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► **To cite this version:**

Claire Hazotte, Baptiste Laubie, Stéphanie Pacault, Olivier Dufaud, Marie-Odile Simonnot. Evaluation of the performance of nickel hyperaccumulator plants as combustion fuel. *Biomass and Bioenergy*, 2020, 140, pp.105671. 10.1016/j.biombioe.2020.105671 . hal-02983609

**HAL Id: hal-02983609**

**<https://hal.science/hal-02983609>**

Submitted on 22 Aug 2022

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2 **Evaluation of the performance of nickel hyperaccumulator plants as combustion fuel**

3

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7

8 **Abstract**

9 Agromining is an emerging technology aiming at recovering metals from soils using hyperaccumulator  
10 (HA) plants. Plant cultivation and pyro- and hydrometallurgical processes have been designed for nickel  
11 (Ni) recovery. In this chain of processes, dry plants are burnt to obtain Ni-rich ashes that are  
12 subsequently treated. To ensure the sustainability and the profitability of the process, energy recovered  
13 at the combustion stage would add some value. The combustion of three Ni HA plants (*Odontarrenha*  
14 *chalcidica*, *Leptoplax emarginata* and *Berkheya coddii*) was investigated. Namely the higher and lower  
15 heating values (HHV and LHV) were measured with a calorimeter bomb and calculated with correlations,  
16 thermo-gravimetric analysis was performed, dry plants and ashes were characterized, and gas emissions  
17 were monitored during combustion at two temperatures. In a complementary approach, the self-heating  
18 behaviour of plants and ashes were compared, and the activation energy of such phenomenon was  
19 determined. These results allowed the identification of the step limiting the self-inflammation of the  
20 plants, which gives relevant information for their safe storage.

21

22 **Keywords:** hyperaccumulator plants; combustion; higher and lower heating values; elemental  
23 composition; gaseous emissions; self-heating

24

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25

## 26 1. Introduction

27 Some plants, called hyperaccumulator (HA) plants, are able to extract metals from soils and store them  
28 in their **harvestable tissues**, at concentrations up to a few tens of grams per kilogram. This property has  
29 been used to advantage to recover metals from soils and secondary resources. The chain of process,  
30 called agromining, consists of cultivating HA plants and extracting the metals by pyro- or  
31 hydrometallurgical processes [1,2]. Agromining has mainly been developed for nickel (Ni), **because i)**  
32 large areas of soils enriched in Ni, called ultramafic soils, are available in many countries, and ii) more  
33 than 450 species of Ni HA plants have been documented. The plant *Alyssum murale*, recently renamed  
34 *Odontarrhena chalcidica* [3], belonging to the *Brassicaceae* family has been widely studied for  
35 agromining. This plant, containing up to 10 g kg<sup>-1</sup> of Ni in its above-ground parts, has been cultivated in  
36 several countries in temperate latitude (e.g. Albania, Greece, Spain, USA) [4–8]. Nickel yield reached  
37 more than 100 kg per hectare [9].

38 Over the past two decades, processes have been developed to recover Ni from the plant biomass to  
39 produce Ni metal, Ni-based catalysts and Ni salts [10–14]. In the 2000s, the very first tests consisted of  
40 introducing ashes from the *O. chalcidica* plant into a Ni-smelter to obtain Ni metal [14]. Then a  
41 hydrometallurgical approach **was** developed. Most often, the first step consists of burning the plant in  
42 order to produce ashes, which are free of organic matter and contain 100 to 200 g kg<sup>-1</sup> of Ni [15,16]. The  
43 metal is extracted by acid leaching and the solution is treated to produce Ni salts. The most common  
44 example is the production of ammonium nickel sulphate hexahydrate (ANSH) from *O. chalcidica*, from  
45 laboratory to pilot scale. The combustion stage appears to be the most sensitive, since it determines the  
46 quality and composition of the ashes, which is very important for the subsequent operations. The  
47 temperature is easy to control at laboratory scale with a few grams of plants burnt in a furnace; it is  
48 generally set at 550 °C, which is high enough to degrade the organic matter. But it may be difficult to

49 control and measure in a boiler at the pilot scale, fed by kilograms of biomass per hour; in these  
50 conditions, it can reach 900 °C. Therefore, the influence of combustion temperature on ash composition  
51 has been studied for *O. chalcidica* [15,16]. Although it has an influence on ash mineralogy,  
52 hydrometallurgical processes are only slightly modified [15]. On the other hand, oxygen content can  
53 have an influence on nickel oxidation state and residence time on the amount of unburnt material.  
54 Moreover, the process upscaling can also lead to safety issues, as large storages are notably more prone  
55 to self-heating than a few grams of plants. In a first approach, the safety parameters can be inferred  
56 from literature data on wood, hay or other cellulosic materials [18]. However, it should be kept in mind  
57 that numerous factors such as the volume, porosity, storage duration, shape of the material or water  
58 content can have a significant influence on the self-heating of the storage. Therefore, this point has to be  
59 addressed on the basis of experimental data and with regard to inherent safety principles [19]. A  
60 common example of the application of these principles is to dry the biomass before storage in order to  
61 limit its water content and reduce the risks related to biological activity.

62 Agromining is commonly presented as an environmentally friendly chain of processes, since it is based  
63 on plant cultivation on soils of low fertility and allows the recovery of metal dispersed in low  
64 concentration matrices. However, these arguments are not sufficient, and this view was supported by  
65 using an objective method: a life cycle assessment (LCA) of the process was conducted to evaluate the  
66 environmental impact of the process, from the resource extraction to the final disposal [20]. This study  
67 has clearly shown the importance of the recovery of the heat generated during the combustion, in order  
68 to lower the environmental impacts. More generally, in the context of global change and energy  
69 transition, it is essential to increase the portion of renewable energy and also to assess the composition  
70 of the emitted gases. As a consequence, in order to reduce greenhouse gas emission, the use of biomass  
71 for energy production is drastically increasing, biomass including wood and wood waste, energy **crops**,  
72 agricultural residues, **biosolids** etc. [21,22].

73 From an application point of view, it may be difficult to implement heat recovery in some agromining  
74 contexts, specifically in isolated areas, but it is important first to examine the extent to which heat  
75 recovery from the combustion of these plants is of interest. According to ISO 17225:2014 standard on  
76 solid biofuels, hyperaccumulator plants from temperate areas could be classified as “herbaceous  
77 biomass from agriculture and horticulture”, and more specifically as “grasses, whole plant” (category  
78 2.1.2.1). These plants could be easily burned in the form of bales. In addition to the parameters of bale  
79 size and density, moisture, chlorine and ash content, net calorific value (LHV, lower heating value) at  
80 reception, and ash melting behaviour should be stated. However, due to the particularity of this  
81 biomass, with its high concentration of metal, other questions arise. Thus, emissions into the  
82 atmosphere during combustion and storage of dry biomass under safe conditions have to be  
83 investigated.

