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Novel energy crops for Mediterranean contaminated lands: valorization of *Dittrichia viscosa* and *Silybum marianum* biomass by pyrolysis

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Abstract

Establishing energy crops could be a cost-efficient alternative towards the valorization of the plant biomass produced in contaminated lands, where they would not compete with food production for land use. *Dittrichia viscosa* and *Silybum marianum* are two native Mediterranean species recently identified as potential energy crops for degraded lands. Here, we present the first characterization of the decomposition of the biomass of these species during thermo-chemical conversion (pyrolysis). Using a greenhouse study we evaluated whether the quality of *D. viscosa* and *S. marianum* biomass for energy production through pyrolysis could be substantially influenced by the presence of high concentrations of soluble trace element concentrations in the growing substrate. For each species, biomass produced in two different soil types (with contrasted trace element concentrations and pH) had similar elemental composition. Behavior during

thermal decomposition, activation energies and concentrations of pyrolysis gases were also similar between both types of soils. Average activation energy values were 295 and 300 kJ mol^{-1} (for a conversion value of α=0.5) for *S. marianum* and *D. viscosa*, respectively. Results suggest that there were no major effects of soil growing conditions on the properties of the biomass as raw material for pyrolysis, and confirm the interest of these species as energy crops for Mediterranean contaminated lands.

Keywords: biofuel; soil remediation; raw material; TGA

Highlights

- *Dittrichia viscosa* and *Silybum marianum* are promising energy crops for contaminated lands
- Biomass obtained from two contaminated soils was examined during pyrolysis
- TGA curves were similar across materials obtained from both soils
- Biomass chemical composition and concentrations of pyrolysis gases were also similar
- Results confirm the interest of both species as energy crops for contaminated lands

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1. Introduction

The establishment of a plant cover in contaminated lands is critical to improve soil quality and to reduce the spread of contaminants through soil erosion (Mendez and Maier, 2008). However, accumulation of contaminants into aboveground biomass often prevents the agricultural use of these lands (Madejón et al., 2009). Establishing energy crops could be an alternative towards the valorization of the plant biomass produced in contaminated lands (Ruttens, 2011; Witters et al., 2012). These crops would not compete with food production for land use in these marginal areas, and would contribute to the attainment of national renewable energy targets.

Due to a long history of mining activities in the Mediterranean Basin, trace-element (TE) contaminated lands are frequent in Mediterranean countries. Extraction and processing of metals have resulted in vast extensions of land where wastes have been deposited and left abandoned, posing a serious threat to environment and local populations in this region (Doumas et al., 2016). Achieving the remediation of these contaminated sites will likely be an obligation for EU Member States in the upcoming years, if the European Soil Framework Directive is finally approved (European Commision, 2006). The use of energy crops in TE contaminated lands would pose an opportunity to generate an added-value product from these degraded sites in

Mediterranean countries.

Many of the most common energy crops, however, have high water requirements and are not suitable for degraded Mediterranean areas. Therefore, there is a necessity to explore native plant species with potential as energy crops for this region. Ideally, these species should: i) be able to tolerate high concentrations of TE in soils; ii) produce high biomass even in nutrient-poor and physically altered soils; and iii) have a valuable biomass, in terms of energy value, that can be handled through the whole process from biomass harvest to biofuel obtainment with low energy inputs. Both the shrub *Dittrichia viscosa* (L.) Greuter and milk thistle *Silybum marianum* (L.) Gaertn. comply with some of these criteria, and have been recently identified as promising bioenergy crop species for Mediterranean lands (Robledo and Correal, 2013). These species might have a particular interest for contaminated sites, given their ability to colonize soils with high concentrations of TE where other plant species fail to establish (Brunetti et al., 2009; Martínez-Sánchez et al., 2012).

Previously, we experimentally showed that *D. viscosa* has the ability to produce a high biomass in highly degraded soils, including extremely acid and TE-contaminated soils, and that this biomass has a relatively high calorific value, similar to that of other common bioenergy crops such as *Arundo donax* and *Miscanthus x giganteus* (Domínguez et al., 2017). This study also found that biomass production of *S. marianum* was less affected by soil contamination than production of *Cynara cardunculus*, another thistle species with a well-known potential as bioenergy crop for Mediterranean lands (Fernandez et al., 2006), and that the calorific value of *S. marianum* biomass was not influenced by soil contamination. The behavior of *D.*

101 *viscosa* and *S. marianum* biomass during energy conversion processes, however, is still
102 to be characterized.
103
104 Main technologies for thermo-chemical conversion of biomass include combustion,
105 gasification and pyrolysis (McKendry, 2002). Pyrolysis presents some advantages over
106 combustion and gasification, such as the relatively lower temperature requirements, the
107 lack of oxygen requirement, and the possibility to obtain liquid bio-oil (Bridgwater et
108 al., 2001). The syngas resulting from pyrolysis, once cleaned, can be used for different
109 purposes such as gas turbines, fuel cells, synthesis of liquid fuels like methanol, or
110 chemicals (Yang et al., 2006). In addition, generation of biochar is obtained during
111 pyrolysis of biomass, which has been shown to have an increasing range of applications
112 in the agriculture and forestry sectors (reviewed in Kuppusamy et al., 2016). For these
113 reasons, pyrolysis is often considered as a practical and effective way of producing
114 bioenergy from raw lignocellulosic materials or biowaste with reduced emissions of
115 greenhouse gases (Ferreira et al., 2016).
116
117 Understanding pyrolysis kinetics of a raw material is important to predict the
118 conversion processes and to optimize the design of reactors (Di Blasi, 2008; Van de
119 Velden, 2010). Thermogravimetric analysis (TGA) is frequently applied to investigate
120 pyrolytic kinetics of lignocellulosic biomass (Chen et al., 2015; Damartzis et al., 2011;
121 Ferreira et al., 2016). Analysis of gases evolved during the pyrolysis is also crucial for a
122 full characterization of the environmental implications of this conversion technology
123 and of the potential syngas production.
124
125 In this work, we assessed the potential valorization of *D. viscosa* and *S. marianum*

126 biomass produced in TE-contaminated soils through pyrolysis to produce syngas. We
127 analyzed elemental composition of biomass, pyrolysis kinetics and composition of gases
128 evolved during the application of this conversion technology, using the biomass
129 obtained in a greenhouse experiment that aimed to test the sensitivity of these plant
130 species to soil contamination. With this, we aimed to evaluate whether the quality of *D.*
131 *viscosa* and *S. marianum* biomass for syngas production through pyrolysis could be
132 substantially influenced by soil conditions during plant growth. As reported for other
133 conversion technologies, such as gasification, soil contamination might result in a lower
134 quality of biomass for biofuel production, by affecting plant chemical composition
135 (Madejón et al., 2016). Analyzing the behavior of the biomass of these species during
136 thermo-chemical conversion is essential for a complete characterization of their
137 potential as bioenergy crops. To our knowledge, this is the first description of a
138 conversion process applied to *D. viscosa* and *S. marianum* biomass.
139

