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1 Pyrolysis of biofuels of the future: sewage sludge and microalgae -

2 Thermogravimetric analysis and modelling of the pyrolysis under different temperature conditions

3 Antonio Soria-Verdugo^{a*}, Elke Goos^b, Andrés Morato-Godino^a, Nestor García-Hernando^a, Uwe Riedel^b

4 ^a *Carlos III University of Madrid (Spain), Energy Systems Engineering Group, Thermal and Fluids*
5 *Engineering Department. Avda. de la Universidad 30, 28911 Leganés (Madrid, Spain).*

6 ^b *Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR, German Aerospace Center), Institute of*
7 *Combustion Technology, Pfaffenwaldring 38-40, 70569 Stuttgart (Germany).*

8 * *corresponding author: asoria@ing.uc3m.es Tel: +34916248465 Fax: +34916249430.*

9 Abstract

10 The pyrolysis process of both microalgae and sewage sludge was investigated separately, by means of non-
11 isothermal thermogravimetric analysis. The Distributed Activation Energy Model (DAEM) was employed to
12 obtain the pyrolysis kinetic parameters of the samples, i.e. the activation energy E_a and the pre-exponential
13 factor k_0 . Nine different pyrolysis tests at different constant heating rates were conducted for each sample in
14 a thermogravimetric analyzer (TGA) to obtain accurate values of the pyrolysis kinetic parameters when
15 applying DAEM. The accurate values of the activation energy and the pre-exponential factor that
16 characterize the pyrolysis reaction of *Chlorella vulgaris* and sewage sludge were reported, together with
17 their associated uncertainties. The activation energy and pre-exponential factor for the *C. vulgaris* vary
18 between 150 - 250 kJ/mol and 10^{10} - 10^{15} s⁻¹ respectively, whereas values ranging from 200 to 400 kJ/mol
19 were obtained for the sewage sludge activation energy, and from 10^{15} to 10^{25} s⁻¹ for its pre-exponential
20 factor. These values of E_a and k_0 were employed to estimate the evolution of the reacted fraction with
21 temperature during the pyrolysis of the samples under exponential and parabolic temperature increases,
22 more typical for the pyrolysis reaction of fuel particles in industrial reactors. The estimations of the relation
23 between the reacted fraction and the temperature for exponential and parabolic temperature increases were
24 found to be in good agreement with the experimental values measured in the TGA for both the microalgae
25 and the sludge samples. Therefore, the values reported in this work for the activation energy and the pre-
26 exponential factor of the *C. vulgaris* can be employed as reference values in numerical studies of the
27 pyrolysis process of this biofuel since its chemical composition is quite homogeneous. In the case of sewage
28 sludge, due to the heterogeneity of its composition, the results reported for the kinetic parameters of the
29 pyrolysis process can be employed to describe the pyrolysis of sludge with similar composition.

30 **Keywords:** Microalgae, *Chlorella vulgaris*, Sewage Sludge, Distributed Activation Energy Model (DAEM),
31 Biomass pyrolysis, Thermal Gravimetric Analysis (TGA).

32 **Nomenclature:**

33 a Heating rate [K min^{-1}].
34 A_p Surface of a fuel particle [m^2].
35 b Constant for the parabolic temperature profile [$^{\circ}\text{C min}^{-2}$].
36 Bi Biot number [-].
37 c Constant for the exponential temperature profile [min^{-1}].
38 c_p Specific heat of the fuel particle [J kg K^{-1}].
39 E_a Activation energy [kJ mol^{-1}].
40 $f(E)$ Probability density function of the activation energy [-].
41 h Convective coefficient [$\text{W m}^{-2} \text{K}^{-1}$].
42 k Reaction rate coefficient [s^{-1}].
43 k_f Fuel particle thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$].
44 k_0 Pre-exponential factor [s^{-1}].
45 R Universal gas constant [$\text{J mol}^{-1}\text{K}^{-1}$].
46 t Time [s].
47 T Temperature [$^{\circ}\text{C}$].
48 T_p Fuel particle temperature [$^{\circ}\text{C}$].
49 T_0 Initial temperature of the fuel particle [$^{\circ}\text{C}$].
50 T_{∞} Temperature of the surrounding of the fuel particle inside a reactor [$^{\circ}\text{C}$].
51 V Volatile mass loss [%].
52 V^* Volatile mass content [%].
53 V/V^* Reacted fraction [%].
54 V_p Fuel particle volume [m^3].
55 ϕ ϕ function [-].
56 ρ_p Fuel particle density [kg m^{-3}].

57 **1. Introduction**

58 A continuous growth of the world population has occurred during the last 50 years, resulting in an increase
59 of the primary energy consumption. Currently, more than 80% of the total primary energy consumption is
60 based on fossil fuels, which are responsible for more than 98% of the carbon dioxide emissions to the

61 atmosphere, causing the current global warming problems [1]. Therefore, there is a need to evaluate the
62 potential of different alternative fuels capable of substituting fossil fuels, with lower associated pollutant
63 emissions. Two of the most promising alternative fuels, due to entirely different reasons, are sewage sludge
64 and microalgae.

65 Sewage sludge is the residue produced during the treatment of industrial or municipal wastewater. The main
66 ways of the disposing of sewage sludge nowadays can be divided into three applications: landfill, agricultural
67 use and incineration or thermochemical conversion [2]. Nevertheless, the European regulations try to limit
68 the amount of sewage sludge employed for landfill. Concerning the agricultural use, sewage sludge contains
69 organic matter, nitrogen, and phosphorus, making them suitable as a fertilizer. However, the sludge may
70 also concentrate heavy metals and pathogens, which could cause significant environmental problems. In
71 contrast, the thermochemical conversion of sewage sludge [3] presents several benefits, such as the
72 possibility to recover energy [4], the reduction of the residue volume by 70% and the thermal destruction of
73 pathogens [5]. Furthermore, the population growth in urban areas causes also the problem of an increase in
74 the sewage sludge production. Therefore, the thermochemical conversion of sewage sludge with energy
75 recovery might solve the issue of the increase in residues produced due to the population growth,
76 contributing to a reduction of the dependence on fossil fuels.

77 Among the potential replacement for fossil fuels, biodiesel is gaining importance in applications such as
78 transport, where other possible substitute fuels count on a limited applicability. The production of biodiesel
79 has been based on different crops, causing social problems as the dilemma regarding the risk of diverting
80 farmland or crops for biofuels production to the detriment of the food supply. The so-called third generation
81 biofuel obtained from microalgae can deal with these social problems since microalgae can be cultivated in
82 freshwater, marine seawater or even wastewater [5]. Microalgae have higher photosynthesis efficiency than
83 energy crops based on terrestrial lignocellulosic biomass, which would help to reduce the concentration of
84 CO₂ in the atmosphere at a faster rate [7]. Besides, microalgae are the fastest-growing photosynthesizing
85 organisms, being able to complete an entire growing cycle in few days [1]. There is a large number of
86 species of microalgae, among them the most widely grown is *Chlorella vulgaris* [8].