84 To our knowledge, no work on the combustion parameters of Ni hyperaccumulators has been done  
85 before. Therefore, the present work was undertaken to compare this biomass to other solid biofuels. It  
86 studied the heat flux released during the combustion of HA plants as well as the gaseous emissions. The  
87 risk of self-heating of dry biomass and ashes during storage was also assessed. Three HA plants were  
88 selected: i) *Odontarrhena chalcidica*, which is the “reference” plant, ii) *Leptoplax emarginata*, belonging  
89 to the same family, and potentially able to accumulate higher amounts of Ni, and iii) *Berkheya coddii*,  
90 from the *Asteraceae* family, which is also a good potential candidate for Ni agromining.

91

## 92 **2. Materials and methods**

### 93 2.1. Biomass samples

94 *O. chalcidica* and *L. emarginata* plants were harvested, collected and dried in 2015-2016 in an ultramafic  
95 area near the village of Eidián, 127 Ponteveda (Galicia, North-West Spain; N 42°49'55,08" W  
96 8°00'14,60") [10]. Soil pH was 5.8 and the total concentration of Ni in soil was 0.86 g kg<sup>-1</sup>. *B. coddii* was

97 cultivated in a growth chamber with the following conditions: photoperiod of 16 h of day/ 8 h of night,  
98 temperatures of 25 °C day/19 °C night, 50% air humidity between July 2015 and July 2016 with a  
99 synthetic soil containing 0.10 g kg<sup>-1</sup> of Ni and 0.01 g kg<sup>-1</sup> of Co [11]. All the concentrations refer to dry  
100 soil. Then, the plants were dried in the oven at 105 °C and ground with a laboratory grinder. The  
101 available amounts were a few kilograms of *O. chalcidica* and of *L. emarginata* and a few grams of *B.*  
102 *coddii*.

103

## 104 2.2. Chemicals and reagents

105 HNO<sub>3</sub> (≥ 65 %) was obtained from Fluka, HNO<sub>3</sub> (64-69% - Trace metal grade) by Fisher Chemical, H<sub>2</sub>SO<sub>4</sub>  
106 (95-97 %) by Sigma Aldrich, H<sub>2</sub>O<sub>2</sub> (50%) by Alfa Aesar, certified solutions for ICP analyses by PlasmaCal,  
107 SCP Science. Ultra-pure water (Elga-Purelab Option) was used for all the experiments.

108

## 109 2.3. Chemical analyses

110 Solid samples of dry plants or ash (approximately 0.10 g) were randomly collected and digested with  
111 8.5 mL of concentrated HNO<sub>3</sub> (Fluka) and 1.5 mL of H<sub>2</sub>O<sub>2</sub>, in a microwave oven (Milestone Start D  
112 Microwave Digestion System Ethos1) for 50 min with a set-point of 200 °C. The resulting solutions were  
113 diluted to 50 mL with ultra-pure water before analysis by ICP-AES (ICAP 6000 Series ICP spectrometer).  
114 Standard solutions from multi-elemental certified liquid sample (1000 mg L<sup>-1</sup>, SCP Science) were used for  
115 calibration and quality controls by dilution with 3 vol. % (v/v) HNO<sub>3</sub> (Fisher). Analyses were repeated  
116 three time for each sample and a quality test was carried out every 10 measurements with a certified  
117 solution. The analysis procedure (digestion and quantification) was controlled by using reference  
118 certified standard (corn powder standard V463-USRAVE-INRA).

119 For each plant, C, H, N, S and O were analysed by CHNS-O Flash Analyser. The samples (1.5 mg) were  
120 used in a tin boat assortment for percentage composition of C, H, N, O and S. These experiments were

121 repeated 5 times at 960 °C. The calibration and quality controls were performed with sulfanilamide  
122 standard (C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S, Thermoscientific). About 1 mg of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>, Thermoscientific) was  
123 added to the samples to determine sulphur content.

124 Chlorine concentrations in the biomass of *O. chalcidica* and *L. emarginata* were measured by ionic  
125 chromatography by Socor (external laboratory, Cofrac accreditation). This was not done for *B. coddii* due  
126 to the small quantities available.

127 Throughout the text, all concentrations of the given elements indicated for plants or ash are on a dry  
128 weight basis.

129

#### 130 2.4. Physical analyses

131 The density of each dry plant (including ground leaves, stems and flowers) was measured by a helium  
132 pycnometer (Micrometrics AccuPyc 1330). This measurement gives the true density (except the internal  
133 porosity). This method was chosen instead of bulk density measurement (standard ISO 17828:2015),  
134 which is very dependent on the grinding stage. The average of ten consecutive measurements was  
135 taken.

136 The moisture content was determined by weight loss: a few grams of dry plants were heated in a furnace  
137 at 105 °C until constant mass. They were calculated on wet basis (standard ISO 18134-1:2015).

138 Thermogravimetric analysis (TGA) of the hyperaccumulator plants was performed using STAR<sup>e</sup> system  
139 METTLER Toledo. Samples of approximately 10 mg of dry plants were heated in standard alumina  
140 crucibles (Al<sub>2</sub>O<sub>3</sub>) from 30 to 1 000 °C at 10 °C min<sup>-1</sup> in air atmosphere (50 mL min<sup>-1</sup>). Each experiment was  
141 repeated three times.

142 The ash fraction was determined according to ISO 18122:2105 standard. The temperature was increased  
143 to 250 °C at 6.25 °C min<sup>-1</sup> and kept constant for 60 min; then, it was increased to 550 °C at 10 °C min<sup>-1</sup>  
144 and kept constant for 120 min. The crucible was placed in a desiccator until temperature decreased to  
145 room temperature (20 °C) and the sample was weighed. This heating and cooling processes were

146 repeated until the weight variation was lower than 0.5 mg. Ash fractions were obtained at 550 and 900  
147 °C. CHONS and ICP-AES analysis were performed to monitor the variation of metallic and organic  
148 contents against temperature.

149 To complete requirements of ISO 17225-1:2014 standard on solid biofuels, ash melting behaviours were  
150 **reported** by Socor (external laboratory, Cofrac accreditation) according to ISO 21404:2020 standard.

151 There were no tests on *B. coddii* because of the small quantities available.

152

### 153 2.5. Higher and lower heating values

154 The higher heating values (HHV) were determined with a static bomb calorimeter (sealed Parr 6100).

155 First, the device was calibrated with 1 g of benzoic acid ( $C_7H_6O_2$ , HHV: 26.45 MJ  $kg^{-1}$ ), calibration was

156 repeated 5 times. Then, samples of 1.0 g of dry biomass previously compacted into pellets using an

157 Instron press, were burnt: the pellets were placed in a steel crucible under the lid of the bomb on which

158 there are also two electrodes and a valve allowing the filling of  $O_2$  or air. The electrodes allowed the

159 firing of the sample. Combustion was performed at constant volume, the oxidant ( $O_2$ ) was added in

160 excess (20 bars). The system was adiabatic and contained 2 L of water whose temperature was

161 measured by thermocouple sensor.

