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# Fly ash characterization from *Cynara cardunculus* L. gasification

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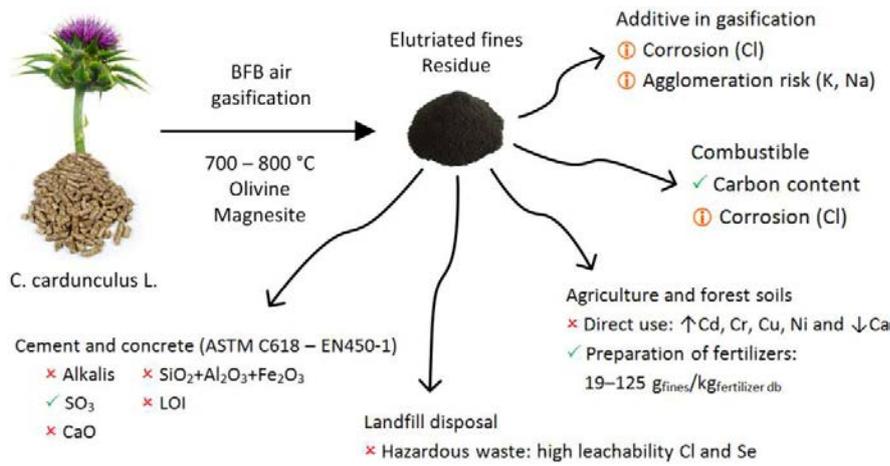
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## ABSTRACT

This study analyzes the characteristics of fines produced during the air-blown gasification of *Cynara cardunculus* L. in a bubbling fluidized bed. These fines are collected by means of two cyclones and a hot filter. The gasification temperature is varied from 700 to 800 °C using olivine and magnesite as bed materials, with an equivalence ratio (ER) of 0.2. Relatively high carbon content is found in the entrained fines for all experiments. The lower heating value (LHV) of the elutriated fines varies from 5.2 to 9.4 MJ/kg<sub>db</sub>. Around 75 % of the fines are captured in the first

cyclone, 5 % in the second cyclone and the remaining 20 % in the hot filter. The concentration of elements such as Se and Cl makes these fly ashes a hazardous material. Based on these properties the potential reuse of fly ashes is evaluated.

## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Gasification is a promising technology to transform biomass into a useful product gas. However, this process generates an ash residue that needs to be disposed of or reused in a different application. This aspect is often overlooked in biomass gasification studies which usually concentrate their attention on gas yields and tar mitigation.

The elements that form the inorganic fraction of the biomass are divided into major elements, minor elements and trace elements mainly formed by heavy metals<sup>1</sup>. However, this composition depends on the origin and handling of the biomass<sup>2</sup>. The composition of the biomass ash plays a major role in the treatment of this residue as different regulations exist depending on the country or region for its use in terms of the content of some toxic elements such as Cd, Hg, Ni, Pb, Se or Zn that can increase the contamination of air, water and soils, or can threaten human health<sup>1,3</sup>.

The final composition of fly ash depends also on the atmosphere, reducing or oxidative, at which the conversion process is carried out <sup>3</sup>. Dong et al. <sup>4</sup> found that a reducing atmosphere promotes the evaporation of Cd and Zn while Pb, Cu, Ni, and Cr volatilization is enhanced under an oxidative atmosphere. In addition, presence of chlorine promotes the evaporation of heavy metals in form of metal chlorides that tend to condense on fine particles, leading into the corrosion of the different parts of the installation <sup>5-8</sup>. Belevi and Moench <sup>9</sup>, on the other hand, found that during the incineration of (household waste or mixed waste?) the content of Al, Ba, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Na, Ni, P, Si and Ti in fly ash is not much influenced by chemical conditions (temperature or redox conditions) whereas Cu and Zn are favored by oxidative conditions.

In the case of biomass combustion, there is an extensive library of literature which deals with ash characterization and utilization <sup>10-14</sup>. However, the information regarding biomass gasification fly ash is very limited <sup>15-17</sup> and its composition is also quite different from that of combustion plants, containing high amounts of unburned carbon, polycyclic aromatic hydrocarbons (PAHs), chlorine and heavy metals. All these features make the use of gasification fly ashes more complicated and suggest that coal combustion fly ash utilization options are not suitable for biomass gasification ash, giving rise to the requirement for some pretreatment <sup>18,19</sup>. Different studies have been performed within the GASASH project <sup>15</sup>, trying to find sustainable and economic methods for gasification ash management. When the carbon content is high, combustion is the most promising method to reduce the un-reacted carbon and the amount of undesirable compounds such as the PAHs, chlorine and some heavy metals as well as recovering energy. This reduces the volume of the fly ashes and applications such as construction products can be considered for the new ash generated <sup>15</sup>.

The use of biomass gasification fly ashes in construction have been investigated by many authors: concrete paving blocks <sup>20</sup>, fire-resistant boards <sup>18</sup>, lightweight bricks <sup>19</sup> or clay bricks <sup>21</sup>. These preliminary studies conclude that fly ashes have high potential as a binding material within different construction components.

The properties of biomass gasification fly ash collected in different locations of the cleaning section was investigated by Liao et al. <sup>22</sup>. They observed that the most volatile compounds (CaO, Na<sub>2</sub>O, MgO, Cl, P<sub>2</sub>O<sub>5</sub>, SrO, As<sub>5</sub>O<sub>3</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub>) were mostly found in the ash scrubber while the less volatile species (NiO, Cr<sub>2</sub>O<sub>3</sub>, PbO, CuO and MnO) stayed in the cyclone. Narayan et al. <sup>23</sup> found that cyclone ash was dominated by K and Ca silicates. They also found high fractions of K and Ca in the second cyclone.