87 In comparison to other thermochemical conversion processes, such as combustion or gasification, pyrolysis
88 presents the advantage of producing mainly an easy to store and transport liquid product, in particular for
89 those fuels characterized by high volatile matter and low fixed carbon content, like sewage sludge and
90 microalgae [9]. Pyrolysis was found to be the optimal thermochemical process for sewage sludge by [10],
91 due to its favorable energy balance, material recovery, and zero-waste conversion. Several methods have
92 been employed in the literature to model the pyrolysis process of biomass, such as the single step model

93 [11], the two parallel reaction model [12], the three pseudo-components model [13], the sectional approach
 94 model [14], or the Distributed Activation Energy Model (DAEM) [15]. [16] and [17] proposed a simplification
 95 for DAEM to easily obtain the activation energy and the pre-exponential factor of a sample from different
 96 thermogravimetric analysis (TGA) tests. This simplified DAEM has been employed, achieving a proper
 97 agreement with experimental measurements, for a wide variety of samples, such as coal [18], charcoal [19],
 98 polymers [20], oil shale [21], medical waste [22], sewage sludge [23], microalgae [24, 25], and several
 99 different types of biomass [26, 27, 28, 29, 30, 31].

100 In this work, the pyrolysis of the *C. vulgaris* microalgae and sewage sludge are investigated separately, by
 101 means of non-isothermal thermogravimetric analysis. Independent TGA tests of both biomasses under
 102 different constant heating rates were conducted and the experimental results were employed as input data
 103 to apply the Distributed Activation Energy Model. Nine different TGA curves were employed for both the *C.*
 104 *vulgaris* and the sewage sludge samples in order to obtain accurate values of pyrolysis kinetic parameters,
 105 i.e. the activation energy and the pre-exponential factor, of the samples when applying DAEM [32]. The
 106 accurate values of the kinetic parameters of the pyrolysis reactions of *C. vulgaris* and sewage sludge are
 107 reported together with their associated uncertainties. Finally, the values of the activation energy and pre-
 108 exponential factor of the samples were employed to simulate the evolution of the pyrolysis process of the
 109 biomasses under exponential and parabolic temperature increases, more typical of the pyrolysis process of
 110 fuel particles in industrial reactors. The comparison of the numerical results with experimental
 111 measurements carried out in the TGA resulted in an excellent agreement.

112 **2. Mathematical model**

113 The simplified Distributed Activation Energy Model was applied to obtain accurate values of the activation
 114 energy E_a and the pre-exponential factor k_0 of *C. vulgaris* and sewage sludge kinetics of pyrolysis. The
 115 activation energy is the energy needed to activate the pyrolysis reactions and the pre-exponential factor
 116 expresses the empirical temperature dependence of the reaction rate coefficient k [33].

117 DAEM considers a complex fuel as a mixture of components, which decompose following first-order
 118 reactions. Thus, a large number of independent irreversible first-order reactions occur simultaneously with
 119 different associated activation energies. The reacted fraction V/V^* in a pyrolysis reaction can be determined
 120 as [16]:

$$121 \quad 1 - \frac{V}{V^*} = \int_0^\infty \exp\left(-k_0 \int_0^t e^{-E/RT} dt\right) f(E) \cdot dE \quad (1)$$

122 where V is the volatile matter content released at time t , V^* is the total volatile matter content of the sample,
 123 k_0 is the pre-exponential factor corresponding to the activation energy E , R is the universal gas constant,
 124 and $f(E)$ is the probability density function of the activation energy. The exponential term in Eq. (1) is the so-
 125 called ϕ function:

$$126 \quad \phi(E, T) = \exp\left(-k_0 \int_0^t e^{-E/RT} dt\right) \quad (2)$$

127 which is typically approximated by a step function at a value of the activation energy $E = E_a$, obtaining for the
 128 reacted fraction:

$$129 \quad \frac{V}{V^*} = 1 - \int_{E_a}^{\infty} f(E) \cdot dE = \int_0^{E_a} f(E) \cdot dE . \quad (3)$$

130 [16] proposed a value for $\phi(E_a, T) = 0.58$, which has been employed for several different types of mineral
 131 carbon and biomass samples obtaining good agreement with experimental measurements. Approximating
 132 the integral in the ϕ function, for a constant heating rate a , to:

$$133 \quad \phi(E, T) = \exp\left(-\frac{k_0}{a} \int_0^T e^{-E/RT} dT\right) \approx \exp\left(-\frac{k_0 RT^2}{aE} e^{-E/RT}\right) \quad (4)$$

134 and using the value proposed by [16] for $\phi(E_a, T) = 0.58$, the widely used Arrhenius equation for the pyrolysis
 135 of a sample under a constant heating rate a can be derived:

$$136 \quad \ln\left(\frac{a}{T^2}\right) = \ln\left(\frac{k_0 R}{E_a}\right) + 0.6075 - \frac{E_a}{R} \frac{1}{T} . \quad (5)$$

137 Based on this Arrhenius equation, [17] proposed a method to determine the activation energy E_a and the
 138 pre-exponential factor k_0 of a sample from TGA curves of the pyrolysis process obtained for different heating
 139 rates a .

140 **3. Experimental Measurements**

141 The pyrolysis tests were performed in a thermogravimetric analyzer TGA Q500 from TA Instruments. A
 142 nitrogen flowrate of 60 ml/min was supplied to the furnace to guarantee the existence of an inert
 143 atmosphere. The temperature profile programmed to the TGA consisted of two processes occurring in
 144 series, first a drying process of the sample at 105 °C and then the pyrolysis process taking place when
 145 increasing the temperature of the sample in the inert atmosphere up to 800 °C. For the pyrolysis tests
 146 conducted to determine the kinetic parameters of the pyrolysis, a constant heating rate was used, and for a

147 more industrial application, a series of consecutive constant heating rates obtaining exponential or parabolic
148 temperature increases, as described in [34], were employed. For the pyrolysis measurements at constant
149 heating rates, nine different tests were carried out, as proposed by [32], using heating rates of 10, 13, 16,
150 19, 22, 25, 30, 35, 40 K/min. These heating rates are low compared to industrial applications, nevertheless
151 similar results were obtained by [31] when applying DAEM to TGA curves obtained at higher heating rates,
152 up to 200 K/min.

153 The sensitivity of the TGA mass measurement is 0.1 μg and the weighing precision is $\pm 0.01\%$. The dynamic
154 baseline drift during a heating process of an empty platinum pan from 50 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ at 20 K/min is lower
155 than 50 μg with no baseline subtraction. The TGA temperature accuracy during an isothermal process is
156 ± 1 $^{\circ}\text{C}$ and the temperature precision is ± 0.1 $^{\circ}\text{C}$. A mass of 10.0 ± 0.5 mg of the sample, sieved previously
157 under 100 μm , was employed in the pyrolysis measurements in the TGA to reduce heat transfer effects in
158 the sample [26, 35]. Each pyrolysis test was conducted three times to guarantee the repeatability of the
159 process (obtaining differences lower than 1 %), and a blank experiment was also run for each heating rate to
160 exclude buoyancy effects.