162 The higher heating value of the sample (heat released during combustion) was calculated according to

163 eq.1.

164

$$165 \quad HHV = \frac{C \times (T_f - T_i)}{m_{sample}} \quad (1)$$

166 with HHV the higher heating value of the sample ( $J \text{ kg}^{-1}$ ), C the calorific capacity of the device ( $J \text{ K}^{-1}$ ),  $T_i$

167 and  $T_f$  the initial and final temperatures of water in the calorimetric vessel (K),  $m_{sample}$  the sample mass

168 (kg).



169 The lower heating values for dry samples were calculated from HHVs as follows according the equation  
170 (2) from the standard ISO 18125:2017 [23]. They were not determined considering the moisture content,  
171 as the analyses were not performed immediately after shipment

$$172 \text{ LHV} = \text{HHV} + 6.15 \times w(\text{H}) - 0.8 \times [w(\text{O}) + w(\text{N})] \quad (2)$$

173 with LH and HHV, the lower and higher heating values ( $\text{J g}^{-1}$ ) and  $w(\text{H})$ ,  $w(\text{O})$  and  $w(\text{N})$ , the hydrogen,  
174 oxygen and nitrogen contents of the moisture-free biomass, respectively.

175 HHV and LHV can also be determined using correlations based on the biomass content in C, H, O, N, S.  
176 Gumz (eq.3) and Boie (eq. 4) correlations have been selected for the calculations of HHV (in  $\text{MJ kg}^{-1}$ )  
177 since they are based on the mass fractions  $w_i$  of the five previous elements [23, 24].

$$178 \text{ HHV} = 35.160 w_{\text{C}} + 116.225 w_{\text{H}} - 11.090 w_{\text{O}} + 6.280 w_{\text{N}} + 10.465 w_{\text{S}} \quad (3)$$

$$179 \text{ HHV} = 34.03 w_{\text{C}} + 124.31 w_{\text{H}} - 9.836 w_{\text{O}} + 6.278 w_{\text{N}} + 19.09 w_{\text{S}} \quad (4)$$

180 Comparison between experimental and calculated values will show whether these correlations can be  
181 used as a first approach to predict HHVs of other hyperaccumulator plants.

182

## 183 2.6. Gaseous emissions

184 Combustion tests were performed in a modified Godbert Greenwald furnace [26], in which a grid was  
185 added to maintain the plant sample until total combustion (Fig. 1). Approximately 0.3 g of crushed plants  
186 were dispersed in an open vertical tube, which can be heated from 20 to 1 000 °C. Combustion  
187 experiments were performed at 550 and 900 °C under air gas for each plant.

188 The combustion gases were sampled in collapsible Tedlar bag and analysed with a four-way micro gas  
189 chromatography (Varian - 490 GC). High purity helium (99.99%) at a flow rate of  $50 \text{ mL min}^{-1}$  was used  
190 for gas flushing. This system allowed the quantification of different gases from  $\text{H}_2$  to  $\text{C}_8$  hydrocarbons.  
191 The gases were separated by four columns: two molecular sieves, one PoraPlot U and on CP Wax.  
192 Column temperature was comprised between 50 and 70 °C and the pressure was equal to 180-200 kPa.

193 The temperature of injectors was 100 °C and the detection was performed by a thermal conductivity  
194 detector.

195

196

*Please insert Fig. 1*

197

## 198 2.7. Self-heating behaviour

199 The self-heating of a powder is due to the presence of an exothermic phenomenon (oxidation, water  
200 condensation, fermentation, *etc.*) whose heat production occurs more rapidly than the heat transfer at  
201 its boundaries. Self-heating can then lead to self-ignition and cause fires or dust explosions in case of  
202 dust lifting.

203 The self-ignition behaviour of *O. chalcidica* and its ashes, obtained after combustion at 900 °C, was  
204 studied by performing tests in an isothermal oven according to EN 15188 [27]. It should be pointed out  
205 here that if the combustion process is complete, the ashes will certainly not burn. However, this is not  
206 always the case in industrial processes and a distinction must be made between the combustibility of fly  
207 ash and "bottom ash". In particular, Amyotte et al. (2005) showed that while fly ash is not explosive,  
208 bottom ash can explode under restrictive experimental conditions [28] . The powder was placed in cubic  
209 baskets of volumes ranging from 8 to 2744 cm<sup>3</sup> and the tests were carried out at temperatures up to  
210 400 °C. For a single basket size, numerous tests are performed to identify the critical temperature at  
211 which an ignition can occur. In addition to the oven temperature, three thermocouples were positioned  
212 into the basket in order to measure the temperature evolution at three different depths (at the powder  
213 surface, at one-third of the basket and at its centre). Ignition criterion is validated if the temperature at  
214 the cube centre exceeds the oven temperature by 60 K.

215 Then, various models can be applied to extrapolate the experimental results to pilot and industrial  
216 scales. The most commonly used model, developed by Frank-Kamenetskii, assumes that the heat

217 generated by the reaction is transferred by conduction within the storage and consider a zero-order  
218 reaction [18]. Subject to the foregoing limitations, its application leads to the estimation of the activation  
219 energy of the exothermic reaction.

220

### 221 **3. Results and discussion**

222

#### 223 3.1. Characteristics of the dry plants

224 The values of the moisture, density and ash fraction of the plants are given in Table 1. *O. chalcidica* and  
225 *L. emarginata*, belonging to the *Brassicaceae* family exhibited close values while *B. coddii* showed a  
226 lower moisture content and a higher density.

227

228 *Please insert Table 1*

229

230 For the three plants, the ash fraction was ~~comprised~~ between 7 and 9%. For *O. chalcidica*, it was  
231 comparable to the value of 7.6% reported in [9]. These results are close to the barley straw, equal to 9.8  
232 % while the ash rates of others plants are generally lower (*e.g.* wheat straw:  $1.3 \pm 0.1$  %, flax straw:  $3.0 \pm$   
233  $0.2$  %, timothy grass:  $1.1 \pm 0.1$  %, pinewood:  $1.5 \pm 0.2$  %) [15].

234 The CHONS and elemental composition of the dry plants are presented in Table 2 and Fig. 2a. The plants  
235 exhibited comparable weight contents in carbon ( $\approx 42$ -46 %), oxygen ( $\approx 40$  %), hydrogen ( $\approx 6$  %), nitrogen  
236 (1-2 %) and sulphur ( $\leq 1\%$ ). The C, H and O contents were close to the ones of wheat straw, barley straw,  
237 flax straw, timothy straw and pinewood (C: 41.4-49.0 %, H: 6.1-6.4 %, O: 44.4-52.1 %), while the N and S  
238 contents were higher for HA plants [29], especially for *L. emarginata*.