140 ## 2. Materials and Methods

141

142 ### 2.1. Raw materials

143 The plant biomass used in this study was produced in a greenhouse experiment that
144 tested the sensitivity of *D. viscosa* and *S. marianum* productivity to soil contamination.
145 In this experiment *D. viscosa* and *S. marianum* plants were grown on four different soil
146 types (acid contaminated, neutral contaminated, and two corresponding uncontaminated
147 soils - acid and neutral-) that were collected from the Guadiamar River Valley (SW
148 Spain), an area that was contaminated by a large mining accident in 1998 (Fig. 1). Plant
149 biomass obtained from the most and the least productive soils (the neutral and the acid
150 contaminated, respectively) were used for this study. Both soil types are classified as

151 fluvisols and had a low organic matter content (< 2 %); pH in the neutral soil was 6.4,
152 while the other soil was extremely acidic (pH = 3.1), due to the oxidation of sulphides
153 deposited onto the soil by the mining accident (Domínguez et al., 2016). In this soil
154 lower pH conditions promoted a higher solubility of TE. Main properties and TE
155 concentrations of the experimental soils are shown in Appendix, Table A1.
156
157 *D. viscosa* and *S. marianum* seeds were germinated in November 2014, in containers
158 filled with 15 kg of each soil type. Ten seeds were sown in each container for *S.*
159 *marianum*, while for *D. viscosa* an amount of 0.05 g, equivalent to 60 seeds, was used.
160 The containers were kept outdoors until March 2015. Then, 8 containers of each
161 combination of plant and soil type were moved into a greenhouse where the plants were
162 grown with irrigation. One of the emerged seedlings per container was left, and the rest
163 removed. As germination rates in the acid soil were very low, an application of sugar
164 beet lime as soil amendment was conducted to correct soil pH. This resulted in an
165 increase in soil pH in the top 5 cm that promoted seed germination, but acid soil
166 conditions remained in lower soil profiles, where most roots developed (Domínguez et
167 al., 2017). Thus roots were exposed to unfavourable acid conditions during plant growth
168 in this acid soil treatment. From March to April plants were irrigated twice weekly with
169 an amount of water equivalent to 4 L m^{-2}. In May, due to the increased
170 evapotranspiration in the greenhouse, sprinkler irrigation was applied, at a dose of 2.8 L
171 m^{-2} day^{-1} per container. See Dominguez et al. (2017) for a full description of the
172 greenhouse experimental design and plant growing conditions over the experiment.
173
174 In summer aboveground biomass in each container was harvested and washed with
175 deionized water, dried at 70 º C for at least 48 h and ground in a stainless mill to < 1

176 mm, then further milled to < 500 μm in a ball mill for pyrolysis experiments. Samples
177 were stored in a small glass bottle to prevent the contact with air moisture. Biomass
178 samples of three individual plants (grown in individual containers) per soil type and
179 species were used for all analyses (N = 12).
180
181 2.2. Elemental composition analysis
182 The determination of contents in C, H, N and S was performed in a LECO TruSpec
183 CHN elemental analyzer. The oxygen content was calculated by the difference of the
184 mole fraction. Each sample was analyzed in duplicate. Dry matter content, metal
185 concentrations in aboveground biomass and gross calorific values were also analyzed as
186 described in Domínguez et al., (2017) and are reported in Appendix, Table A2.
187
188 2.3. Pyrolysis and TGA experiments
189 A laboratory-scale reactor was used to study the gases evolved from pyrolysis of
190 biomass. The experimental system consisted of a quartz tube, 10 mm wide, where the
191 sample (approximately 2g, < 500 μm particle size) is uniformly introduced inside a tube
192 of 35 cm length. A horizontal actuator introduced the tube with the biomass into a
193 furnace maintained at 550ºC at constant velocity, and with 2 s of residence time.
194 Nitrogen (20 cm^3 min^{-1}) was used as transport gas. Hydrogen, CO and CO_2
195 determinations were performed by using a previously calibrated multi-gas analyzer
196 (MultiRAE IR PGM-54, RAE Systems, San José, CA, USA), and were done in
197 triplicate, using an integrated sampling pump with a flow rate of 0.2 L min^{-1}.
198
199 Thermo-chemical decomposition behavior was assessed using a thermo-gravimetric
200 analyzer (TGA, Mettler Toledo TGA/DSC1 STARe System). The TGA experiments

were performed by heating a 50-130 mg sample from 25°C to 800°C at four heating rates (5, 10, 15 and 20°C min^{-1}, respectively) under a nitrogen flow of 20 cm^3 min^{-1}. TGA data were analyzed to determine the Arrhenius activation energy (E_a) and the pre-exponential constant (A) using the Flynn-Wall-Ozawa iso-conversion method (see section 2.4).

2.4. TGA kinetic analysis

Activation energy (E_a) has been studied with different mathematical methods (Damartzis et al., 2011; Fernández et al., 2016). Among these, the use of the iso-conversion method has been successfully documented for pyrolysis kinetics determination (Mehrabian et al., 2012; El-Sayed et al., 2015). For a single-reaction mechanism, E_a should be a constant value throughout the weight loss region. Activation energy values for the degradation process were determined by the iso-conversional Flynn-Wall-Ozawa (FWO) method (Flynn and Wall, 1966; Ozawa, 1965) defined by Eq. 1:

$$\ln(\beta) = \ln\left(\frac{A\,E_a}{R\,g(\alpha)}\right) - 2.315 - 0.4567\,\frac{E_a}{R\,T} \quad \text{(Eq 1)},$$

where β is the heating rate, A is the pre-exponential factor, g(α) is a function of the conversion, E_a is the activation energy, T is temperature and R is the gas constant. For different heating rates (β) and a given degree of conversion (α), a linear relationship is observed when plotting the natural logarithm of heating rates (ln β) against 1/T. Activation energy can be calculated from the slope of the straight line describing this relationship (-0.4567 (E_a/RT)). The underlying assumption is that the reaction model, g(α), is identical at a given degree of conversion (α) for a given reaction under different thermal conditions. This method can be used for determination of the E_a values without any knowledge of the reaction mechanisms (El-Sayed et al., 2015). Disadvantage of this

method is the requirement of a series of measurements at different heating rates, which must be made with the same samples mass and the same volume flow of inert gas, with inherent fluctuations that can be source of errors (Opfermann, et al., 2002). In this study four replicates of each material were tested to prevent these errors.

2.5. Data analysis

For each species, differences in the elemental composition of the biomass obtained from the two types of soils were explored by applying one-way Anova and Duncan´s multiple range tests (three replicates for each species and soil type). Likewise, these analyses were applied to test for significant differences in the composition of the gas resulting from pyrolysis, as well as in activation energies for different conversion values. For *S. marianum*, activation energy data did not met the homoscedasticity assumption, and Kruskal-Wallis tests were applied to analyze differences in E_a values between samples with different soil origin. All these analyses were conducted using R 3.3.2.