*C. cardunculus* L. is a perennial energy crop native to Mediterranean regions (Spain, Portugal or Greece), and is commonly known as cardoon or thistle. However, it also grows as weed in other parts of the world like Argentina or California <sup>24</sup>. Cardoon is suitable for cultivation in the dry soils of the Mediterranean region and has some distinct advantages over other biomass plants: low water irrigation requirement, enhancement of soil characteristics, low cost, and the possibility to grow in lands that are not suitable for food purposes <sup>25,26</sup>. The cultivation of *C. cardunculus* L. has been studied by different authors due to its importance for biomass production <sup>25-29</sup>. They show a cardoon production of between 1.4 and 25 t<sub>db</sub>/ha·year, depending on the irrigation and annual rainfall with annual costs of around 65 €/t, including establishment and operating costs. Further information can be found in a recently published review which considers the research carried out with this feedstock in the last 30 years <sup>30</sup>. Different gasification studies have been performed using *C. cardunculus* L. as a feedstock <sup>31-37</sup>. However,

to the authors' knowledge, the properties of the entrained fines from gasification of cardoon have never been investigated.

Therefore, the objective of this work is to analyze the entrained fines collected from cardoon air gasification in a BFB pilot plant and focus the attention on this residue which has been not always considered as has been recently reported by Thomsen et al. <sup>17</sup>. For this purpose, a multi-layer characterization: CHN-S, loss on ignition (LOI), moisture, ash, lower heating value (LHV), chlorine and metal composition, has been carried out on the samples as well as a A mass balance of the 18 elements retained in the solid by products of gasification. Based on these characteristics, the different possible applications employed for combustion fly ashes are evaluated for cardoon gasification fly ashes in order to determine if they meet the specific requirements for each application and to check how toxicity of these fines in case they have to be landfilled.

## 2. EXPERIMENTAL SETUP

**2.1. Biomass and bed material.** Cardoon pellets are used as the feedstock. Table 1 shows the chemical characteristics of the fuel. Cardoon is characterized by relatively high ash content when compared to other biomass crops such as *Miscanthus* or Reed Canary Grass (Phyllis database, <https://www.ecn.nl/phyllis2/>). Typical ash content reported for cardoon are 11.3 % <sup>38</sup>, 15.4 % <sup>34</sup> and 7.2 % <sup>25</sup>. The high volatile matter content and higher heating value (HHV) make cardoon a good option for gasification. However, high the sodium and potassium content in the ash exposes cardoon to a high risk of bed agglomeration <sup>39</sup>. In order to avoid this undesirable problem 3 wt.% of kaolin ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) is added to the cardoon prior to gasification as suggested by Llorente et al. <sup>40</sup> and Weber and Quicker <sup>41</sup>.

**Table 1.** Biomass properties (cardoon ar. with 3 wt.% of added kaolin).

<i>Proximate analysis [wt.% ar]</i>		<i>Ultimate analysis [wt.% db]</i>	
Moisture	9.69	Carbon	48.91
Volatile Matter	69.83	Hydrogen	5.90
Fixed Carbon	10.21	Nitrogen	0.58
Ash	10.27	Sulphur	0.09
		Chlorine	0.91
		Oxygen <sup>a</sup>	32.24
<i>Higher heating value [MJ/kg db]</i>	17.50		
<i>Ash composition [g/kg ash db]</i>			
Al	110.76	Mg	18.13
Ca	151.06	Na	247.73
Cu	5.14	Se	5.54
Fe	9.37	Si	312.19
K	86.61		
<i>Minor elements [mg/kg ash db]</i>			
Cd	201.41	Mo	805.64
Co	221.51	Ni	413.90
Cr	100.70	Pb	10.07
Mn	508.56	Zn	312.19

ar: as received, db: dry basis, <sup>a</sup> by difference

Olivine, supplied by Magnolithe, Austria, and magnesite, obtained from MINELCO, U.K., are employed as bed materials (Table 2). Both olivine and magnesite are commonly used as bed materials in biomass gasification showing good operational performance in terms of agglomeration and improvements in gas composition and tar mitigation <sup>42,43</sup>.

**Table 2.** Bed materials composition.

	Olivine	Magnesite
MgO [wt.%]	2.69	74.05
SiO <sub>2</sub> [wt.%]	88.33	21.10
Fe <sub>2</sub> O <sub>3</sub> [wt.%]	6.59	0.63
CaO [wt.%]	–	0.84
Al <sub>2</sub> O <sub>3</sub> + Cr <sub>2</sub> O <sub>3</sub> + Mn <sub>3</sub> O <sub>4</sub> [wt.%]	2.69	3.35

**2.2. Experimental facility.** A pilot scale air-blown bubbling fluidized bed gasifier is used for the experimental campaign. This facility is located at the University of Limerick. The fluidized bed consists of a lower section of 134.5 mm internal diameter and a freeboard of 211.6 mm internal diameter, with a total height of 3000 mm. The entire facility including reactor and

downstream cleaning section are heated, insulated and monitored with temperature and pressure sensors. Further information about this setup can be found elsewhere <sup>37,44</sup>.

**2.3. Experimental procedure.** The reactor is loaded with olivine or magnesite to a bed height of 26.90 cm. The air flow rate is kept at a constant value of 63 Ndm<sup>3</sup>/min for all the experiments and the electrical furnaces are set to the experimental temperature for each test i.e. 700, 760 or 800 ° C. When the desired temperature is reached, biomass feeding commences leading to a stable operation approximately 40 min after the introduction of the biomass. The selected air and biomass rates result in a constant ER, defined as the ratio between the air flow rate introduced into the reactor and the stoichiometric air flow rate needed for the complete combustion of the biomass, of 0.20. This value has been chosen according to an approximate  $u/u_{mf}$  ratio of 3, a typical value for BFB gasifiers, and a biomass feeding rate of 4.5 kg/h which was easily maintained by the feeding system.