161 The mono-cellular green microalgae *C. Vulgaris* have a diameter of 4-10 μm and a spherical form. They
162 grow in flowing or standing fresh and brackish water and contain as dried samples around 50% of proteins
163 and a high amount of a multitude of unsaturated fatty acids, such as alpha-linolenic acid and carotenoids, as
164 lutein. Additionally, they contain minerals with iron, calcium, magnesium, zinc, potassium, manganese and
165 sulfur. The *C. vulgaris* microalgae samples employed for the study were cultivated and dried by the
166 company AlgaEnergy S.A. in 2016 in Madrid.

167 The sludge was obtained from the municipal sewage treatment plant of Loeches (Madrid, Spain) in February
168 2016. The sludge was taken after the pre-drying process at 80 $^{\circ}\text{C}$ in a fluidized bed in the sewage treatment
169 plant. This sewage sludge sample is quite different to that investigated earlier [23], which was obtained from
170 the municipal sewage treatment plant of La China (Madrid, Spain) in 2012.

171 The samples of *C. Vulgaris* and sewage sludge were characterized by proximate and elemental analyses.
172 The proximate analysis was performed in the TGA Q500 from TA Instruments to determine the moisture,
173 ash, volatile matter, and fixed carbon contents of the samples. The moisture content was characterized as
174 the mass released by the sample at 105 $^{\circ}\text{C}$. The ash content was determined as the percentage of mass
175 remaining after a heating of the sample up to 550 $^{\circ}\text{C}$, supplying the furnace with an oxygen flow rate of 60
176 ml/min using a heating rate of 10 K/min, and an isothermal process at 550 $^{\circ}\text{C}$ until the mass of the sample
177 stabilized. The volatile matter content of the samples was measured as the percentage of mass released by

178 the sample during a heating process at a heating rate of 10 K/min from 105 °C to 900 °C and an isothermal
179 process at 900 °C in an inert atmosphere which was obtained introducing a flux of 60 ml/min of nitrogen in
180 the furnace, until the mass of the sample stabilized. Finally, the fixed carbon content was obtained from the
181 difference between these two procedures.

182 The elemental analysis of the sample was carried out in a LECO TruSpec CHN analyzer, where the carbon
183 and hydrogen content of the sample are measured using an infrared absorption detector for the exhaust
184 gases obtained from a complete combustion of the sample. The nitrogen content is determined conducting
185 the exhaust gases through a thermal conductivity cell. The carbon and nitrogen contents are measured with
186 a precision of $\pm 0.5\%$, while the precision of the measurement of the hydrogen content is $\pm 1\%$. Heating value
187 tests of the samples were also conducted in an isoperibolic calorimeter Parr 6300 with an instrument
188 precision of 0.10% relative standard deviation. Control limits were based on 99% confidence (3 sigma)
189 values. The calorimeter has a temperature resolution of 0.0001 °C (data obtained from the manufacturer
190 Parr Instruments).

191 **4. Results and Discussion**

192 The results of the chemical, thermogravimetric and kinetic analysis of microalgae and sewage sludge as
193 potential biofuels of the future are shown and discussed in the following sections.

194 **4.1. Physical and chemical properties of *Chlorella Vulgaris* and Sewage sludge**

195 The results obtained from the proximate analysis, the ultimate analysis and the heating value tests of the
196 microalgae *C. vulgaris* and sewage sludge samples are reported in Table 1.

197 Table 1: Results obtained from the characterization of the *C. vulgaris* and the sewage sludge samples (d:
198 dry basis, daf: dry ash free basis, * obtained by difference).

199 Table 1 shows that the volatile matter content of both the *C. vulgaris* and the sewage sludge is high, and
200 therefore the pyrolysis study of these biofuels is justified. Concerning the elemental analysis, the carbon and
201 hydrogen contents of *C. vulgaris* are higher than those of sewage sludge samples, resulting therefore in a
202 higher heating value for the microalgae sample. The nitrogen content of both samples is high, which
203 indicates a high pollution level of NO_x emission if direct combustion of these biomasses is selected as the
204 thermochemical conversion method. Therefore, an appropriate NO_x after-treatment system is necessary to
205 satisfy EU emission regulations. Additionally, the ash content, especially in sewage sludge, needs to be
206 considered as it influences the optimal operation and maintenance conditions of pyrolysis, gasification, and
207 combustion systems for instance through the formation of slag, which affect the heat transfer to the wall [36].

208 Also ash compounds like heavy metals should not end up in the environment due to their negatively impact
209 on health of humans, animals, plants and microorganism.

210 The composition of *C. vulgaris* samples from different sources, shown in Table 2, is quite homogeneous.

211 Table 2: Comparison of characterization results of *C. vulgaris* samples. M: Moisture, V: Volatile matter, A:
212 Ash, FC: Fixed Carbon, C: Carbon, H: Hydrogen, N: Nitrogen, S: Sulfur, O: Oxygen, w: wet, d: dry, daf: dry
213 ash free, * obtained by difference.

214 As can be seen from Table 3, sewage sludge samples are quite heterogeneous. The reason is that sewage
215 sludge is a complex mixture of water, organic compounds (such as carbohydrates, lipids, and proteins),
216 microorganisms which can be pathogenic before they were destroyed through heating processes, and
217 inorganic substances e.g. silicates and metal containing compounds, which are left over as ash after a high-
218 temperature heating process. The composition of sewage sludge depends strongly on the origin of the
219 wastewater, e.g. industrial, agricultural or rain water and the season, as well as the used pretreatment
220 methods, such as aerobic, anaerobic, chemical or thermal stabilization, dewatering, thickening and drying
221 processes [45]. This influences, for instance, the pyrolysis product distribution as shown by [2] for three
222 samples of anaerobically digested sewage sludge obtained from three different urban wastewater treatment
223 plants.