3. Results and Discussion

3.1. Chemical characterization

D. viscosa was able to produce a significant amount of biomass in the acid soil (24.7 ± 4.2 g dw plant^{-1}; mean ± st. error), being comparable to the production in the neutral soil (22.2 ± 1.5 g dw plant^{-1}), despite that the conditions in the rooting zone of the acid soil promoted the solubilization of toxic TE in the rhizosphere (Domínguez et al., 2017). Elemental analysis of a subset of plants grown in these two types of soils revealed that C, H, N, O and S composition of *D. viscosa* biomass was neither affected by the soil type (one-way Anova with soil type as categorical factor non-significant, Table 1).

Mean values (± std. error, %) were 41. 5 ± 0.3 (C), 5.60 ± 0.10 (H), 1.02 ± 0.04 (N), 51.5 ± 0.03 (O) and 0.33 ± 0.04 (S).

Biomass produced by *S. marianum* was lower than that produced by *D. viscosa*, without significant differences in production between the two soil types (5.24 ± 1.13 g dw plant^{-1} and 6.93 ± 2.63 g dw plant^{-1} in the neutral and acidic soils, respectively). For this species there was only a slight difference in the content of S between samples with different soil origins, being higher in those plants grown in the neutral soil (mean of 0.33 %) than in the acidic soil (mean of 0.32 %). Mean values (± std. error, %) were 41.9 ± 0.6 (C), 5.71 ± 0.06 (H), 1.32 ± 0.05 (N), and 50.7 ± 0.06 (O).

Both materials had, therefore, similar elemental composition, although the O/C ratio was higher for *S. marianum*. On average, H/C and O/C ratios were 0.13 and 1.11, respectively, in *D. viscosa*, and 0.14 and 1.21, respectively, in *S. marianum*. As the O/C value is closely related to the calorific value of the material (decreasing with increased O/C ratio; Ferreira et al., 2016), this could explain the higher calorific value of *D. viscosa* (17.20 MJ kg^{-1}) in comparison to *S. marianum* biomass (16.3 MJ kg^{-1}; Appendix Table A3). In comparison to other works with different materials, the O/C ratio of both *D. viscosa* and *S. marianum* biomass was slightly higher than some agricultural residues from Mediterranean crops, but lower than some industrial residues that have been proposed as raw material for pyrolysis, in order to promote the valorization of residues commonly produced in the Mediterranean region (Ferreira et al., 2016). Regarding the S content, both materials showed very low levels in comparison with conventional fuels (0.7–4.9%, Gräbner, 2014), which is a positive feature, as it reduces the risk of forming S compounds with negative environmental

276 implications, such as H_2S and SO_2.

277

278 3.2. Thermogravimetric analysis of the pyrolysis process

279 The TGA curves show mass losses of the studied materials (mean of the three replicates
280 per soil type and plant species) over the range of temperature from 27 ºC to 800 ºC, at
281 four heating rates (5, 10, 15 and 20 ºC min^{-1}) under nitrogen atmosphere (Fig. 2). For
282 both *D. viscosa* and *S. marianum* materials, the TGA curves exhibit the three thermal
283 degradation zones typical of lignocellulosic biomass samples (Gašparovič et al., 2010;
284 Giudicianni et al., 2013), related to moisture evaporation, primary decomposition, and
285 secondary decomposition, respectively. The first zone, from 60 ºC to 180 ºC, is related
286 to the extraction of moisture and water adsorbed into samples. The second region (main
287 decomposition stage) took place in the temperature range from 180 to 570ºC, where
288 hemicellulose and cellulose decomposition occurs (200-400 ºC for hemicellulose and
289 250-380 ºC for cellulose; Dantas et al., 2013). As expected, this was the most active
290 region, where the greatest mass losses were observed. In the third zone (570-800ºC)
291 decomposition rates were low, and possibly attributed to the gasification of the char
292 formed over the conversion process (Vuthaluru, 2004). In addition, lignin is
293 decomposed in the range from 180 to 850 ºC without characteristic peaks (Van de
294 Velden et al. (2010), and therefore some of the mass loss in this third region could be
295 also attributable to lignin decomposition. The TGA curves were rather similar for all the
296 studied heating rates, although for both plant species residual mass values at 800 ºC
297 were lower at 5 ºC min^{-1} (< 20 %) than at the other heating rates (≈ 25 %), possibly
298 indicating a greater volatilization of biomass at a low heating rate. Similar residual mass
299 values at 800 ºC have been obtained in the pyrolysis of different biomass samples, such
300 as Camel grass (Mehmood et al., 2016), rice straw (Xu and Chen, 2013) and agricultural

301 residues such as walnut shells and olive waste from olive oil production (Ferreira et al.,
302 2016). For each species, TGA curves obtained from samples with different soil origins
303 were rather similar (Fig. 2).
304
305 Inspection of derivative thermogravimetric (DTG) curves confirmed that, for each
306 species, biomass produced in both types of soils had a similar behavior during thermal
307 degradation (Fig. 3). For both *D. viscosa* and *S. marianum* the peak of maximum
308 thermal decomposition was observed at ≈ 350 °C, with maximum weight loss rates
309 around 9 % min^{-1} at a heating rate of 20 ºC min^{-1}. As mentioned above, heating rates
310 had a modest effect on the dynamics of thermal decomposition, so that decomposition
311 peaks occurred at similar temperatures under all the tested heating rates. However,
312 shoulder peaks occurred in the region of hemicellulose degradation (180-350 ºC; Dantas
313 et al., 2013) at high heating rates (< 15-20 ºC min^{-1}), especially in *D. viscosa* samples.
314 According to Gaur and Reed (1998), these shoulder peaks could be due to the
315 interaction among wood biomass polymers (cellulose, hemicellulose and lignin); within
316 the range of 150 -180 ºC the stability of cellulose is reduced, and it might react with
317 hemicelluloses, while at greater temperatures (300°C to 400°C) cellulose decomposes
318 quickly (Stefanidis et al., 2013), with a large decomposition peak. Flat tailing sections
319 were observed in the DTG curves at the range of 400 ºC to 750 ºC, likely associated to
320 lignin decomposition, which is known to decompose slowly over a broad temperature
321 range. Small decomposition peaks were observed at 800 ºC, being higher in *S.*
322 *marianum* than in *D. viscosa* samples, likely revealing differences in the amount of
323 lignin between the two types of biomass.
324
325 3.3. Analysis of pyrolysis kinetics