The feeding system is pressurized with a nitrogen flow of 2 Ndm<sup>3</sup>/min to prevent the backflow of gases from the gasifier. The gas leaves the reactor passing through two hot cyclones and a hot filter (Candle element, Pyrotex BWF-Envirotec) whose temperatures are kept at 400 and 450 °C, respectively, to prevent tar from condensing. Entrained particles, such as fine bed particles, char and fly ash are stored in these devices. The principal operating conditions can be found in Table 3.

**Table 3.** Main operating conditions and gasification results.

<i>Operating conditions</i>		
Bed material	Olivine, 5.38 kg	Magnesite, 5.70 kg
Biomass feeding rate [kg <sub>daf</sub> /h]	3.55	3.56
Air flow rate [Ndm <sup>3</sup> /min]	63.07	63.47
ER [—]	0.20	0.20
Inlet air temperature [°C]	227 – 320	270
Gasification temperature [°C]	700 – 800	800

Freeboard temperature [°C]	500	500
Cyclones temperature [°C]	400	400
Hot filter temperature [°C]	450	450

When the experiments are completed the facility is cooled to ambient temperature using an N<sub>2</sub> purge. Fly ash and entrained particles from cyclones and filter are discharged, weighed and retained for analysis.

**2.4. Methods of fines analysis.** All samples from the two cyclones and the hot filter are analyzed using a CHN-S elemental analyzer, a drying oven and an ash furnace in order to get the ultimate analysis, and moisture and ash contents. The HHV is also measured using an isoperibolic calorimeter, and the LHV is calculated using the moisture and hydrogen content of the sample, M and H, respectively, and the latent heat of steam,  $h_g$ , (Eq. 1) <sup>45</sup>. Ash (at 550 °C according to CEN/TS 14775:2004) is obtained from the samples and digested following the procedure described by Serrano et al. <sup>37</sup>. Bed materials are also digested according to the same procedure. The inorganic elemental composition is determined using an atomic absorption spectrometer (AAS) or inductive coupled plasma atomic spectroscopy (ICP-OES) for Hg, As, Sb and S. The LOI of the fly ash is determined as the weight loss between the dry samples and the weight of the samples after being kept at 550 °C for 90 minutes.

$$LHV = HHV - h_g \left( \frac{9H}{100} + \frac{M}{100} \right) \quad (1)$$

In order to test the metal mobility, 5 g of dry fines are mixed with deionised water, in a liquid to solid ratio (L/S) of 10. The mixture is continuously agitated for 24 h and then filtered as indicated in the DIN 38414-S4 standard for leaching tests. Finally, the liquid samples/leachates are analyzed by AAS.

### 3. RESULTS AND DISCUSSION

In this section, the characteristics of the ashes collected in the two cyclones and the hot filter are presented and analyzed. An extensive discussion of the gasification results, gas composition, tar analysis and catalytic effect of bed materials, can be found in a previous publication <sup>37</sup>.

Different amounts of fines are collected by the three cleaning devices: around 75 wt.% of the total in the first cyclone, 5 wt.% in the second cyclone and 20 wt.% in the hot filter. Table 4 shows the amount of fines accumulated in the different devices, over the lifetime of each experiment.

### 3.1. Ash characterization

*3.1.1. Elemental composition, ash and moisture.* The fines escaping the reactor are mainly composed of ash, more than 69 wt.% db, and to a lesser extent by carbon (Table 4). The carbon content of the samples is moderately high (13 – 25 wt.% db). The negative values for the oxygen content in the magnesite experiments are due to the temperature differences in the determination of the elemental composition (850 °C) and ash content (550 °C).

**Table 4.** Elemental composition, moisture and ash content, and LHV of the fines from the cyclones and hot filter.

	m <sub>fines</sub> [g/h]	C [wt.% db]	H [wt.% db]	N [wt.% db]	S [wt.% db]	Cl [wt.% db]	O <sup>a</sup> [wt.% db]	Moisture [wt.% ar]	Ash [wt.% db]	LHV [MJ/kg db]
Cardoon + kaolin Olivine 700 °C		48.91	5.90	0.58	0.09	0.91	32.24	9.69	11.37	15.81
Cyclone 1	162.8	24.67	0.62	0.25	0.07	2.32	2.13	1.38	69.94	9.54
Cyclone 2	11.7	16.53	0.36	0.24	0.04	2.03	2.10	1.55	78.70	6.44
Filter	44.1	19.66	0.40	0.17	0.07	3.33	0.44	0.22	75.93	6.67
Olivine 760 °C										
Cyclone 1	164.7	24.85	0.60	0.37	0.07	2.85	1.55	0.75	69.71	9.02
Cyclone 2	12.4	17.73	0.32	0.27	0.04	2.63	2.46	2.28	76.55	6.45
Filter	48.8	21.36	0.45	0.22	0.05	3.60	0.67	0.00	73.65	7.94
Olivine 800 °C										
Cyclone 1	175.8	18.41	0.30	0.31	0.14	3.75	7.00	1.59	70.09	7.15
Cyclone 2	18.0	13.41	0.17	0.24	0.09	3.33	3.64	2.08	79.12	5.28
Filter	27.0	14.19	0.13	0.35	0.08	3.70	5.00	1.02	76.55	5.24
Magnesite 800 °C										
Cyclone 1	217.2	25.79	0.25	0.21	0.09	2.90	-3.38	1.38	74.14	8.53

Cyclone 2	17.5	23.05	0.09	0.21	0.10	2.93	-3.47	2.23	77.09	7.35
Filter	62.2	24.49	0.15	0.19	-	-	-	0.66	75.40	7.50

ar: as received, db: dry basis, <sup>a</sup> by difference

The carbon content is higher from ash collected in the first cyclone than in the second one and the filter. Furthermore, the carbon content in the second cyclone always shows the lowest value. On the other hand, the highest amount of ash is obtained in the second cyclone while the lowest ash concentration is found in the first cyclone. It should be noted that the mean carbon content in the two cyclones and the hot filter decreases with temperature. Olivine and magnesite show some differences in terms of carbon content at the same temperature, with the value being higher for magnesite. The LOI of the cardoon ashes ranges from 19 to 33 wt.% db (Figure 1a), which are very similar to those obtained in full-scale gasifiers. These results are in agreement with the higher carbon conversion when the temperature is increased and when olivine is used instead of magnesite at the same temperature <sup>37</sup> and with the values reported in other works <sup>16</sup>.