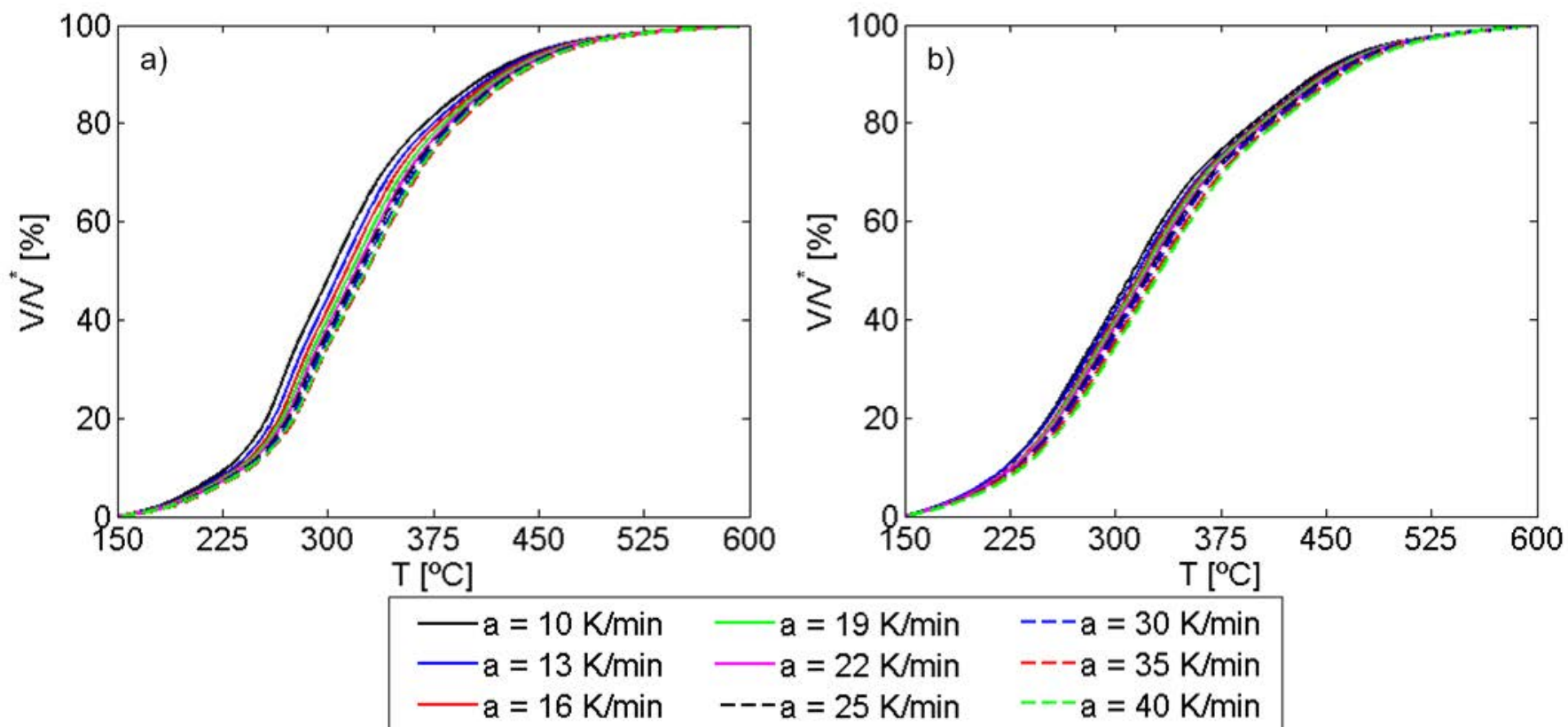
224 Table 3: Comparison of characterization results of sewage sludge samples. M: Moisture, V: Volatile matter,
225 A: Ash, FC: Fixed Carbon, C: Carbon, H: Hydrogen, N: Nitrogen, S: Sulfur, O: Oxygen, w: wet, d: dry, daf:
226 dry ash free, * obtained by difference.

227

228 **4.2. Determination of the kinetic parameters of the pyrolysis**

229 The pyrolysis tests using constant heating rates were conducted under a controlled atmosphere in the
230 thermogravimetric analyzer. The procedure described by [32] was followed to obtain accurate values of the
231 kinetic parameters of the pyrolysis, i.e. the activation energy E_a and the pre-exponential factor k_0 . Following
232 this procedure, tests using nine different heating rates ($a = 10, 13, 16, 19, 22, 25, 30, 35, 40$ K/min) were
233 performed. The evolution of the reacted fraction V/V^* , defined as the percentage of the total volatile matter
234 released by the sample, with temperature T is shown in Figure 1 a) for the *C. vulgaris* and in Figure 1 b) for
235 the sewage sludge sample, up to a temperature of 600 °C. Under a constant nitrogen flow, carbonaceous
236 compounds, measured as fixed carbon amount, volatilize between 500 - 700 °C and the ash melts at
237 temperatures above around 800 °C, which was not investigated in this study.

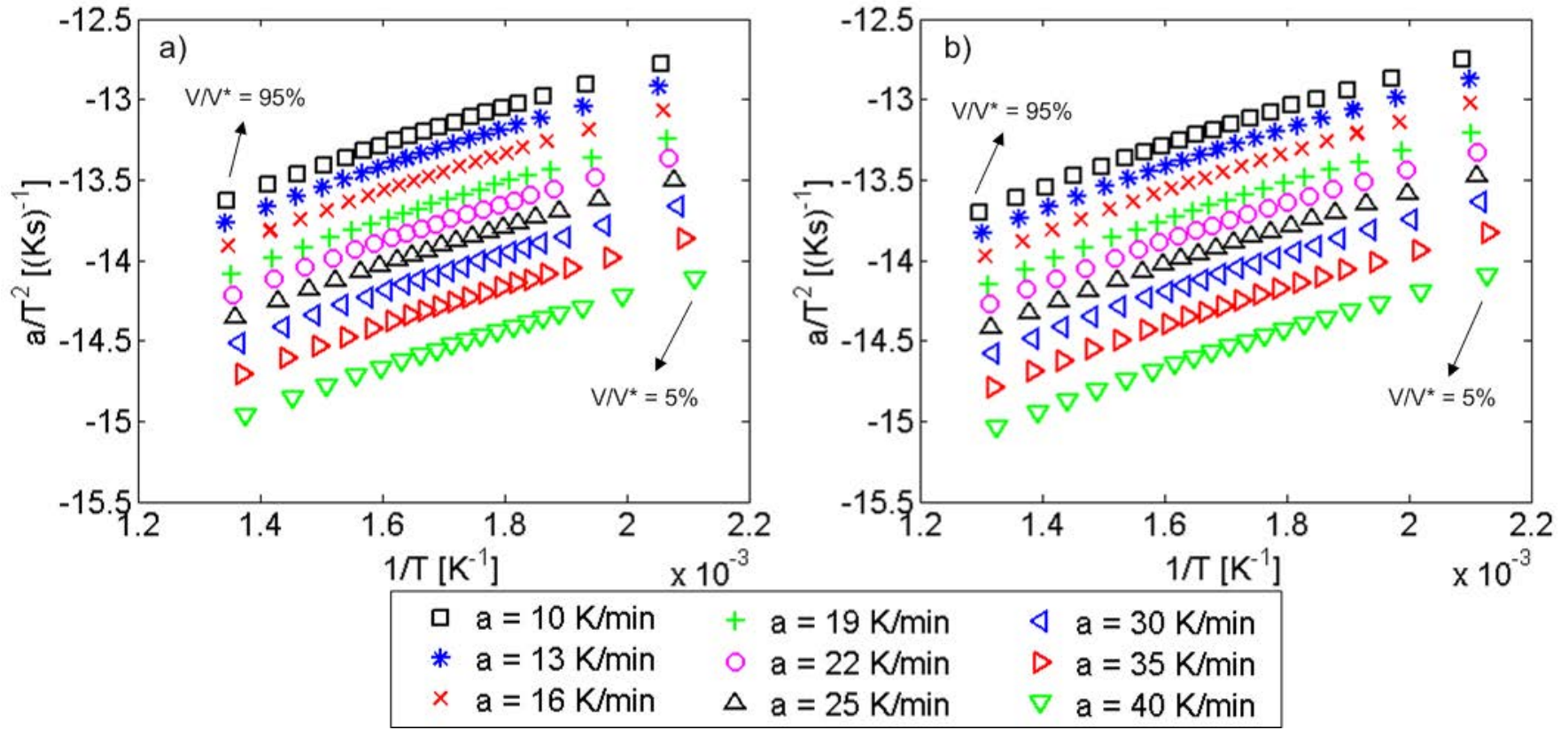
238 The pyrolysis of both samples occurred between 150 and 600 °C, nevertheless the evolution of the reacted
 239 fraction of sewage sludge with temperature is more progressive than that of the microalgae sample, for
 240 which the pyrolysis takes place faster for temperatures in the range 250 - 450 °C. Furthermore, the effect of
 241 the heating rate variation on the reacted fraction is higher for the *C. vulgaris* sample, obtaining a
 242 displacement of the curve to higher temperatures when increasing the heating rate, a typical result for non-
 243 isothermal pyrolysis reactions [59, 60]. This effect is slighter for the sewage sludge, resulting in a collapse of
 244 the reacted fraction curves for the different heating rates in a narrow zone.