239 The other elements represented 7 to 10% of the biomass; the major ones were nickel (Ni), calcium (Ca),  
240 potassium (K), magnesium (Mg) and phosphorus (P). The mineral composition of species varied. For

241 nickel, concentrations are higher than 1 g kg<sup>-1</sup> (hyperaccumulation threshold) for both *Brassicaceae*  
242 (10.2 and 4.5 g kg<sup>-1</sup> for *O. chalcidica* and *L. emarginata* respectively). *B. coddii* is on the verge of that  
243 threshold. The amount of Na (<2 g kg<sup>-1</sup>), Mg (<3 g kg<sup>-1</sup>), Ca (5 - 10 g kg<sup>-1</sup>), Fe (<2 g kg<sup>-1</sup>), Zn (<1 g kg<sup>-1</sup>), and  
244 P (≈3 g kg<sup>-1</sup>) and were similar for the three plants. However, the K level in the biomass was lower for  
245 *O. chalcidica* than *L. emarginata* and *B. coddii*.

246 The chlorine concentration by weight was 0.25 and 0.80 % for *O. chalcidica* and *L. emarginata*,  
247 respectively. These values are typical values for straw from wheat, rye, barley and oilseed rape [30].  
248 Chlorine is a normative parameter for solid biofuels as it causes corrosion of combustion devices and  
249 pipes. It should be put into perspective with potassium: indeed, KCl is also a volatile compound [31]. It is  
250 found in large quantities in herbaceous plants compared to woody materials (1 to 40 times more) [30].  
251 Thus, in addition to the amount of nickel which can be highly dependent on soil composition, it seems  
252 that *O. chalcidica* is a better candidate for combustion than *L. emarginata*, because it had lower KCl  
253 levels.

254

255 *Please insert Table 2 and Fig. 2*

256

### 257 3.2. Thermogravimetric profiles of the plants and characteristics of the ashes

258 All three plants exhibited similar thermogravimetric profiles (Fig. 3). The masses of water evaporated in  
259 the first stage were in agreement with the values in Table 1, the differences were attributed to the  
260 different sample sizes. The second stage (200-300 °C) corresponded to the degradation of hemicellulose  
261 and cellulose. The third stage (420 °C) was the degradation of the remaining organic matter above 500  
262 °C. Weight losses (250-900°C) were similar for all three plants (comparable amounts of hemicellulose,  
263 cellulose and lignin). At 550°C, more than 95% of the organic matter was degraded.

264

*Please insert Fig. 3*

265  
266 The composition of the ash obtained after combustion at 550 and 900 °C is presented in Table 2 and  
267 Figure 2, the results are comparable with those of Zhang et al. [16]. In Fig.2b., metal concentrations in  
268 plants and ashes at 550 and 900 °C were normalized relatively to the initial mass of the plant samples to  
269 allow comparison.

270 At 550 °C, N had disappeared. At standard pressure and temperature,  $19.2 \pm 5.8 \text{ L kg}^{-1}$  (for *O. chalcidica*  
271 and *B. coddii*) and  $32.0 \pm 1.6 \text{ L kg}^{-1}$  (for *L. emarginata*) of NO<sub>2</sub> could be formed. The ashes contained  
272 approximately 4-6 % of C, 4-9 % of O and 1-3 % of S. The oxygen fraction is a total value including  
273 organically bound oxygen and oxygen in mineral matter (oxides, sulphates and carbonates). The mineral  
274 composition represented 83-89 % of the ashes weight. At 900 °C, the C content has decreased to 1 % of  
275 the ashes; the O fraction was lower in *O. chalcidica* (2 %) than in *L. emarginata* (13 %) or *B. coddii* (8 %),  
276 and the mineral fraction represented 82 to 94 %.

277 Mass balances indicate that around 99.0 % and 99.9 % of C was eliminated at 550°C and 900°C  
278 respectively for all three plants. The slight decrease in mass observed on thermogravimetric profiles was  
279 assigned to the loss of KCl (especially for *B. coddii*), but mainly to the transformation of carbonates to  
280 oxides (with CO<sub>2</sub> release). While the ashes became enriched in oxygen very slightly, sulphur remained  
281 stable in the ashes (not volatilized under SO<sub>x</sub> form). Contrary to N, which is a normative parameter (due  
282 to NO<sub>x</sub> formation), S is not mandatory by the standard in case of bale combustion.

283 Only small variations are observed between the mass fractions of the main minerals in the biomass and  
284 in the ash, except for potassium in *B. coddii*. This indicates that only traces of nickel can be found in the  
285 fumes (absorbed on the fly ash). Zinc is partially volatilized. Biomasses do not contain lead, which may  
286 also be removed during combustion. The concentrations of trace metals in the gas phase should be  
287 further investigated, but this should only be done in real combustion appliances. This depends on the  
288 combustion conditions, as air flows, chamber geometry, filters etc.

289 The melting behaviour of the ash must be indicated as an informative parameter according to ISO 17225  
290 standard. A high temperature **reached** during combusting can lead to clinker and many dynamic  
291 problems in the chamber. For *O. chalcidica* and *L. emarginata*, the shrinkage starting temperature are  
292 very close (1365 and 1377 °C respectively). All other parameters (deformation, hemisphere and flow  
293 temperatures) are above 1500 °C.

294

### 295 3.3. Higher and lower heating values

296 The results of the experimental and calculated calorific values (HHVs and LHVs) of the three HA plants  
297 are given in Table 3. The experimental and calculated values of the HHVs are in good agreement,  
298 confirming the validity of the chosen correlations. Thus, Gumz or Boix correlations can be used to predict  
299 the HHV of other plants as a first approach. The calorific values of the three plants are very close, in the  
300 range 16.7-17.3 MJ kg<sup>-1</sup>.

301 *Please insert Table 3*

302

303 Calorific values of others fuels are given in Table 4 [2, 3, 15, 17-19]. The HHVs of the HA plants are 15 to  
304 20% lower than HHVs of wood, straws and eucalyptus. They are similar to the HHVs of Chinese cabbage,  
305 poplar leaf or banana peel and from 13 to 30% higher than the ones of mahua tree peel branch, ginkgo  
306 leaf or water hyacinth [17], the latter being used to produce energy. By considering the average annual  
307 energy consumption in France (e.g. 11,000 kWh for a 4-person household in a 75 m<sup>2</sup> apartment),  
308 approximately 2.3 tons of plants **per household** would be necessary for heating and domestic hot water  
309 production only.

310 *Please insert Table 4*

311 [32–37]

### 312 3.4. Gaseous emissions

313 Exhaust emissions of H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, O<sub>2</sub> and CH<sub>4</sub> were recorded in order to  
314 estimate the impact of the combustion. The average values of the gas concentrations at 550 and 900 °C  
315 are given in Fig 4. for each plant.