*3.1.2. Chlorine and sulphur content.* Sulphur and chlorine contents are shown in Table 4. Sulphur content is similar in all samples, on average around 0.08 wt.% (dry basis). In the case of the chlorine concentrations, values of between 2 and 4 wt.% are observed. The content of Cl is higher in fly ash collected in hot filter since more Cl containing compounds condense on finer particles, which have higher surface area. The contents of S and Cl are in the range of other fines collected from different biomasses and gasifiers reported in the literature <sup>15</sup>.

*3.1.3. Energy content.* The LHV of the samples collected in the first cyclone is higher than the fines collected in the filter and in the second cyclone (Table 4). The mean values for each experiment are between 5 and 10 MJ/kg<sub>db</sub>, and are lower than the values obtained from full-scale gasifiers which are in the range of 14-25 MJ/kg <sup>15</sup>. However, these values are, more or less, half of the LHV of the original biomass. Therefore, a considerable amount of energy per unit of mass,

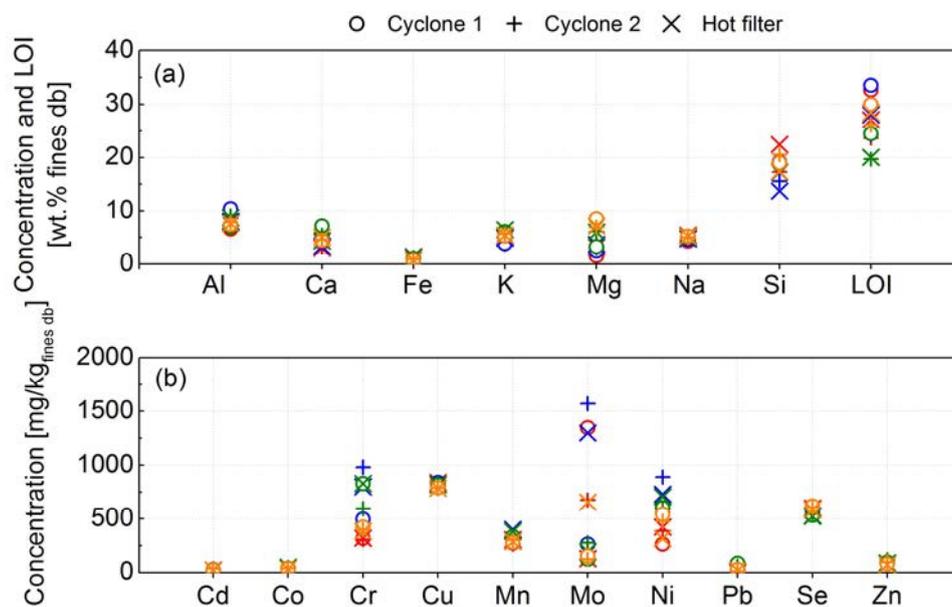
2-3 % of the energy introduced with the biomass, remains in the fines. This amount of energy can be important in industrial scale plants, and can be recovered for other applications.

The LHV of fines collected in first cyclone is from 13 to 33 % higher than in second cyclone and hot filter. There are negligible differences between the mean LHV at 700 and 760 °C in the case of olivine. However, the differences increase when the temperature is raised to 800 °C, with a considerable decrease of the LHV. There is also a significant difference in the LHV between the bed materials at this temperature. When magnesite is used, the LHV of the fines is higher than for olivine at the same temperature. These trends resemble carbon content since calorific value refers to carbon content in fines.

*3.1.4. Distribution of elements/metals in the solid streams from gasification.* The main ash forming inorganic elements found in fines are Al, Ca, K, Mg, Na, Si, and, to a lesser extent, Fe (Figure 1a). Si is the most abundant element which is in accordance with the amount of Si in the cardoon and kaolin mixture. Jordan and Akay<sup>46</sup> reported a similar composition for the main ash forming elements in bagasse gasification ash. Gasification temperature affects the distribution of Ca, K and Mg whose concentration increases with temperature at all sampling points while Na and Fe remain more or less constant. Similar results are observed for Al in cyclone 2 and the hot filter. Concentration of Si does not change with temperature in the samples collected at cyclone 1, but greater fluctuation is observed for the samples from cyclone 2 and the hot filter where the differences are very marked.

Considering both bed materials, the Mg content is clearly higher for magnesite because of possible entrainment of the bed particles (Table 2) and/or enrichment of cyclone fines in magnesium due to abrasion.

The concentrations of some major elements such as Al, Na, K and Si are higher in *C. cardunculus* fines than reported in other experiments<sup>15</sup>. Mg is similar to other biomasses while Ca and Fe concentrations are rather smaller. These differences are influenced by the ash composition of the original biomass. Additionally, the bed material employed also has an influence as some elements become detached from the bed material surface due to abrasion or catalytic action with, and contribute to enrichment in the fines.