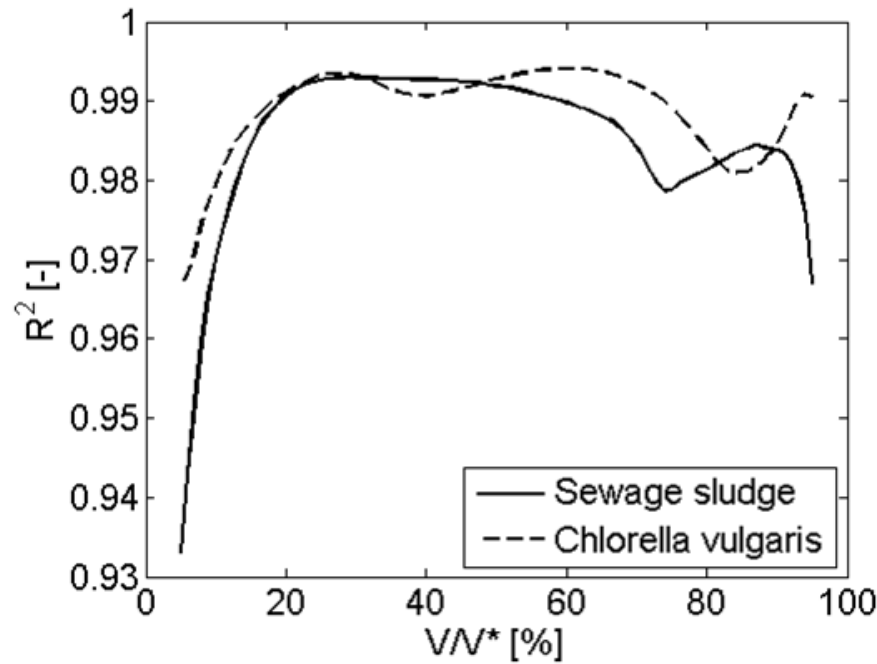
245
 246 Figure 1: Evolution of the reacted fraction, V/V^* , with temperature, T , during the pyrolysis process at
 247 constant heating rates. a) *C. vulgaris*, b) Sewage sludge.

248 From the reacted fraction curves shown in Figure 1, and given the Arrhenius equation (Eq. 5), the Arrhenius
 249 plot can be built by plotting $\ln(a/T^2)$ as a function of $1/T$ for different values of the reacted fraction V/V^* . Even
 250 though all calculations within this paper were carried out using intervals of 1% for the conversion rate, Figure
 251 2 shows the Arrhenius plots of the *C. vulgaris* (a) and the sewage sludge (b), built using conversion rate
 252 intervals of 5% to improve data visualization. The Arrhenius plot of sewage sludge is wider because of the
 253 more progressive evolution of the reacted fraction with temperature observed in Figure 1 b). The Arrhenius
 254 plots can be employed to determine the activation energy E_a and the pre-exponential factor k_0 of the
 255 samples by linearizing the points obtained for the different reacted fractions V/V^* . Both for the microalgae
 256 and the sludge samples, the points in the Arrhenius plot present a high linearity. To quantify the linearity of
 257 the Arrhenius plots, the determination coefficient of the linear fitting of the points, R^2 , was calculated. The
 258 results can be observed in Figure 3, both for the *C. vulgaris* and the sewage sludge. A high linearity, i.e. high
 259 values of R^2 , can be observed for a wide range of reacted fractions between 20% and 80%, whereas the

260 values of the determination coefficient of the fitting decrease for low and high reacted fractions, where the
 261 slope of the curve V/V^*-T is smooth, as shown in Figure 1.



262
 263 Figure 2: Arrhenius plot obtained using conversion rate intervals of 5%. a) *C. vulgaris*, b) Sewage sludge.