316 At 550 °C, the main gases were CO<sub>2</sub> and N<sub>2</sub> and at 900 °C, the combustion of plant emits CO<sub>2</sub>, CO, H<sub>2</sub> and  
317 N<sub>2</sub> with the same order of magnitude. It should be underlined that the presence of nitrogen in the  
318 exhaust gases is due to air flushing, and can be related to the amount of oxygen consumed by the  
319 reaction. NO<sub>x</sub> can potentially be emitted by the plant combustion, but such compounds were not  
320 analysed here. As expected, the gas emissions from biomass are strongly influenced by the temperature:  
321 at 550 °C, the amount of CO<sub>2</sub> was higher than at 900 °C. In fact, it is even more relevant to analyse the  
322 evolution of the CO/CO<sub>2</sub> ratio as a function of the temperature. The CO/CO<sub>2</sub> ratio increases both when  
323 the fuel equivalent ratio increases, which is due to incomplete combustion, but also when the oven  
324 temperature increases from 550 to 900°C. Indeed, Boudouard equilibrium is shifted towards the carbon  
325 monoxide when the temperature exceeds about 700°C. During the combustion of the biomass, water  
326 vapour is also generated, but was not quantified in this work. However, as the combustion of the plants  
327 implies a preliminary step of pyrolysis, the influence of steam reforming reaction cannot be ignored at  
328 high temperatures. Reaction between water vapour and methane generated by pyrolysis can lead to  
329 hydrogen formation, which is clearly observed in Fig. 4 at 900°C.

330 By comparing the gases generated by the combustion of the three plants, it appears that only slight  
331 variations can be observed at 900 °C. However, at 550 °C, the ratio CO/CO<sub>2</sub> is higher for *B. coddii* than for  
332 the other plants, which can be assigned to a lower availability of the oxygen contained by this HA plant.

333 Figure 4 also shows that at low temperature, the carbon dioxide concentration is significantly higher for  
334 *O. chalcidica* than for *L. emarginata*. In particular, Veznikova et al. (2017) demonstrated that the gases  
335 generated by self-heating were dependent on the moisture content of the cellulosic material [38].  
336 Therefore, a higher moisture content tends to increase the carbon dioxide concentration, whereas the

337 CO concentration appears to be less affected by the presence of water. This is consistent with the results  
338 shown in Figure 3, with the water content being higher for *O. chalcidica* (7.8%wt.) than for *L. emarginata*  
339 (4.4%wt.).

340 *Please insert Fig. 4*

341

342 3.5. Self-heating behaviour of *O. chalcidica* and its ashes

343 The thermal stability of *storage* of *O. chalcidica* plants and ashes is described in Fig. 5. It appears that the  
344 plants are more prone to self-heating and ignition than their ashes, which was expected considering the  
345 organic content of the powders. Frank-Kamenetskii model was successfully applied to the experimental  
346 results obtained for both samples. It should be noted that the critical dimension corresponds to the half-  
347 edge of the cube (1, 2.5, 3.5, 5 and 7 cm), which is the characteristic dimension with regard to the heat  
348 and mass transfers. The thermal conductivity of the powders beds was determined by using a Thermal  
349 Conductivity Analyzer TCi (CTherm) in order to evaluate the Biot number. By considering an average  
350 convection coefficient of  $25 \text{ W m}^{-2} \text{ K}^{-1}$  [27], **Biot number** ranges from 5 to 50 for the various cubes,  
351 which validates one of the assumptions of the model: the convective transfer can be neglected  
352 compared to conduction. As a consequence, the critical parameter  $\delta_c$  of Frank-Kamenetskii model was  
353 set at 2.569 [18]. It can be deduced that, for a storage of 1 m of half-edge, the critical temperature  
354 leading to self-ignition is 405 and 375 K for the ashes and plants, respectively. The critical temperature  
355 obtained for plant *storage* corresponds to that of hardwood chips or cork sawdust and is greater than,  
356 for instance, that of hops *storage* [39]. Furthermore, for *storage* at room temperature, the critical size is  
357 always greater than 100 m of half-edge, which implies that the self-heating risk is low under such  
358 conditions. It should be stressed that the propensity to self-heating of the ashes strongly depends on  
359 their volatile matter and fixed carbon contents, but also on their metal content in the case of ashes  
360 collected for HA plant combustion. Concerning plant *storage*, their initial moisture content also has a



361 strong influence on their self-heating behaviour at low temperatures. The impact of water can be mostly  
362 negative on the thermal stability of storage, due to biological reactions or acid hydrolysis of  
363 hemicellulose, but Gray et al. (1984) also state that water can have a positive impact on the thermal  
364 diffusivity of storage [40]. In addition, completely dry plants are hygroscopic, which can increase the rate  
365 of heat release due to condensation of water vapour. However, these effects cannot be shown here.  
366 Indeed, in experiments carried out at laboratory scale and at temperatures above 373 K, the  
367 temperature increase slows down for a period corresponding to the evaporation of water. Under such  
368 normalized conditions, the influence of moisture is reduced, and the dried biomass finally reacts with the  
369 surrounding oxygen.

370 Using Frank-Kamenetskii model, the activation energies calculated for the plants and ashes are 113 and  
371 128  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. These results are consistent with the activation energy associated to the  
372 combustion of other lignocellulosic compounds, e.g. 110  $\text{kJ}\cdot\text{mol}^{-1}$  for Douglas fir, 125  $\text{kJ}\cdot\text{mol}^{-1}$  for wheat  
373 straw and 147  $\text{kJ}\cdot\text{mol}^{-1}$  for beech wood [41]. Nevertheless, some limitations should be kept in mind,  
374 notably the fact that the oxidation is assumed to be a zero-order reaction, i.e. independent from the fuel  
375 equivalent ratio. Fig. 6 shows the temperature evolution of *O. chalcidica* samples at various heights of  
376 the basket and for two experiments: a cube of 1 cm half-edge at 280 °C and a cube of 7 cm half-edge at  
377 220 °C.

378 *Please insert Fig. 5 and 6*

379  
380 Fig. 6 clearly shows that, for small **storage**, ignition occurs at the centre of the sample, whereas ignition  
381 takes place first at one-third of the largest basket. Focusing on the latter cube, it can be seen that self-  
382 heating occurs at the centre of the sample after 2 hours, but that ignition (main peak at 760°C) is  
383 delayed. Ignition is then clearly visible at one-third of the sample (peak at 650°C). This behaviour  
384 characterizes a diffusional-limitation of oxygen within the sample, which is not consistent with a zero-

385 order reaction. For instance, reducing oxygen accessibility, by compaction, by choosing the best  
386 orientation with regard to prevailing winds for outdoor piles, by creating a protective layer with an ash-  
387 water slurry or by inerting are relevant solutions to manage the risk of self-heating for such compounds  
388 [42].