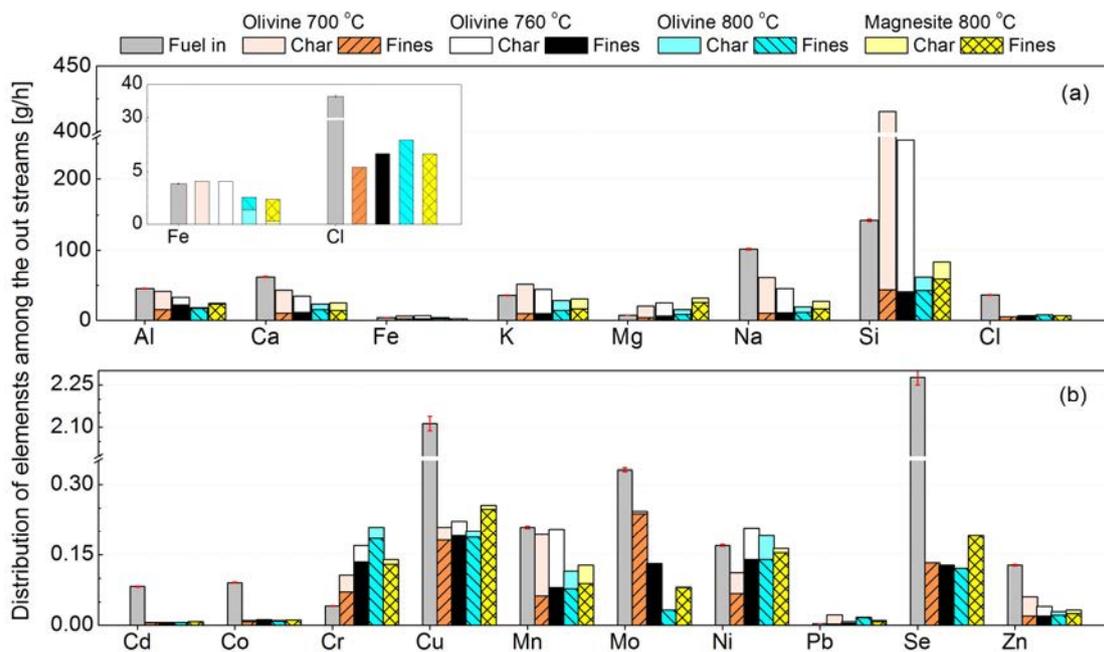
**Figure 1.** a) Main inorganic elements found in the collected fines at the different locations (as oxides in wt.% fines<sub>db</sub>) and b) minor elements concentration in collected fines for different temperatures, bed materials, and sampling locations: (red) olivine 700 °C, (blue) olivine 760 °C, (green) olivine 800 °C, (orange) magnesite 800 °C.

The concentration of minor elements (Figure 1b) shows little variation with temperature, sampling location and bed material with exception of Cr, Mo and Ni which show significant differences. No As and Sb were observed in the samples analyzed. Higher content of Cr, Mo and Ni are observed for gasification tests at higher temperature.

An attempt is made to perform mass balances for the 18 elements collected in the solid streams, where biomass with kaolin is the input stream and the entrained fines and the bed char are the outputs (Figure 2). Metal recovery, defined as the ratio between the mass flow of an element collected in the char and in the cleaning system with that of and the inlet mass flow of that element in the biomass was calculated for all elements. The recovery for K, Ca, and to a lesser extent, Mg is slightly influenced by process temperature due to their lower boiling points compared to metals like Al, Fe and Si (Figure 2a). For magnesite test and in a lesser extent for olivine tests, Mg enrichment in the fines is observed caused by abrasion of magnesite particles during the operation of the fluidized bed or entrainment of small bed material particles. The chlorine recovery is rather low, with only 15-22 % captured on fly ash particles, indicating this element is volatilized and released in the gas phase as HCl, KCl and NaCl <sup>47</sup>. Some of this chlorine is captured by other elements that condense in the downstream devices. Chlorine under reducing/pyrolysis conditions is released mostly as CH<sub>3</sub>Cl at 350 °C with minor amounts of HCl <sup>48</sup>. At temperatures above 700 °C, gaseous Cl is recaptured by either K salts (KCl, (KCl)<sub>2</sub>) or K in the char matrix <sup>49-51</sup>. Gaseous KCl condenses and forms aerosols.

In the case of bed char, higher mass retention of the different elements is observed at lower gasification temperatures. This shows an effect of temperature on the release of inorganics from biomass, regardless of whether olivine or magnesite is used. The fate of the different metals cannot be accurately determined because it was impossible to separate and analyze the bottom ash from bed material and char particles while the metal emissions in the product gas were not measured. The high values of Fe and Si in char composition, coming from bed materials, are an indication of this difficulty.

It is worth noting the high recovery values for Cr, Mn, Mo and Ni in the fines (Figure 2b, raster filled bars) which is probably due to the abrasion of bed materials particles, in particular Cr and Ni from olivine<sup>52</sup> and the decomposition of the reactor walls releasing lubricants and residuals from previous tests<sup>53,54</sup>. The high recovery values for Pb are related to the inherently high volatility of this element combined with the reducing atmosphere that enhances its volatility<sup>4</sup>. At a temperature of 850 °C, Pb is completely vaporized as PbCl<sub>4</sub> and PbCl<sub>2</sub><sup>55</sup> and capture by Al and Si oxides when the temperature decreases<sup>56</sup>. The Cu was mainly retained/captured in the fines. The distribution of heavy metals is shifted towards the entrained fines, with their mass in the char being much lower than in the fines.



**Figure 2.** Mass balance for fines composition: a) major elements and b) minor elements and d) out/in balance for minor elements.

Taking into account the fuel input, the char and the entrained fines, the closure of the mass balance was less than 100 % for all major elements except for the elements mentioned above. The excess in Mg and Si mainly comes from the char composition as it is observed in Figure 2a,

where some bed particles could be retained in the char pores. In the case of Cr, the surplus could be produced from attrition of bed particles with the reactor walls in which trace particles are mainly retained in the first cyclone. The overall mass balance is not complete due to the lack of information from the ash inside the gasifier as it is difficult to and the elements which are volatilized and deposited on downstream colder surfaces. However, these values are within the limits reported in the literature <sup>54,57,58</sup>.

The corresponding enrichment factors (EF) <sup>59</sup> (Eq. 2), for all elements are calculated and presented in Table 5.

$$EF = \frac{\text{element concentration in fines}}{\text{element concentration in fuel}} \cdot \frac{\% \text{ as in fuel}}{100} \quad (2)$$

In the case of fly ash from cardoon gasification, the metals has been classified according to Meij's classification for fly ash <sup>59</sup> into group I (non-volatile elements): Al, Ca, Cd, Co, Cu, Fe, K, Mg, Se, Si and Zn; group II (semi-volatile elements with possible occurrence of the condensation phenomena): Cr, Mn, Mo, Na, Ni and Pb, aswell as group III (very volatile elements, with a limited capacity for condensing on the surface of submicron particles of ash): Cr.