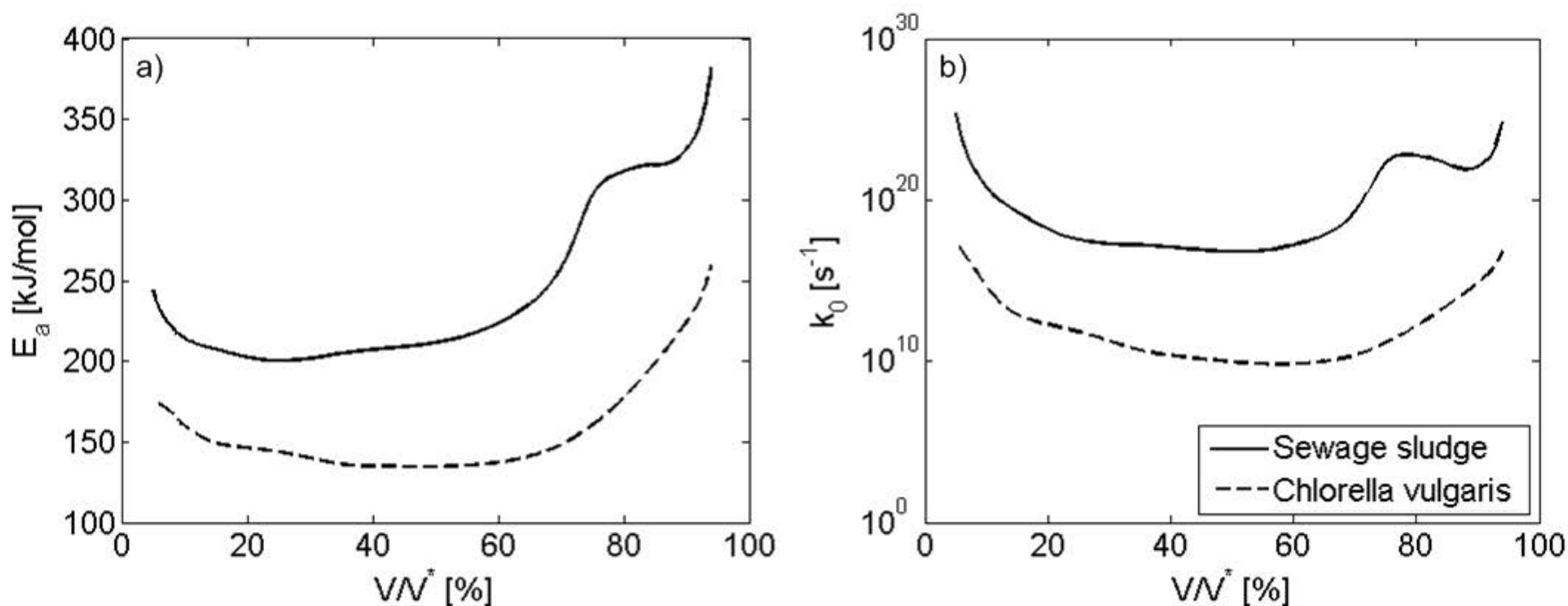
264
 265 Figure 3: Determination coefficient of the linear fitting of the Arrhenius plot.

266 Considering the Arrhenius equation for constant heating rates (Eq. 5), the kinetic parameters of the pyrolysis
 267 reaction, i.e. the activation energy E_a and the pre-exponential factor k_0 , can be obtained for each reacted
 268 fraction from the linear fitting of the values of the Arrhenius plot ($\ln(a/T^2) = m \cdot (1/T) + n$). Equating terms of
 269 Eq. 5 with the linear fitting, the activation energy E_a and the pre-exponential factor k_0 of the samples can be
 270 calculated from the slope m and the intercept n of the linear fitting as:

$$271 \quad E_a = -m \cdot R \quad (6)$$

$$272 \quad k_0 = -m \cdot \exp(n - 0.6075) \quad (7)$$

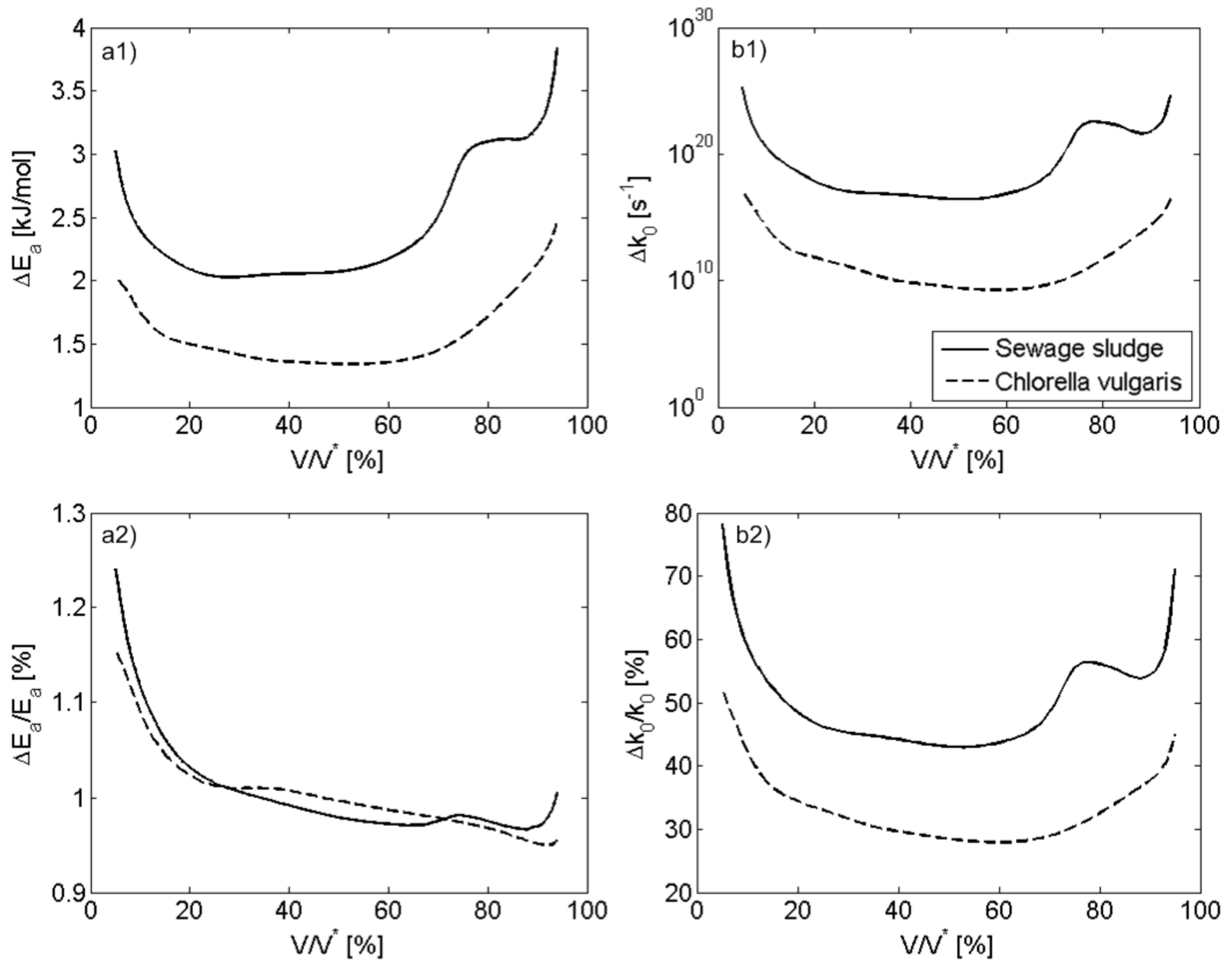
273 Accurate values of the activation energy E_a and the pre-exponential factor k_0 can be calculated using the
 274 nine different reacted fraction curves shown in Figure 1, obtained for different constant heating rates, and
 275 considering the uncertainties of the mass, the temperature T and the heating rate a for the linearization of
 276 the values of the Arrhenius plot, as stated by [32]. The accurate values of E_a and k_0 for the *C. vulgaris* and
 277 the sewage sludge are shown in Figure 4. The activation energy of the *C. vulgaris* varies between around
 278 150 and 250 kJ/mol, while its pre-exponential factor is in the range from 10^{10} to 10^{15} s⁻¹. Similar values for
 279 the kinetic parameters of the pyrolysis reaction were obtained for samples of the *Chlorella* microalgae by
 280 [44, 38, 61–66], and for different microalgae species such as *Nannochloropsis oculata* and *Tetraselmis sp.*
 281 by [24]. In contrast, higher values for both E_a , ranging from 200 and 400 kJ/mol, and k_0 , varying between
 282 10^{15} and 10^{25} s⁻¹, were obtained for sewage sludge. These values of the kinetic parameters for sewage
 283 sludge are in accordance with the measurements of different authors [58, 67–70]. In a previous work, [23]
 284 slightly lower values were obtained for the activation energy and pre-exponential factor of sewage sludge.
 285 Nonetheless, it should be noticed that the sewage sludge analyzed in [23] was obtained from a different
 286 municipal sewage treatment plant, La China (Madrid, Spain), and were collected in 2012. Furthermore, the
 287 values of E_a and k_0 reported in [23] were obtained from just three TGA curves and thus, a higher uncertainty
 288 could be expected for these values.