326 Kinetic parameters were calculated according to Eq. (1) at three conversion (α) values
327 (0.25, 0.5 to 0.75) for all curves (different heating rates), following the FWO method.
328 The FWO equations (slope and R^2) describing the relationship between ln (β_i) and $1/T_{\alpha i}$,
329 as well as apparent activation energy (E_a) values calculated from the slopes of these
330 equations (individual samples) are shown in Appendix Tables A3 and A4.
331
332 In general, the calculated E_a values at the different conversion rates were similar for
333 both *D. viscosa* and *S. marianum* (Table 2). With the exception of one *S. marianum*
334 sample, R^2 values were > 0.93 at all conversion rates. The obtained E_a values were
335 highly dependent on the extent of conversion, which could indicate that the pyrolysis
336 process in these materials is a multi-step reaction and not a single reaction mechanism
337 (Sonobe and Worasuwannarak, 2008). As with elemental composition, there were not
338 significant differences in E_a values between biomass samples obtained from different
339 soils at any conversion rate (Table 1).
340
341 At low conversion (α <0.25), which corresponds to the thermal degradation of the
342 hemicellulose and the beginning of cellulose degradation (Nada and Hassan, 2000), E_a
343 varied between 126 and 171 kJ mol^{-1} in the samples of both plant species. In
344 comparison with published data on E_a, slightly higher E_a values (213 kJ mol^{-1}) have
345 been reported by Lv et al., (2010) for hemicellulose activation energy, using the same
346 kinetic method. Cellulose activation energy is usually reported to be greater than
347 hemicellulose E_a (Gašparovič et al., 2010), with reported values ranging between 178.7
348 kJ mol^{-1} (Saddawi et al., 2010) and 226 kJ mol^{-1} (Lin et al., 2013), while lignin
349 activation energy has been reported in the range of 237.1-266.6 kJ mol^{-1} under
350 isothermal heating conditions (Junmeng et al., 2013). Maximum E_a values in this study

were observed at α=0.5, ranging from 273 to 429.4 kJ mol^{-1} in *D. viscosa* (average around 300 kJ mol^{-1}), and from 204 to 370 kJ mol^{-1} in *S. marianum* (average around 295 kJ mol^{-1}). Activation energies between 118.8 and 150.9 kJ mol^{-1} in *D. viscosa*, and between 101 and 151 kJ mol^{-1} in *S. marianum* were found for α=0.75.

In comparison to previously reported E_a values, calculated E_a of *D. viscosa* and *S. marianum* (α=0.5) were found to be higher than other common raw materials, such as Miscanthus (113–143 kJ mol^{-1}; Cortés and Bridgwater, 2015), *Eucaliptus grandis* (218 kJ mol^{-1}; Poletto et al., 2012) or poplar (198 kJ mol^{-1}; Slopiecka et al., 2011). The similar E_a of both *D. viscosa* and *S. marianum* biomass suggest that these two raw materials could be pyrolyzed together; likewise other common raw materials with lower E_a could be used for co-firing with *D. viscosa* or *S. marianum* biomass.

3.4 Gases obtained during pyrolysis

The concentrations of gases (CO, CO_2 and H_2) obtained during pyrolysis of *D. viscosa* and *S. marianum* biomass are shown in Table 3. Although the composition of syngas depends on the biomass properties and gasifier operating conditions (Basu, 2013), under fixed conditions obtained data may be useful for comparison among different treatments. In relation to our treatment (different soil types in the growing substrate), slightly higher H_2 values were found for some samples of *D. viscosa* produced in the neutral soil, although differences with the pyrolysis gases of those samples produced in the acid soil were not statistically significant (Table 1). For *S. marianum*, differences in pyrolysis gases between soil types were neither observed (Table 1). We could have expected a significant increase in H_2 concentrations in the gas obtained from biomass produced in the neutral soil (more favorable for plant growth), as found in a previous

work with *Paulownia fortuneii* biomass obtained from the same experimental soils (Madejón et al., 2016). However, in that work differences in plant growth and status between soil types were larger than those detected for *D. viscosa* and *S. marianum* in this study.

When E_a values were compared with the composition of the gas obtained during the pyrolysis process, a negative relationship between H_2 concentration and E_a was observed for α=0.5, which in most cases corresponded to the maximum activation energy of the process (Fig. 4). Ideally, optimal features as raw material for pyrolysis would include a high concentration of H_2 in the resulting syngas and minimal activation energy required during pyrolysis. All analyzed samples spanned broadly over the curve describing this H_2-E_a relationship, without a clear distinction between *D. viscosa* or *S. marianum* samples, or between samples obtained from the different experimental soils. This suggests, together with the similar behavior of biomass decomposition as indicated by TGA analysis, and with the similar elemental composition of biomass between soil types, that the properties of *D. viscosa* and *S. marianum* biomass relevant for energy conversion processes would not be particularly affected by the plant growing conditions, in particular by acidic soil conditions that promote the availability of toxic trace elements in the rhizosphere. Although C, H, O, N and S concentrations were not affected by the soil type, concentrations of some trace elements, particularly Cd, increased in those plants grown in the acid soil (Domínguez et al., 2017). This issue should be further evaluated before establishing these species as energy crops in contaminated lands, given than metal-enriched ash could be produced during energy conversion processes, which may reduce the environmental sustainability of the bioenergy crop system.

401

402 3.5 Future recommendations

403 The results suggest that the quality of *D. viscosa* and *Silybum marianum* for bioenergy
404 production through pyrolysis is not severely affected by conditions of acidity and trace
405 element contamination in the growing substrate. Given the relatively low water
406 requeriments of these species (Ledda et al., 2013; Robledo and Correal, 2013) and their
407 ability to grow in highly degraded soils (Gómez-Ros et al., 2013; Río-Celestino et al.,
408 2006), there is a potential for establishing these species as bioenergy crops in
409 contaminated Mediterranean lands, if adequate soil preparation is accomplished to
410 reduce the inhibition of seed germination imposed by low pH in acidic soils
411 (Domínguez et al., 2017). Besides the benefits of lignocellulosic biomass production,
412 the establishment of these species could promote the recovery of soil quality in the
413 contaminated lands; short-term effects of *S.marianum* plantation included a stimulation
414 of soil enzyme activities, possibly due to a high release of exudates by *S. marianum*
415 roots that could stimulate the activity of its rhizospheric microbial community
416 (Domínguez et al., 2017). In addition, *D. viscosa* had an ability to develop an extensive
417 root system shortly after its plantation (Domínguez et al., 2017), which contributes to
418 the physical stabilization of the soil, thus reducing the risk of spreads of contaminants
419 through soil erosion.

420

421 Nevertheless, further studies are needed to confirm the suitability of these species for
422 bioenergy production purposes. Firstly, a complete assessment of the accumulation of
423 metals into aboveground biomass under field conditions must be conducted, as exposed
424 above, including an evaluation of potential problems associated to the production of
425 metal-enriched ash during thermo-chemical conversion. Secondly, a complete

426 characterization of the energy balance during crop establishment and biomass
427 processing is required to estimate the costs associated to the management of these new
428 crops. Therefore, longer-term and field-scale experimental studies would be needed to
429 support the evidences of suitability of these species as energy crops for contaminated
430 lands. Finally, other technical factors and variables involved in the pyrolysis of biomass
431 should be analyzed more in detail for a full characterization of these raw materials,
432 including the production of oil and biochar, as well as the release of tar during the
433 pyrolysis process.
434

435 **4. Conclusions**

436

437 Biomass of *Dittrichia viscosa* and *Silybum marianum* produced in two different
438 contaminated Mediterranean soils (with contrasted trace element concentrations and
439 acidity conditions) had similar elemental composition. TGA curves revealed similar
440 peaks of decomposition (with a maximum at ≈ 350 °C) in both species. In addition, E_a
441 values were similar in both types of biomass. For each plant species TGA curves were
442 similar in samples obtained from both types of soils, as well as concentrations of
443 pyrolysis gases (CO, CO_2 and H_2). These results suggest that there were no major
444 effects of the soil growing conditions on the properties of the biomass as raw material
445 for pyrolysis. A complete characterization of the energy balance during crop
446 establishment and biomass processing, as well as an evaluation of potential problems
447 associated to the production of metal-enriched ash during thermos-chemical conversion
448 would be needed to confirm the suitability as energy crop species for TE-contaminated
449 lands in the Mediterranean region.
450

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6. References

Basu P. Biomass co-firing and torrefaction. In: Basu P, editor. Biomass gasification, pyrolysis and torrefaction, Amsterdam: Eselvier; 2013, p. 353–373.