The enrichment factor as originally proposed by Meij et al. <sup>59</sup> refers mainly to the elements volatility. If the EF is higher than 1 for non-volatile metals this means that there is a different source for them in the process other than the feedstock ash, e.g. bed material such as olivine for Fe, Cr, Ni or magnesite for Mg (abrasion or entrainment) <sup>60</sup> or alternatively corrosion of parts of the gasification equipment in the case of Cr, Ni or Pb enrichment <sup>61</sup> or the relatively high content of Cl in cardoon could significantly reduce the volatilization temperature of Ni and Pb. If the EF is lower than 1 for very volatile metals such as K and Na this suggests that they did not condensed on fly ash particles as it is shown in Figure 2a (small amount of these materials are found in the fines) but instead on the heat exchanger walls.

**Table 5.** EF for fines collected in cyclones and hot filter.

	Olivine 700 °C			Olivine 760 °C			Olivine 800 °C			Magnesite 800 °C			Group <sup>a</sup>
	C1	C2	HF	C1	C2	HF	C1	C2	HF	C1	C2	HF	
Al*	0,54	0,73	0,65	0,85	0,71	0,66	0,58	0,75	0,72	0,61	0,65	0,63	I (I/III)
Ca*	0,32	0,19	0,18	0,33	0,25	0,20	0,43	0,33	0,26	0,27	0,27	0,30	I (III)
Cd	0,11	0,12	0,11	0,12	0,13	0,11	0,12	0,17	0,11	0,12	0,16	0,11	I (III)
Co*	0,14	0,17	0,19	0,16	0,19	0,20	0,16	0,16	0,20	0,15	0,16	0,14	I (III)
Cr*	2,87	2,78	2,90	4,49	8,89	7,25	7,50	5,40	7,51	3,85	3,62	3,47	II (II)
Cu*	0,14	0,14	0,15	0,15	0,14	0,15	0,15	0,15	0,15	0,14	0,14	0,14	I (III)
Fe*	0,95	1,05	1,24	1,03	1,15	1,38	1,05	1,06	1,31	0,72	0,86	0,71	I (I)
K	0,44	0,40	0,54	0,41	0,59	0,52	0,65	0,62	0,69	0,56	0,59	0,58	I (I/III)
Mg*	0,77	1,27	1,63	1,21	1,53	1,86	1,64	3,06	3,03	4,28	3,49	3,62	I (I/II)
Mn*	0,49	0,47	0,55	0,60	0,61	0,72	0,60	0,60	0,69	0,50	0,54	0,52	II (I/III)
Mo*	1,53	0,76	0,15	0,30	1,78	1,47	0,14	0,31	0,22	0,17	0,14	0,74	II (I/III)
Na*	0,16	0,17	0,20	0,17	0,17	0,18	0,18	0,20	0,19	0,19	0,18	0,19	II (III)
Ni*	0,58	0,85	0,94	1,22	1,96	1,60	1,32	1,30	1,56	1,20	1,05	0,70	II (I)
Pb*	1,30	0,37	0,09	1,93	2,50	1,27	7,68	5,21	1,37	2,66	1,11	1,64	II (I/II)
Se	0,10	0,10	0,10	0,09	0,09	0,09	0,09	0,09	0,09	0,10	0,10	0,10	I (III)
Si*	0,49	0,46	0,59	0,50	0,41	0,36	0,50	0,49	0,46	0,50	0,54	0,46	I (III)
Zn*	0,26	0,27	0,25	0,26	0,26	0,25	0,27	0,35	0,26	0,23	0,28	0,22	I (III)

<sup>a</sup>According to Meij's classification for fly ash <sup>59</sup>, \*Not volatile at tested gasification conditions according to the element boiling point.

Some of the elements are present in cardoon fly ash because they are in the original feedstock (Cu, Se or Ni) and became concentrated in the ash. Other elements appear as a consequence of the bed material used but also as a result of reactor wall decomposition. Some of the Al in the fly ash arises from kaolin addition while the Pb is a result of attrition of the auger or different parts of the experimental facility. Therefore, the selection of the most appropriate bed material in terms of catalytic properties, ability to mitigate agglomeration while not contributing to an increase of heavy metals in fly ash is very important. In addition, the refractory materials which are used for building industrial scale gasification systems seem to also be important as they can cause ash contamination.

3.1.5. *Leaching characteristic of fines.* Leachability of heavy metals from gasification fines has been tested according to the DIN 38414-S4 standard as this is required under the waste acceptance criteria (WAC 2003/33/EC) to test if heavy metals tend to be removed by water and transferred to the soil, becoming a hazardous material. The results suggest that both cyclone and filter fines are classified as hazardous according to the European landfill directive 1999/31/CE <sup>62</sup> (Table 6). Even though, the majority of the metal concentrations are well within the limit values for non-hazardous landfill. The leachability of Se and in particular Cl exceeds the limits established by the European landfill directive. Consequently, the elutriated fines are unsuitable for direct land filling and will require pretreatment before disposal is permitted. Despite the fact that carboon does not contain large amounts of heavy metals, elements such as Cl promote their volatilization and subsequent condensation into fine particles as metal chlorides <sup>7</sup>. The content of calcium and iron oxides in the fly ash also has an influence on the leaching behavior of selenium, enhancing or inhibiting its mobility from the solid residue to the aqueous solution <sup>63-65</sup>. From the results in Table 6, there is an indication that more Se is leached from fly ash containing higher iron concentration, when olivine was used as a bed material.