289
 290 Figure 4: Kinetic parameters of the pyrolysis process: a) activation energy and b) pre-exponential factor.

291 The absolute and relative uncertainties associated with the kinetic parameters, E_a and k_0 , of *C. vulgaris* and
 292 sewage sludge are reported in Figure 5. The mathematical procedure to determine the uncertainties
 293 associated with the activation energy and the pre-exponential factor is described in detail in [32]. As can be
 294 observed, the absolute uncertainties of the activation energy depend on the stage of pyrolysis process and
 295 can be as low as 1.35 kJ/mol for the *C. vulgaris* algae and 2.03 kJ/mol for the sewage sludge, respectively.
 296 They are, for all the reacted fractions, lower than 2.5 kJ/mol for the *C. vulgaris*, and 4 kJ/mol for sewage

297 sludge over the whole pyrolysis process, resulting in similar relative uncertainties of less than 1.3% for the
 298 activation energy of both samples. Nevertheless, the relative uncertainties for the pre-exponential factor
 299 differ, obtaining larger values for sewage sludge, as a result of its higher activation energy, shown in Figure
 300 4 a), which means a higher slope of the linearization that would lead to a higher uncertainty in the intercept
 301 of the linearization. For both the *C. vulgaris* and the sewage sludge, the relative uncertainty of the pre-
 302 exponential factor is higher for low and high values of the reacted fraction V/V^* , as a consequence of the
 303 lower linearity of the Arrhenius plot values in these zones, which can be proved by the lower determination
 304 coefficient R^2 obtained for low and high V/V^* (Figure 3). Even though the values of the relative uncertainty of
 305 k_0 might seem to be high, the effect of this parameter in the pyrolysis reaction is much lower than that of E_a
 306 due to the exponential function (see Eq. 1). Therefore, the values shown in Figure 4 for the activation energy
 307 and the pre-exponential factor of the *C. vulgaris* and the sewage sludge are accurate enough for most
 308 modelling and optimization purposes and could be employed to model the pyrolysis process of these types
 309 of biomass.



310
 311 Figure 5: Uncertainties associated with the kinetic parameters of the pyrolysis process: a) activation energy,
 312 b) pre-exponential factor, 1) absolute uncertainty, 2) relative uncertainty.

313

314 4.3. Validity of the kinetic parameters of pyrolysis for typical temperature increases of fuel particles

315 The values of the kinetic parameters of the pyrolysis process reported in Figure 4 and their associated
316 uncertainties, shown in Figure 5, correspond to pulverized samples, with particles diameter below 100 μm .
317 However, in industrial applications, the fuels to be pyrolysed are typically larger particles, such as pellets,
318 and thus the temperature inside the fuel particles is subjected to heat transfer effects.

319 The evolution of the interior temperature of the fuel particles with time is governed by the Biot number, Bi ,
320 which relates the convective heat transfer between the solid surface and the surrounding with the heat
321 transfer by conduction inside the particle. The Biot number is defined as:

$$322 \quad Bi = \frac{h \cdot L_c}{k_f}, \quad (8)$$

323 where h is the convective coefficient, L_c is the characteristic length and k_f is the thermal conductivity of the
324 fuel particle. The value of the thermal conductivity is characteristic of the fuel analyzed, however the
325 convective coefficient and the characteristic length could vary in different applications. The convective
326 coefficient can vary depending on the technology employed for the thermochemical conversion process
327 between around 5 and 100 $\text{W/m}^2\text{K}$. Furthermore, the characteristic length of the fuel may vary from a couple
328 of centimeters for pellet particles to tens or hundreds of micrometers when the fuel is supplied to the reactor
329 as powder. The range of variation of both h and L_c causes a wide range of variation for the Biot number.

330 When the thermal conduction inside the fuel particle is much faster than the convective heat transfer at the
331 particle surface, i.e. $Bi \ll 1$, the temperature variation inside the fuel particle can be neglected, assuming
332 that the whole particle is at the surface temperature. In such cases, the Lumped Capacitance Method can be
333 applied to determine the temperature variation inside the particle, equaling the energy increase inside the
334 particle to the heat exchanged by convection on its surface. The result of the Lumped Capacitance Method
335 is an exponential variation of the fuel particle temperature $T_p(t)$ from its initial value T_0 to the temperature of
336 the environment inside the reactor T_∞ , in the form:

$$337 \quad \frac{T_p(t) - T_\infty}{T_0 - T_\infty} = \exp\left[-\frac{h \cdot A_p}{\rho_p \cdot V_p \cdot c_p} t\right] \quad (9)$$

338 with the surface of a fuel particle A_p , the fuel particle density ρ_p , the fuel particle volume V_p and the specific
339 heat of the fuel particle c_p .

340 In contrast, when the thermal conduction inside the fuel particle cannot be considered to be much faster
341 than the convective heat transfer at the particle surface, the Lumped Capacitance Method is no longer valid,
342 and the temperature inside the fuel particle differs from that of its surface. In these cases, the temperature
343 distribution inside the fuel particle can be assumed to be parabolic.

344 Therefore, different tests were conducted in the TGA to characterize the pyrolysis of the *C. vulgaris* and the
345 sewage sludge under exponential and parabolic temperature increases, following the trends of the
346 temperature increases inside the fuel particles in industrial applications. Both the exponential and parabolic
347 temperature increases were obtained in the TGA as a sequence of 25 short constant heating rate increases,
348 as described in [34].