389

390

#### 391 **4. Conclusion**

392 The thermal behaviour of three contrasted hyperaccumulator plants was studied in this work, and the  
393 main conclusions are as follows:

- 394 - the combustion step allows the degradation of organic matter and the concentration of metals,  
395 without significant loss up to 900 °C,
- 396 - these plants can be considered as combustion fuel: their higher heating value, around 17 MJ kg<sup>-1</sup>  
397 is lower than wood but comparable to other plants or agro-wastes; therefore, they can be used  
398 for heating,
- 399 - From a regulatory point of view, the biomass of *Brassicaceae*'s would be globally classified M10  
400 A10.0 ClO.10+.
- 401 - This biomass could not be marketed as a simple solid biofuel due to the very high nickel content.  
402 In the case of pellet manufacture (which could be considered in this case), the concentration of  
403 nickel must be less than 10 mg kg<sup>-1</sup>. The ISO standard is therefore not suitable for agromining.  
404 Installations must be adapted for the combustion of hyperaccumulators.
- 405 - it was very important to confirm this point, since the life cycle assessment of the agromining  
406 chain has shown low environmental impacts provided that energy was recovered according to  
407 Frank-Kamenetskii model,

- 408 - the results concerning gas composition show the importance of the control of temperature and  
409 oxygen; also, the released gases depend on the plant composition,  
410 - self-ignition is not likely to occur with conventional amounts of plants or ashes stored at room  
411 temperature, and even in case of temperature increase in summer.

412 The results are important both from scientific and applied point of view and pave the way of **agromining**.  
413 Future work will be done at the pilot scale, to measure dust and gas emissions from the boiler used to  
414 burn high amounts of plants. The air flow and residence time influence on ash qualities will also be  
415 assessed. Tests will be performed on a larger scale to assess the influence of the moisture content on the  
416 self-heating of plant **storage**.

417

#### 418 **Acknowledgements**

419 We gratefully acknowledge our colleagues, Dr M. Rue, Dr R. Saad (LSE, University of Lorraine-INRA,  
420 Nancy, France), Pr A. Bani (UAT, Tirana, Albania) and Dr P. Kidd (CSIC, Santiago de Compostela, Spain) for  
421 providing the HA plants, Dr B. Brandelet, Dr P. Girods and Pr Y. Rogaume (LERMAB, University of  
422 Lorraine, Nancy, France) for calorimetric analysis. This research was conducted as part of the EU LIFE-  
423 AGROMINE Project (LIFE15 ENV/FR/000512); we gratefully acknowledge for this support.

424

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530

## Figure captions

**Fig.1.** Photography (a) and schematic drawing (b) of the combustion furnace

**Fig.2.** Comparison between the element concentrations in the dried biomass (a1), in ashes obtained at 550 (a2) and 900°C (a3) for the three hyperaccumulators, and normalized relatively to concentrations in the biomass of *O. chalcidica* (b1), *L. emarginata* (b2) and *B. coddii* (b3).

**Fig.3.** Thermogravimetric analysis of biomass samples (a) *O. chalcidica*, (b) *L. emarginata*, (c) *B. coddii*

**Fig.4.** Composition of the gases obtained from hyperaccumulator plants combustion

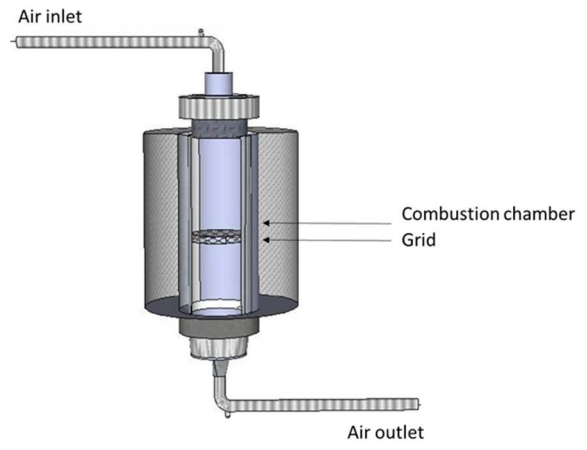
**Fig. 5.** Thermal stability of *O. chalcidica* and its ashes: experimental points and application of Frank-Kamenetskii model

**Fig. 6.** Time evolution of the temperature of *O. chalcidica* samples as a function of the basket size and thermocouple location

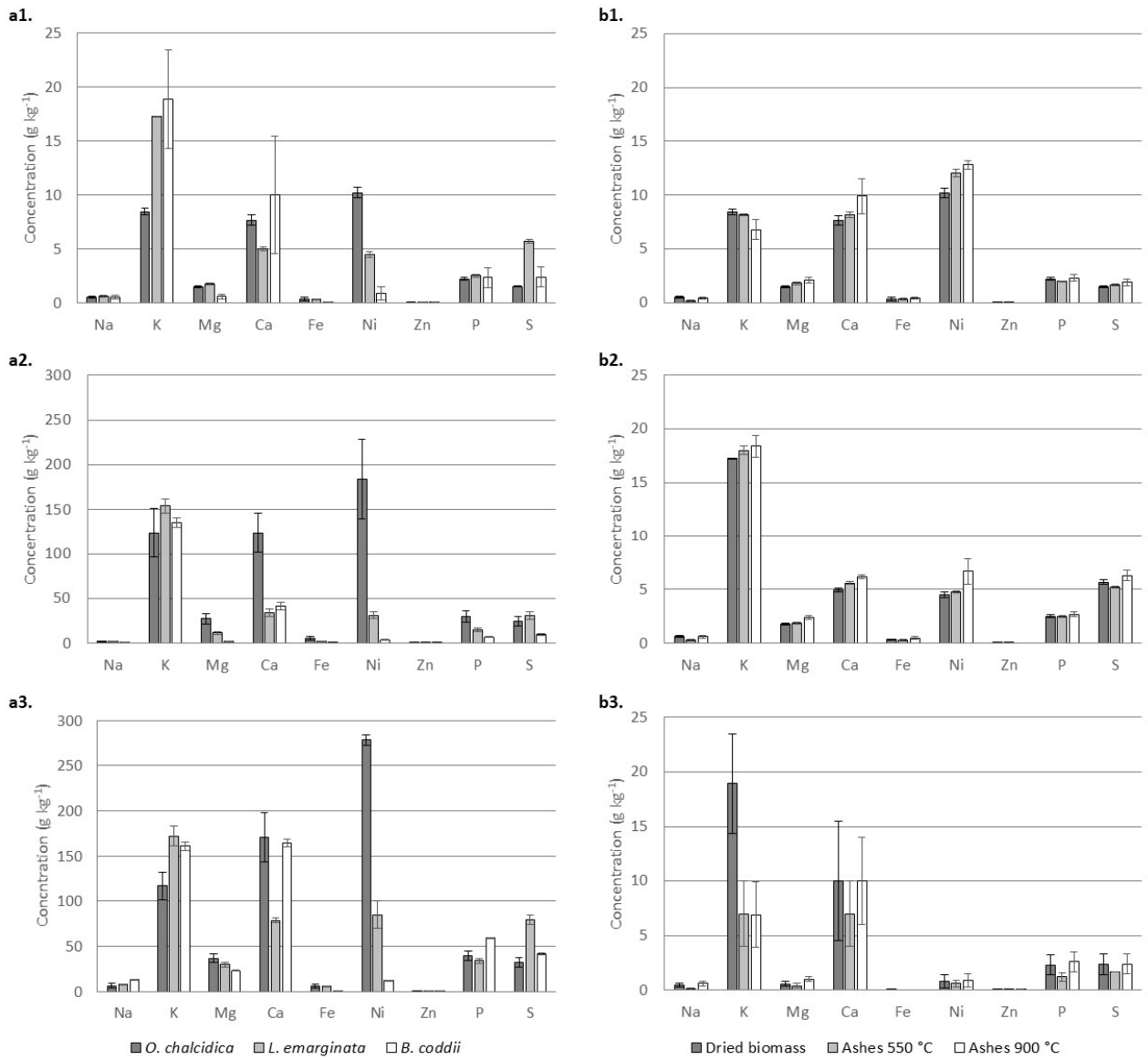
a.



b.