Bridgwater AV, Czernik S, Piskorz J. An Overview of Fast Pyrolysis. In: Bridgwater AV, editor. Progress in thermochemical biomass conversion, Oxford: Blackwell Science Ltd; 2001, p. 977–997.

Brunetti G, Soler-Rovira P, Farrag K, Senesi N. Tolerance and accumulation of heavy metals by wild plant species grown in contaminated soils in Apulia region, Southern Italy. Plant Soil 2009; 318: 285–298.

Chen C, Miao W, Zhou C, Wu H. Thermogravimetric pyrolysis kinetics of bamboo waste via Asymmetric Double Sigmoidal (Asym2sig) function deconvolution. Bioresour Technol 2017; 225: 48–57.

Cortés AM, Bridgwater A. Kinetic study of the pyrolysis of miscanthus and its acid hydrolysis residue by thermogravimetric analysis. Fuel Process Technol 2015;

476 138: 184–193.
477 Damartzis T, Vamvuka D, Sfakiotakis S, Zabaniotou A. Thermal degradation studies
478 and kinetic modeling of cardoon (*Cynara cardunculus*) pyrolysis using
479 thermogravimetric analysis (TGA). Bioresour Technol 2011; 102: 6230–6238.
480 Dantas, G. A., Legey, L. F., Mazzone, A. Energy from sugarcane bagasse in Brazil: An
481 assessment of the productivity and cost of different technological routes. Renew.
482 Sust. Energ. Rev. 2013; 21: 356–364.
483 Di Blasi C. Modeling chemical and physical processes of wood and biomass pyrolysis.
484 Prog Energy Combust Sci 2008; 34: 47–90.
485 Domínguez MT, Alegre J, Madejón P, Madejón E, Burgos P, Cabrera F, Marañón T,
486 Murillo J M. River banks and channels as hotspots of soil pollution after large-
487 scale remediation of a river basin. Geoderma 2016; 261: 133–140.
488 Domínguez MT, Montiel-Rozas MM, Madejón P, Diaz MJ, Madejón E. The potential
489 of native species as bioenergy crops on trace-element contaminated
490 Mediterranean lands. Sci Total Environ 2017; 590–591: 29–39.
491 Doumas P, Munoz M, Banni M, Becerra S, Bruneel O, Casiot C, Cleyet-Marel J-C,
492 Gardon J, Noack Y, Sappin-Didier V. Polymetallic pollution from abandoned
493 mines in Mediterranean regions: a multidisciplinary approach to environmental
494 risks. Reg Environ Change 2016. doi:10.1007/s10113-016-0939-x
495 El-Sayed SA, Mostafa ME. Kinetic parameters determination of biomass pyrolysis fuels
496 using TGA and DTA techniques. Waste Biomass Valori 2015; 6: 401–415.
497 European Commission. Proposal for a Directive of the European Parliament and of the
498 Council establishing a framework for the protection of soil and amending
499 Directive 2004/35/EC /* COM/2006/0232 final - COD 2006/0086 * 2006.
500 http://eur-lex.europa.eu/legal-

content/EN/TXT/HTML/?uri=CELEX:52006PC0232&from=EN). [accessed: 14.12. 16].

Fernández A, Saffe A, Pereyra R, Mazza G, Rodriguez R. Kinetic study of regional agro-industrial wastes pyrolysis using non-isothermal TGA analysis. Appl Therm Eng 2016; 106: 1157–1164.

Fernández J, Curt MD, Aguado PL. Industrial applications of *Cynara cardunculus* L. for energy and other uses. Ind Crops Prod 2006; 24: 222–229.

Ferreira C I, Calisto V, Cuerda-Correa EM, Otero M, Nadais H, Esteves V I. Comparative valorisation of agricultural and industrial biowastes by combustion and pyrolysis. Bioresour Technol 2016; 218: 918–925.

Flynn J H, Wall LA. General treatment of the thermogravimetry of polymers. J Res Nat Bu. Stand 1966; 70A: 487.

Gašparovič L, Koreňová Z, Jelemenský Ľ. Kinetic study of wood chips decomposition by TGA. Chem Pap 2010; 64: 174–181.

Gaur S, Reed TB. Thermal data for natural and synthetic fuels. New York: Marcel Dekker; 1998.

Giudicianni P, Cardone G, Ragucci R. Cellulose, hemicellulose and lignin slow steam pyrolysis: Thermal decomposition of biomass components mixtures. J Anal Appl Pyrolysis 2013; 100: 213–222.

Gómez-Ros, J.M., Garcia, G., Peñas, J.M. Assessment of restoration success of former metal mining areas after 30 years in a highly polluted Mediterranean mining area: Cartagena-La Unión. Ecol. Eng. 2013; 57: 393–402.

Gräbner M. Coal characterization for gasification. In: Gräbner M, editor. Industrial coal gasification technologies covering baseline and high-ash coal, Weinheim: Wiley-VCH Verlag GmbH & Co; 2014, p. 25–106.

526 Hanif MU, Capareda SC, Iqbal H, Arazo RO, Baig MA. Effects of pyrolysis
527 temperature on product yields and energy recovery from co-feeding of cotton gin
528 trash, cow manure, and microalgae: A simulation study. Plos One 2016; 11:
529 e0152230 doi:10.1371/journal.pone.0152230
530 Junmeng C, Wu W, Liu R, Huber G W. A distributed activation energy model for the
531 pyrolysis of lignocellulosic biomass. Green Chem 2013; 15: 1331-1340.
532 Kuppusamy S, Thavamani P, Megharaj M, Venkateswarlu, K, Naidu R. Agronomic and
533 remedial benefits and risks of applying biochar to soil: Current knowledge and
534 future research directions. Environ Int 2016; 87: 1–12.
535 Ledda, L., Deligios, P.A., Farci, R., Sulas, L. Biomass supply for energetic purposes
536 from some Cardueae species grown in Mediterranean farming systems. Ind.
537 Crops Prod. 2013; 47: 218–226.
538 Lin T, Goos E, Riedel U. A sectional approach for biomass: Modelling the pyrolysis of
539 cellulose. Fuel Process Technol 2013; 115: 246–253.
540 Lv G, Wu SB. Lou R. Kinetic study of the thermal decomposition of hemicellulose
541 isolated from corn stalk. BioResources 2010; 5: 1281-1291.
542 Madejón P, Domínguez MT, Díaz MJ, Madejón E. Improving sustainability in the
543 remediation of contaminated soils by the use of compost and energy valorization
544 by *Paulownia fortunei*. Sci Total Environ 2016. 539: 401–409.
545 Madejón P, Domínguez MT, Murillo JM. Evaluation of pastures for horses grazing on
546 soils polluted by trace elements. Ecotoxicology 2009; 18: 417–428.
547 doi:10.1007/s10646-009-0296-3.
548 Martínez-Sánchez MJ, García-Lorenzo ML, Pérez-Sirvent C, Bech J. Trace element
549 accumulation in plants from an aridic area affected by mining activities. J
550 Geochem Expl 2012; 123: 8–12.

