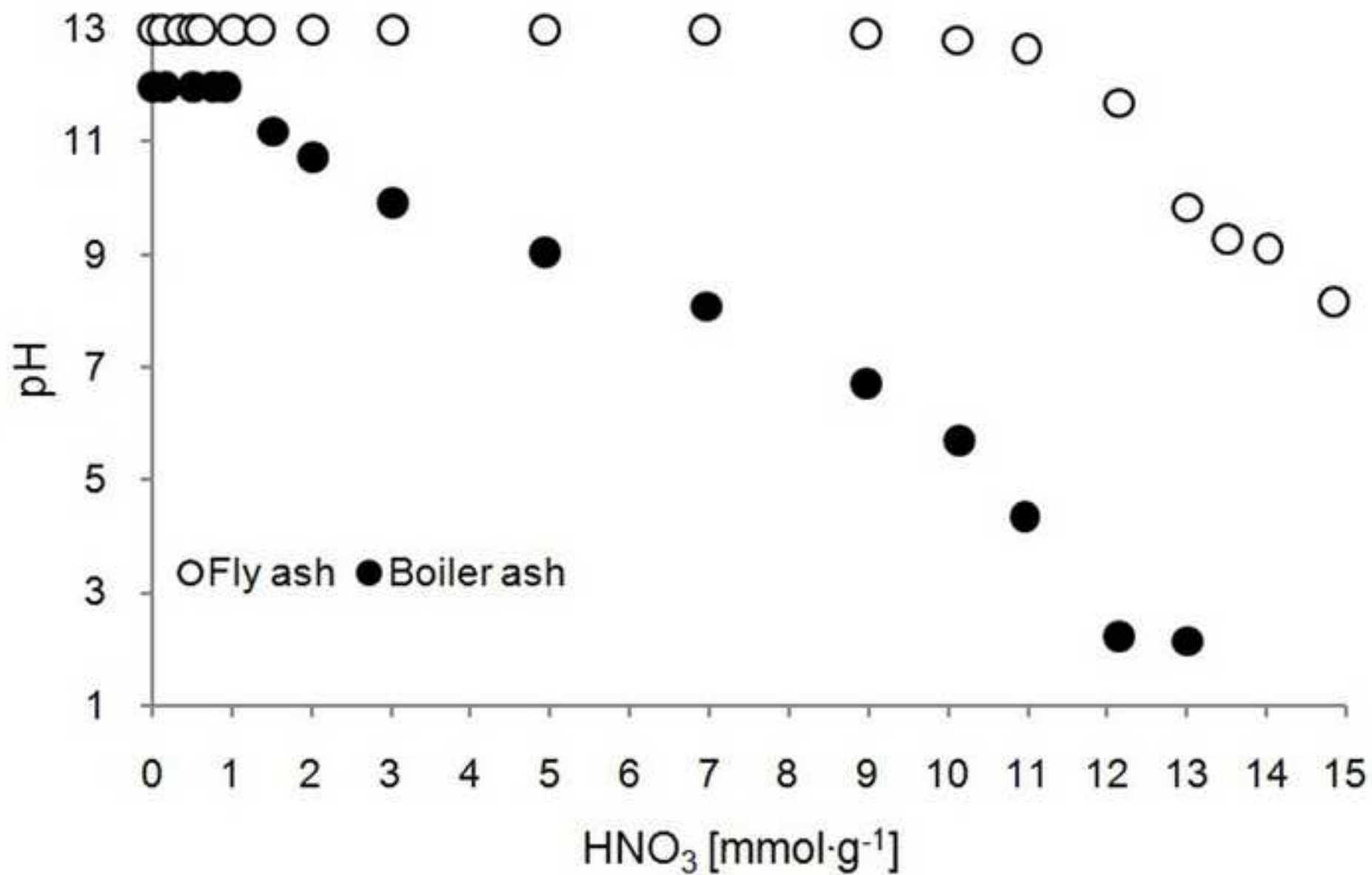


Figure 4
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1 Figure captions

2 Figure 1. Schematic diagram of the biomass combustion plant.

3 Figure 2. Biomass combustion residues: a) BTA; b) BOA; c) FA.

4 Figure 3. X-ray diffraction of a) BTA, b) BOA and c) FA.

5 Figure 4. ANC curves conducted on BOA and FA.

6 Figure 5. Particle size distribution of BTA and BOA (a) and LOI at 550°C for each particle size class (b).