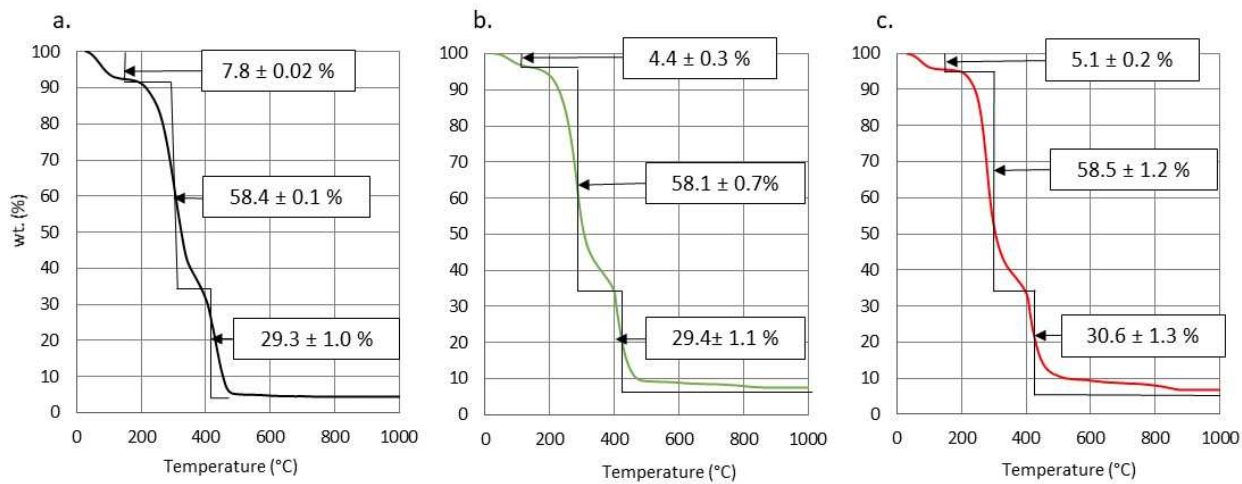


**Fig. 1**

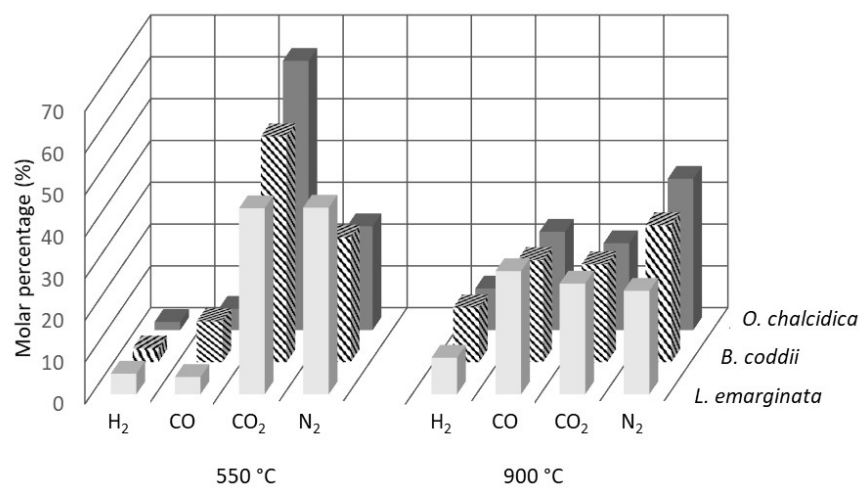


**Fig.2.**





**Fig.3.**



**Fig. 4.**

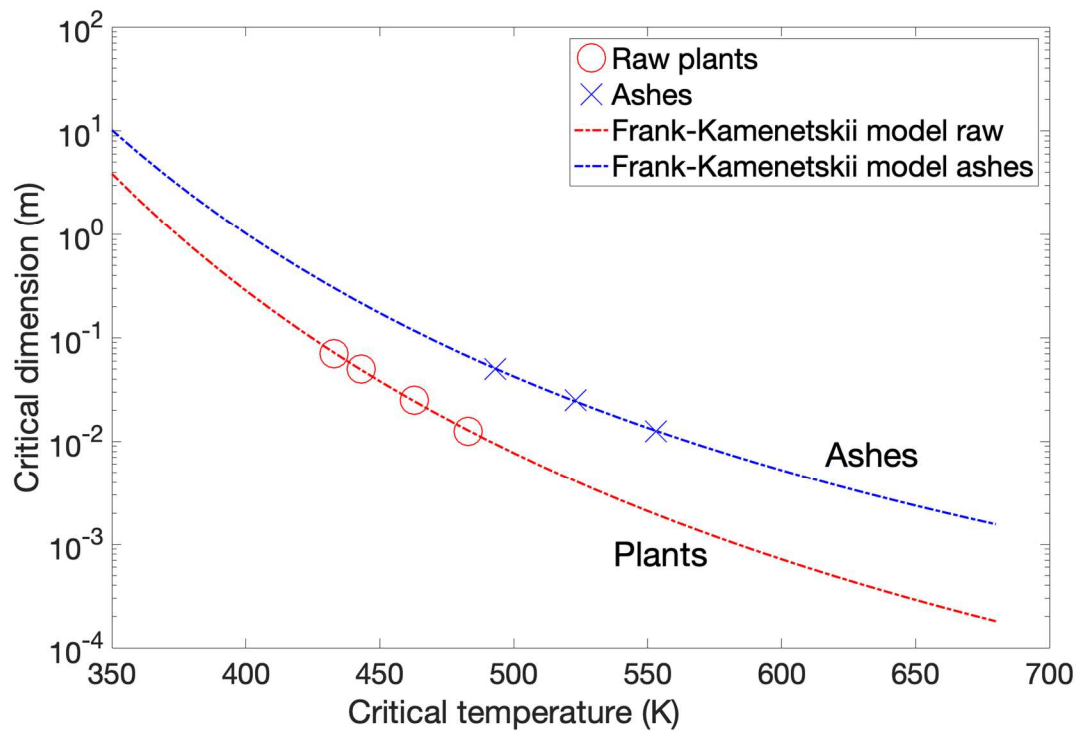


Fig. 5.