551 Mckendry P. Energy production from biomass (part 2): conversion technologies.
552 Bioresour Technol 2002; 83: 47–54.
553 Mehmood MA, Ye G, Luo H, Liu C, Malik S, Afzal I, Xu J, Ahmad MS. Pyrolysis and
554 kinetic analyses of Camel grass (*Cymbopogon schoenanthus*) for bioenergy.
555 Bioresour Technol 2017; 228: 18–24.
556 Mehrabian R, Scharler R, Obernberger I. Effects of pyrolysis conditions on the heating
557 rate in biomass particles and applicability of TGA kinetic parameters in particle
558 thermal conversion modelling. Fuel 2012; 93: 567–575.
559 Mendez MO, Maier RM. Phytostabilization of Mine Tailings in Arid and Semiarid
560 Environments—An Emerging Remediation Technology. Environ Health Persp
561 2007; 116: 278–283.
562 Nada A, Hassan ML. Thermal behavior of cellulose and some cellulose derivatives.
563 Polym Degrad Stabil 2000; 67: 111–115.
564 Opfermann J, Kaisersberger E, Flammersheim H. Model-free analysis of
565 thermoanalytical data-advantages and limitations. Thermochim Acta 2002; 391:
566 119–127.
567 Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn
568 1965; 38: 1881–1886.
569 Poletto M, Zattera AJ, Santana RMC. Thermal decomposition of wood: Kinetics and
570 degradation mechanisms. Bioresour Technol 2012; 126: 7–12.
571 Río-Celestino, M., Font, R., Moreno-Rojas, R., Haro-Bailón, A. Uptake of lead and zinc
572 by wild plants growing on contaminated soils. Ind. Crops Prod. 2006; 24: 230–
573 237.
574 Robledo A, Correal E. Cultivos energéticos de segunda generación para la producción
575 de biomasa lignocelulósica en tierras de cultivo marginales. Murcia: Instituto

576 Murciano de Investigación y Desarrollo Agrario y Alimentario; 2013
577 Ruttens A, Boulet J, Weyens N, Smeets K, Adriaensen K, Meers E, Slycken SV, Tack
578 F, Meiresonne L, Thewys T, Witters N, Carleer R, Dupae J, Vangronsveld J.
579 Short Rotation Coppice Culture of Willows and Poplars as Energy Crops on
580 Metal Contaminated Agricultural Soils. Int J Phytoremediation 2011; 13: 194–
581 207.
582 Saddawi A, Jones JM, Williams A, Wójtowicz MA. Kinetics of the thermal
583 decomposition of biomass. Energy Fuels 2010; 24: 1274–1282.
584 Slopiecka K, Bartocci P, Fantozzi F. Thermogravimetric analysis and kinetic study of
585 poplar wood pyrolysis. Third International Conference on Applied Energy:
586 Perugia, Italy; 2001, p.1687-1698.
587 Sonobe T, Worasuwannarak N. Kinetic analyses of biomass pyrolysis using the
588 distributed activation energy model. Fuel 2008; 87: 414–421.
589 Stefanidis SD, Kalogiannis, KG, Iliopoulou EF, Michailof CM, Pilavachi PA, Lappas
590 AA. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose,
591 hemicellulose and lignin. J Anal Appl Pyrolysis 2014; 105: 143–150.
592 Van de Velden M, Baeyens J, Brems A, Janssens B, Dewil R. Fundamentals, kinetics
593 and endothermicity of the biomass pyrolysis reaction. Renew Energy 2010; 35:
594 232-242.
595 Vuthaluru H B. Investigations into the pyrolytic behaviour of coal/biomass blends using
596 thermogravimetric analysis. Bioresour Technol 2004; 92: 187–195.
597 Witters N, Mendelsohn R, Slycken SV, Weyens N, Schreurs E, Meers E, Tack F,
598 Carleer R, Vangronsveld J. Phytoremediation, a sustainable remediation
599 technology? Conclusions from a case study. I: Energy production and carbon
600 dioxide abatement. Biomass Bioenerg 2012; 39: 454–469.

601 Xu Y, Chen B. Investigation of thermodynamic parameters in the pyrolysis conversion
602 of biomass and manure to biochars using thermogravimetric analysis. Bioresour
603 Technol 2013; 146: 485–493.
604 Yang YB, Sharifi VN, Swithenbank J. Biomass and municipal solid wastes.
605 Substoichiometric conversion of biomass and solid wastes to energy in packed
606 beds. Aiche J 2006; 52: 809-817.

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621 **Figure captions**

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623 **Fig. 1** Location of the Guadiamar River Valley in SW Spain, where experimental soils
624 were collected. AC = acid contaminated soil; NC = neutral contaminated soil.

625

626 **Fig. 2** TGA curves at different heating rates (5, 10, 15 and 20 ºC min^{-1}) of *D. viscosa*
627 (A, B) and *S. marianum* biomass (C, D), obtained from neutral and acid contaminated
628 soils.

629

630 **Fig. 3** DTG curves at different heating rates (5, 10, 15 and 20 ºC min^{-1}) of *D. viscosa*
631 (A, B) and *S. marianum* biomass (C, D), obtained from neutral and acid contaminated
632 soils.

633

634 **Fig. 4** Relationship between H_2 concentration in pyrolysis gases and activation energy
635 (E_a) calculated for a conversion value (α) of 0.5 in the analyzed materials. Samples
636 represented by grey and white symbols correspond to biomass obtained from acid and
637 neutral contaminated soils, respectively.

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Tables

Table 1 Results of the one-way Anova tests applied to *D. viscosa* and *S. marianum* biomass chemical composition, activation energy (at a conversion factor of $\alpha = 0.05$) and composition of pyrolysis gases, with soil type as categorical factor. [a] For S. *marianum*, activation energy data did not met the homocedasticity assumption, and Kruskal-Wallis test was applied to analyze differences in E_a values between samples with different soil origin (chi-square and p-values shown).