**Table 6.** Leachability results according to DIN 38414-S4 in [mg/kg<sub>db</sub>].

	Ba	Cd	Cl	Cr	Cu	F	Hg	Ni	SO <sub>4</sub>	Se	Zn
Olivine 700 °C											
Cyclone 1	0.00	0.41	25999.24	0.74	4.77	13.27	0.00	0.45	1706.22	0.74	0.02
Cyclone 2	0.00	0.43	27391.87	0.78	6.48	9.40	0.00	0.30	1680.67	35.09	0.02
Filter	0.00	0.37	28934.08	0.76	7.17	7.41	0.00	0.31	1538.22	2.27	0.02
Olivine 760 °C											
Cyclone 1	0.00	0.47	28691.34	2.29	5.68	19.09	0.00	0.54	838.53	15.27	0.02
Cyclone 2	0.00	0.45	31229.37	3.04	6.45	9.99	0.00	0.43	1747.71	31.92	0.02
Filter	0.00	0.43	30543.55	0.76	8.03	21.20	0.00	0.56	1770.05	2.28	0.02
Olivine 800 °C											
Cyclone 1	7.19	0.55	31466.92	10.79	7.80	14.68	0.00	0.64	1184.47	6.47	0.02
Cyclone 2	0.00	0.52	34945.18	11.87	6.55	29.51	0.00	0.63	1586.40	23.74	0.02
Filter	2.33	0.60	35613.53	2.33	8.25	31.87	0.00	0.71	1989.83	20.21	0.03
Magnesite 800 °C											

Cyclone 1	1.52	0.37	30803.27	29.72	6.80	18.99	0.00	0.34	1629.71	0.76	0.02
Cyclone 2	0.00	0.39	26664.87	7.60	3.81	7.20	0.00	0.27	1184.93	19.00	0.01
Filter	0.00	0.43	32825.04	1.55	8.50	41.37	0.85	0.53	23058.73	0.00	0.02
<i>EU landfill directive</i>											
<i>Inert</i>	<i>20.00</i>	<i>0.04</i>	<i>800</i>	<i>0.50</i>	<i>2.00</i>	<i>10.00</i>	<i>0.01</i>	<i>0.40</i>	<i>1000</i>	<i>0.10</i>	<i>4.00</i>
<i>Non-hazardous</i>	<i>100.00</i>	<i>1.00</i>	<i>15000</i>	<i>10.00</i>	<i>50.00</i>	<i>150.00</i>	<i>0.20</i>	<i>10.00</i>	<i>20000</i>	<i>0.50</i>	<i>50.00</i>
<i>Hazardous</i>	<i>300.00</i>	<i>5.00</i>	<i>25000</i>	<i>70.00</i>	<i>100.00</i>	<i>500.00</i>	<i>2.00</i>	<i>40.00</i>	<i>50000</i>	<i>7.00</i>	<i>200.00</i>

In order to reduce the leaching behavior of fly ash metals, it would be desirable to treat this hazardous material: immobilization of trace metals within the fly ash <sup>66</sup>, pelletization combined with thermal treatment <sup>67</sup> or controlled leaching <sup>15</sup>.

**3.2. Is it possible to valorize cardoon fly ash?** The differences between fly ashes from gasification and combustion (intensively studied) motivates the investigation of their properties in order to provide information about its capacity to comply with waste regulations and other standards for utilization. All current regulations typically focus on combustion ashes from biomass or sewage sludge. In this case, although the fly ashes under investigation come from gasification and fall outside the direct scope of current standards, the available directives and regulations are chosen in order to evaluate potential use of cardoon fly ashes.

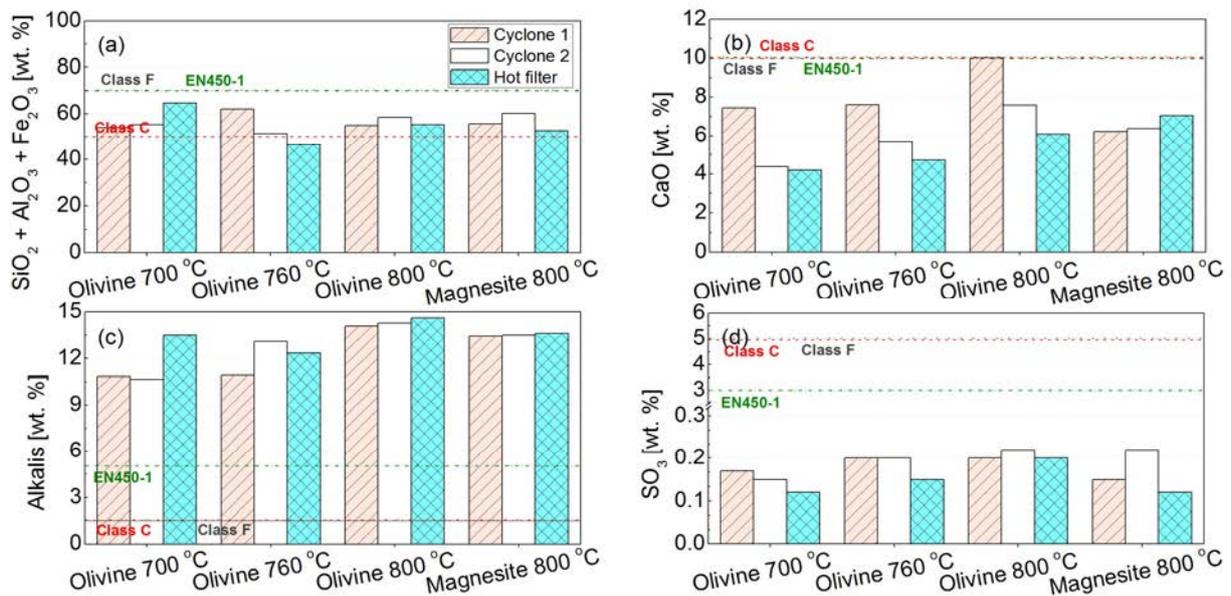
*3.2.1. Use as combustible feedstock.* Since the collected fines contain almost half of the LHV of the original biomass, a significant amount of energy can be recovered from cyclone and hot filter fines when combusted. However, its use is limited and a water pre-wash would be required prior combustion as the K and Cl have a propensity to cause corrosion in the boilers <sup>19</sup>.