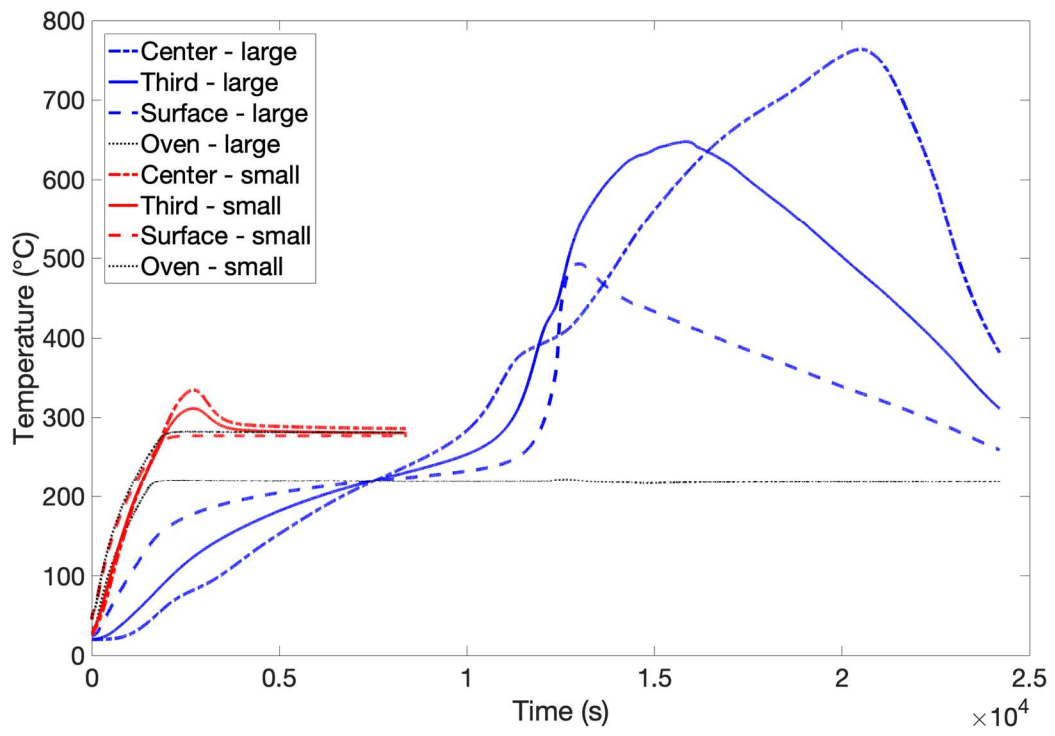


Fig. 6.

**Table 1.**

Moisture, density and ash content of the hyperaccumulator plants

Plants	Moisture (wt. %)	Density (g cm <sup>-3</sup> )	Ash (wt %)
<i>O. chalcidica</i>	8.9 ± 0.2	1.39 ± 0.01	7.3 ± 0.1
<i>L. emarginata</i>	8.5 ± 1.7	1.35 ± 0.01	9.2 ± 0.2
<i>B. coddii</i>	5.0 ± 0.5	1.44 ± 0.01	8.3 ± 0.3

**Table.2.**

Composition of the dry biomass and ashes obtained at 550 and 900 °C of the hyperaccumulator plants

		<i>O. chalcidica</i>	<i>L. emarginata</i>	<i>B. coddii</i>
Dried biomass (100°C)	C	46.0 ± 0.9	42.1 ± 1.1	43.0 ± 1.1
	H	5.0 ± 0.1	5.6 ± 0.2	5.8 ± 0.1
	O	40.7 ± 1.4	39.3 ± 0.6	40.8 ± 4.7
	N	1.2 ± 0.3	2.0 ± 0.1	1.2 ± 0.3
	S	0.3 ± 0.1	0.9 ± 0.1	0.5 ± 0.1
Ashes (550°C)	C	5.9 ± 0.3	3.5 ± 0.2	6.1 ± 0.2
	H	< LD	< LD	< LD
	O	9.1 ± 0.8	7.4 ± 0.5	3.7 ± 0.4
	N	< LD	< LD	< LD
	S	2.5 ± 0.5	3.1 ± 0.5	1.1 ± 0.1
Ashes (900°C)	C	1.0 ± 0.3	0.8 ± 0.3	1.1 ± 0.1
	H	0.16 ± 0.06	0.14 ± 0.03	0.4 ± 0.1
	O	1.6 ± 0.3	12.5 ± 2.3	8.3 ± 2.6
	N	< LD	< LD	< LD
	S	3.2 ± 0.4	4.3 ± 0.9	4.1 ± 0.5

LD: limit detection

**Table 3.**

Calorific value of the three Ni hyperaccumulator plants determined by calorimeter bomb, Boie and Gumz correlations

		<i>O. chalcidica</i>		<i>L. emarginata</i>		<i>B. coddii</i>	
		HHV	LHV	HHV	LHV	HHV	LHV
		(MJ kg <sup>-1</sup> )	(MJ kg <sup>-1</sup> )	(MJ kg <sup>-1</sup> )	(MJ kg <sup>-1</sup> )	(MJ kg <sup>-1</sup> )	(MJ kg <sup>-1</sup> )
Exp.	mean	16.4	15.1	17.3	16.1	17.0	15.7
	std. dev.	0.4	0.4	0.3	0.3	0.2	0.2
Boie	mean	17.5	16.3	17.0	15.8	17.3	16.2
	std. dev.	0.9	0.8	1.1	1.0	0.7	0.6
Gumz	mean	18.0	16.8	17.6	16.4	17.9	16.8
	std. dev.	0.9	0.8	1.1	1.0	0.6	0.6

**Table 4.**

HHVs of different fuels

Fuels	HHV (MJ kg <sup>-1</sup> )	References
Torrefied wood pellet	22.1	[30]
Pinus wood pellets	20.6	[31]
Wheat straw	20.3 ± 0.2	[28]
	18.9 ± 0.3	[32]
Eucalyptus (stem, branch, leaf)	19.2 ± 0.3	
	22.0 ± 0.2	
Red pepper	19.5	[33]
Sugarcane bagasse pellets		[31]
Elephant grass pellets	18.5	
Bayan, Pippal, Mahua tree	Leaf ≈19.5 Peel-branch ≈ 13-15	[34]
<i>Leptoplax emarginata</i>	17.3	this work
<i>Berkheya coddii</i>	17.0	
Chinese cabbage	17.0	[35]
Poplar leaf	16.9	[35]
<i>Odontarrhena chalcidica</i>	16.4	this work
Banana peel	16.4	[35]
Ginkgo leaf	15.3	[35]
Water hyacinth	14.6	[30]



## Agromining: nickel and heat recovery from plants