	D. viscosa		*S. marianum*	
Chemical composition	F	p	F	p
C	2.90	0.163528	2.744	0.172981
H	0.027	0.876595	4.00	0.116189
N	0.9356	0.388192	2.8246	0.168123
S	3.36158	0.140661	2.824650	0.168123
O	0.57	0.493324	2.449	0.192631
Activation energy				
E_a	0.28610	0.621082	0.666[a]	0.414200
Pyrolysis gases				
CO	5	0.101192	2	0.230200
CO_2	1.13	0.348641	0.46	0.536039
H_2	1.688	0.263751	0.893	0.398208

Table 2 Activation energies (E_a, kJ mol^{-1}) obtained by the analysis of pyrolysis kinetics ($\ln(\beta_i)$ vs. $1/T_{\alpha i}$, FWO method), at different values of conversion (α). Mean ± standard error for each species and soil type.

	D. viscosa		*S. marianum*	
	Neutral soil	Acid soil	Neutral soil	Acid soil
α= 0.25	136.4 ± 4.9	147.8 ± 9.4	152.8 ± 12.5	133.9 ± 19.7
α= 0.50	299.5 ± 41.8	333.7 ± 48.4	295.2 ± 39.9	295.1 ± 11.8
α= 0.75	120.6 ± 0.98	132.3 ± 9.42	117.4 ± 3.9	126.1 ± 14.2

693 **Table 3** Composition of pyrolysis gases obtained from *D. viscosa* and *S. marianum*
694 samples (expressed as volume percentage, $\%_v$).
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Gas	Neutral soil		Acid Soil	
	D. viscosa	*S. marianum*	*D. viscosa*	*S. marianum*
CO	24.7 ± 0.1	24.6 ± 0.1	24.8 ± 0.1	24.7 ± 0.1
CO_2	18.4 ± 0.3	18.5 ± 0.1	18.7 ± 0.1	18.3 ± 0.1
H_2	8.0 ± 0.2	7.9 ± 0.1	8.1 ± 0.1	7.7 ± 0.1

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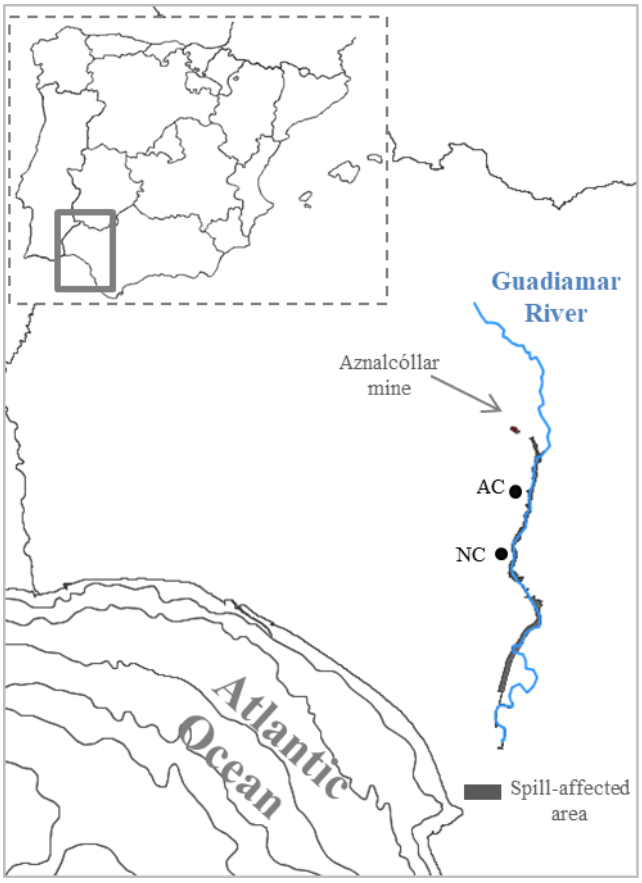
Guadiamar
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AC
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Ocean
Spill-affected
area