*3.2.2. Use as an additive in gasification.* The alkali elements in the fines could serve as catalysts for other biomass under gasification conditions. Sodium and potassium are known to have a positive effect on gasification rate and hydrogen production at specific operating conditions <sup>68</sup>. Evidence for this can be found from the hydrogen content in the product gas obtained from these experiments which is moderately higher compared with other biomasses gasified with air <sup>37</sup>. Apart from adding extra quantities of Cl, the increased risk of bed

agglomeration should be considered. A compromise solution or the use of additives or lower temperatures to prevent agglomeration should be adopted in any case.

*3.2.3. Use in cement and concrete.* The use of fly ashes in the cement and concrete industry is regulated by European and American standards (EN450-1 and ASTM C618) <sup>69,70</sup>. One of the most important parameters for cement and concrete applications is the LOI. Depending on the value of this parameter, fly ashes are divided into three categories <sup>69</sup>: (cat. A) LOI < 5 wt.%, (cat. B) LOI < 7 wt.%, and (cat. C) LOI < 9 wt.%. The LOI of cardoon fly ash is too high to fulfill any of these requirements. However, some studies have demonstrated that the addition of 0 – 25 wt.% of a high-carbon fly ash is feasible in cement manufacturing <sup>71,72</sup>. Moreover, this value could be reduced by burning the fines, obtaining extra energy and ashes with similar characteristics to combustion.

**¡Error! No se encuentra el origen de la referencia.** shows the content of different species in the entrained fines that impact their use for cement and concrete applications. The limits for the total alkali content as well as for the chlorine content are also significantly below the values obtained for cardoon fly ashes, although a pre-wash, may help to satisfy the requirements. The sum of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  is higher than 50 wt.%, suitable for class C component materials according to ASTM C618, but less than the 70 wt.% required for class F and for the European regulation (EN450-1). The amount of  $\text{SO}_3$  is also within the limits, however the amount of CaO is lower than the 10 wt.% required for class C. In this case, cardoon fly ashes comply with low calcium ashes, suitable for class F and EN450-1 standard. In view of these results, cardoon fly ashes are not suitable as component materials for the cement and concrete industry as some requirements for the different regulations are not satisfied.



**Figure 3.** Content of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , CaO, alkalis and  $\text{SO}_3$  of cardoon fly ashes and corresponding limits for their use in cement and concrete industry according to the European and American standards (EN450-1 and, class C and F according to ASTM C618) <sup>69,70</sup>.

3.2.4. *Use in agricultural and forest soils.* Use in agriculture and forestry is a common application for coal combustion fly ashes where they are used directly as fertilizers or as a raw material in the production of these types of products. This use is regulated by different European and national directives and standards <sup>73,74</sup>. There are two main requirements which must be fulfilled: a minimum quantity of the main nutrients (K, P, Ca and Mg), and a maximum amount of contaminants (heavy metals) <sup>75</sup>. For most of the regulations consulted for this study the Cd, Cr, Cu and Ni contents in cardoon fines always exceeded the limits for contaminants while Pb and Zn do not seem to be problematic. The concentration of Ca does not however fulfill the minimum value for nutrients. As a consequence, cardoon fly ashes cannot be used as fertilizer in Austria, Denmark, Sweden or Finland.

In Spain, the Government Decree 506/2013 for fertilizers <sup>76</sup> establishes three different limits for heavy metals in fertilizers obtained from organic waste. Cardoon fly ashes could be utilized in the preparation of fertilizer although the quantity of fly ash to be used is limited by the final Cd content: 19–29 (class A), 54–83 (class B), and 81–125  $\text{g}_{\text{fines}}/\text{kg}_{\text{fertilizer db}}$  (class C), depending on the fly ash origin (cyclone 1, cyclone 2 or hot filter). Despite the differences between biomass fly ashes and sewage sludge, both can contain high amounts of heavy metals. Considering this fact, the Government Decree 1310/1990 for sewage sludge utilization can be used as an indication for the possible hazards when using the cardoon gasification fly ashes directly in agricultural soils according to the soil pH. The content of Cr, Cu, Pb and Zn in the cardoon fly ashes would allow them to be used for both acid and alkaline soils. Nevertheless, the high concentration of Cd limits the direct use of cardoon fly ashes to alkaline soils while the Ni content is over the limits in both cases. Therefore, according to the Spanish regulations, the cardoon fly ashes cannot be employed directly on agricultural soils although some amounts could be used in the preparation of agricultural fertilizers.

#### 4. CONCLUSIONS

The very high chlorine content as well as the selenium content, and what is even more important, the very high leachability of these elements, make the fly ash from cardoon gasification to be classified as hazardous. Due to the high LOI, the total alkali and chlorine content, the direct use of the cardoon fly ash as raw material in cement and concrete industry is not possible. The high content of Ni, Cd, Cu and Cr in the ash excludes its application on the agricultural land.

Some of the elements are present in cardoon fly ash because they are in the original feedstock and become concentrated in the ash. Other elements are enriched in the fly ash as a consequence

of the bed material used in BFB gasification due to abrasion or entrainment but also as a result of reactor wall decomposition. Therefore, the selection of appropriate bed material which will exhibit catalytic properties, mitigate agglomeration and will not contribute to an increase of heavy metals in fly ash is very important. In addition, the refractory materials which are used for building industrial scale gasification systems seem to be also important as they can cause ash contamination.

#### ASSOCIATED CONTENT

**Supporting Information.** Nutrients, heavy metals concentration in the elutriated fines, and limit values for different European regulations for the use of fly ashes and sewage sludge as soil amendments and fertilizers.

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