Fig. 1

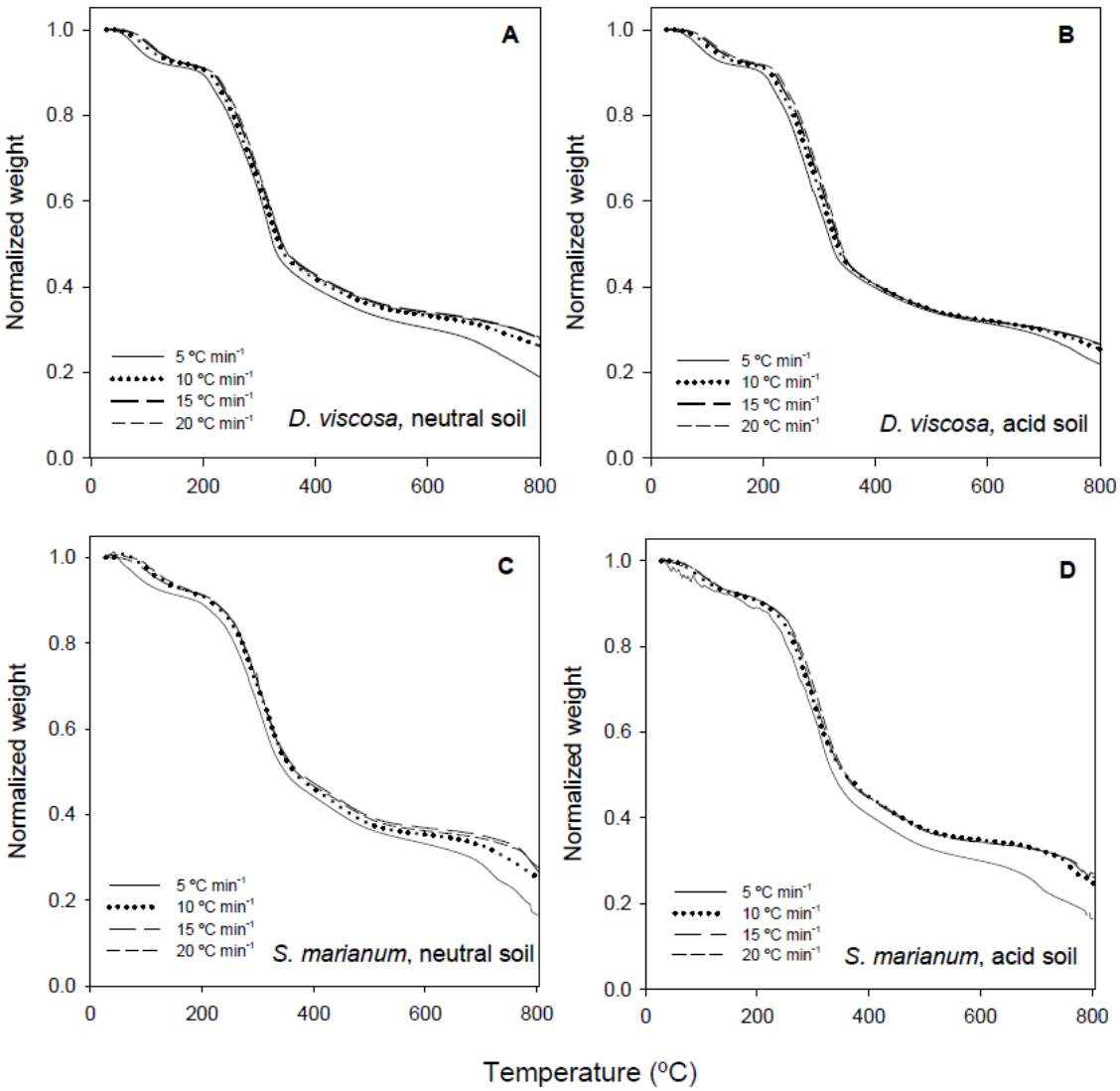
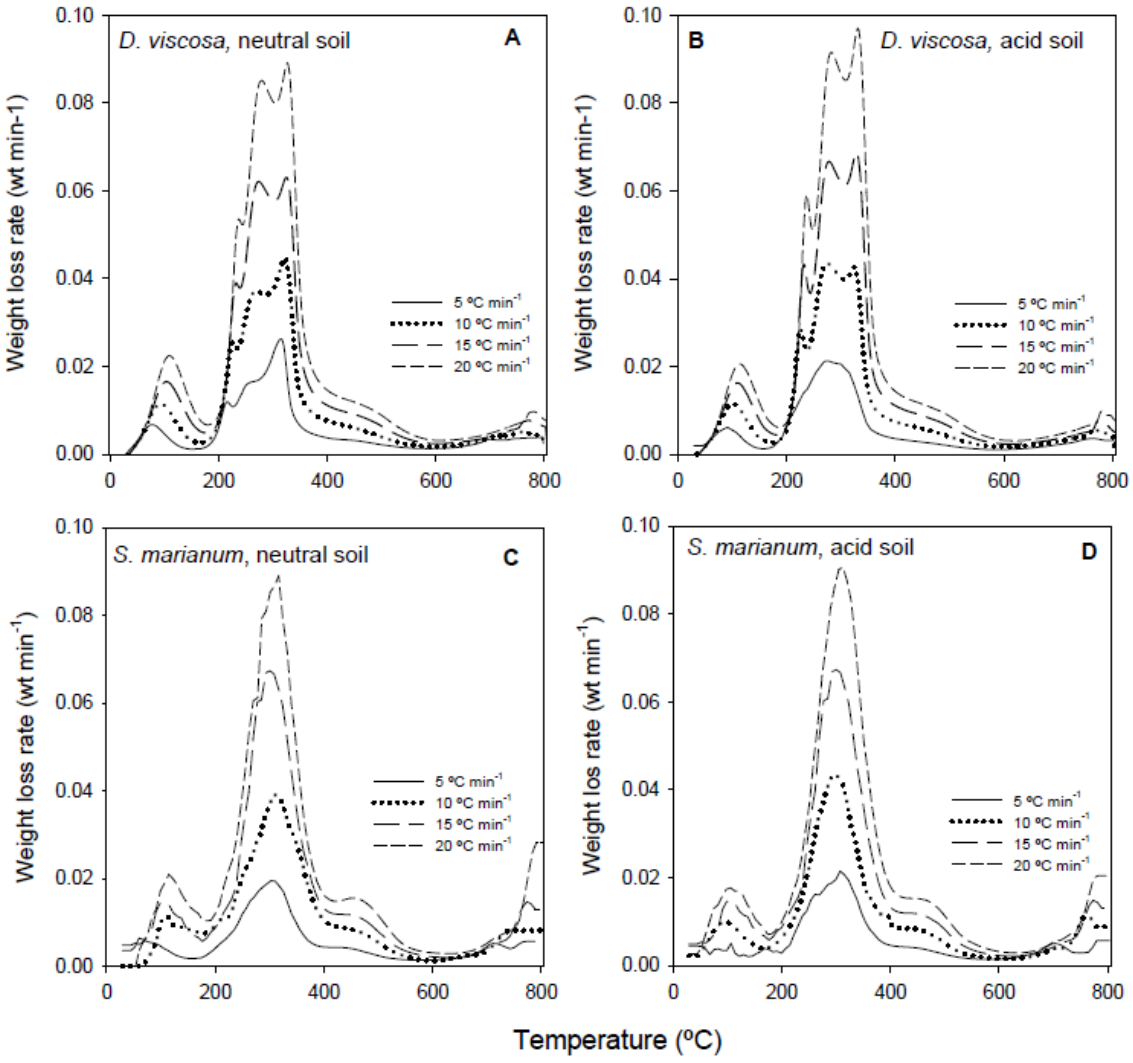

A
B
C
D
Normalized weight
Temperature (°C)
5 °C min-1
10 °C min-1
15 °C min-1
20 °C min-1
D. viscosa, neutral soil
D. viscosa, acid soil
S. marianum, neutral soil
S. marianum, acid soil

Fig. 2



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739 **Fig. 3**

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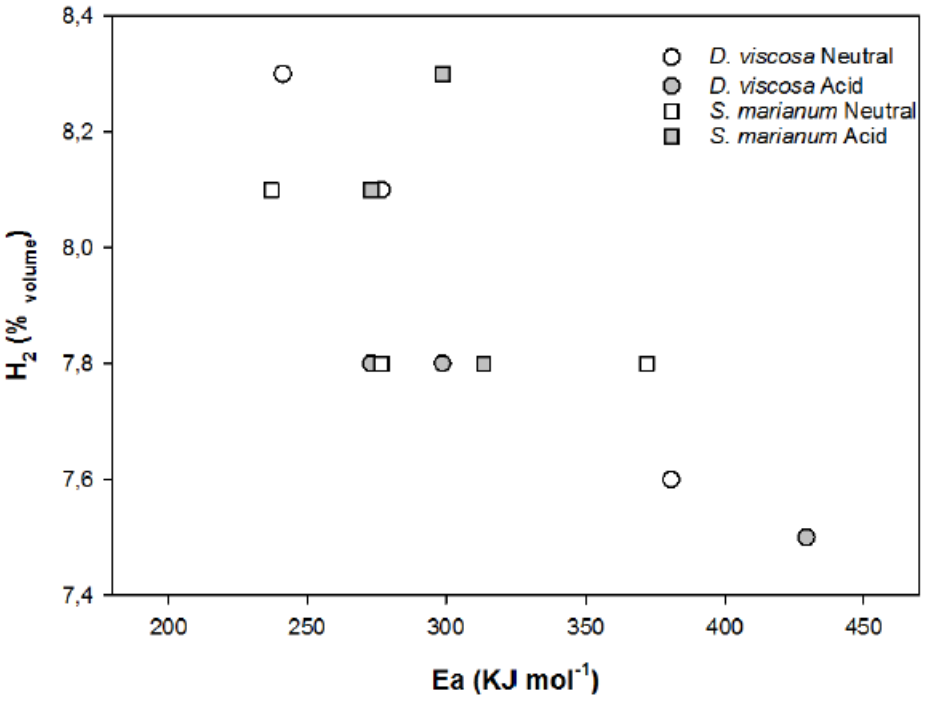
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H2 (% volume)
Ea (KJ mol-1)
D. viscosa Neutral
D. viscosa Acid
S. marianum Neutral
S. marianum Acid

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751 **Fig. 4**