349 4.4. Exponential temperature increases

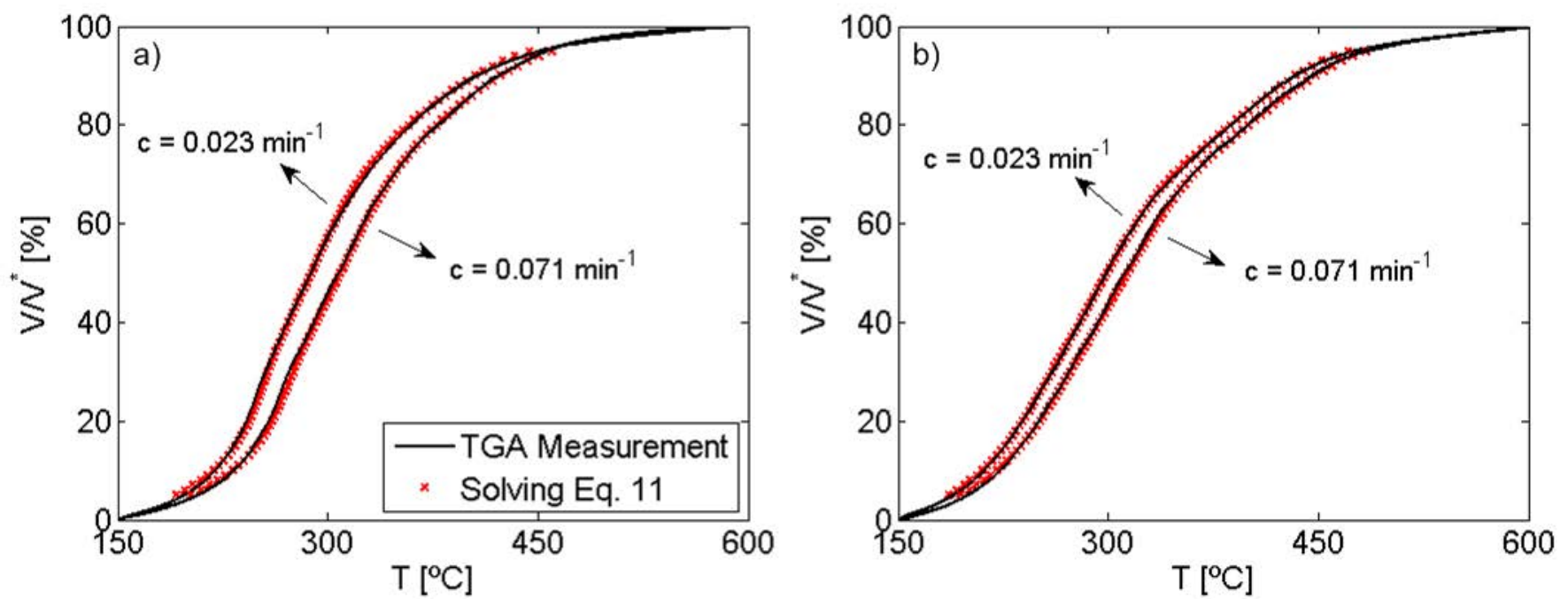
350 The exponential temperature increases tested during the pyrolysis of the samples in the TGA were in the
351 form:

$$352 \quad T[^\circ\text{C}] = 146.5 + 3.5 \cdot \exp(c \cdot t). \quad (10)$$

353 Two different exponential temperature increases were programmed for each sample, varying the value of c ,
354 $c = 0.023 \text{ min}^{-1}$ and $c = 0.071 \text{ min}^{-1}$, these being the limit values studied in [34]. The Arrhenius equation
355 derived from the simplified Distributed Activation Energy Model for exponential temperature increases was
356 obtained by [34]:

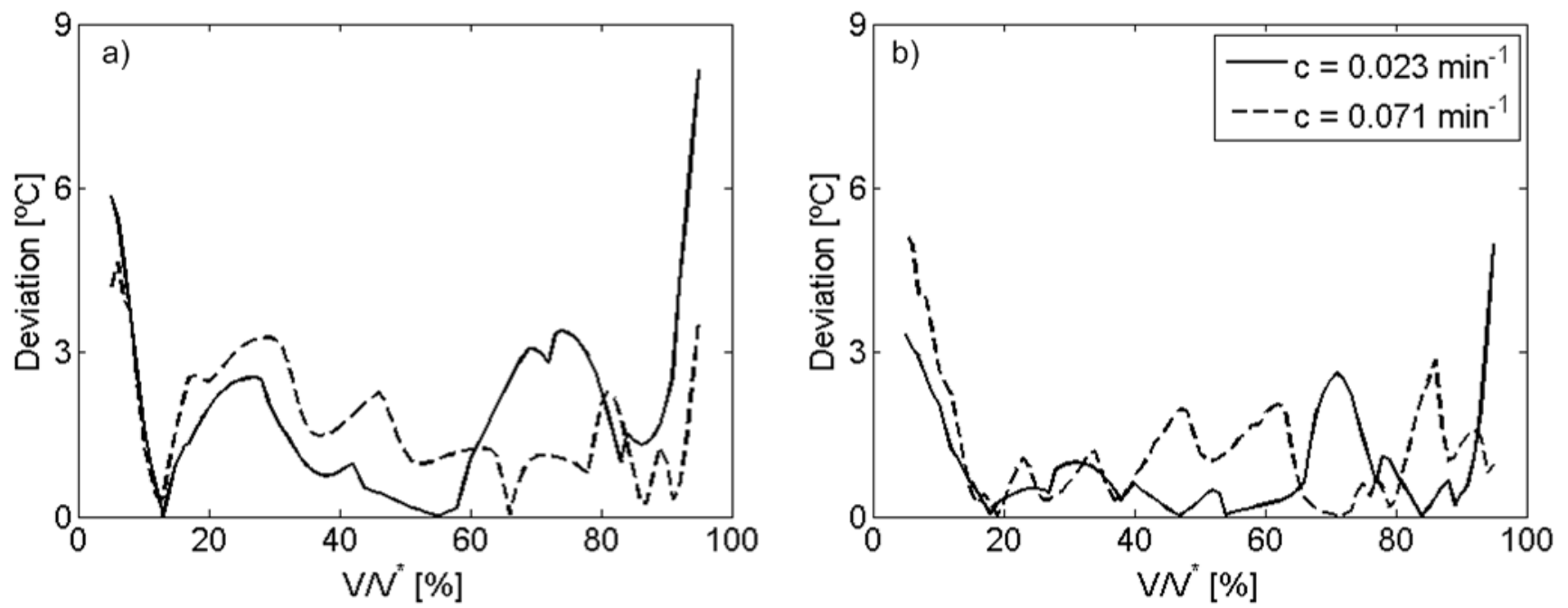
$$357 \quad \ln\left(\frac{c}{T}\right) = \ln\left(\frac{k_0 R}{E_a}\right) + 1.7467 - \frac{E_a}{R} \frac{1}{T}. \quad (11)$$

358 Therefore, Eq. 11 can be solved using the values of the activation energy E_a and the pre-exponential factor
359 k_0 of the sample, shown in Figure 4, to obtain the temperature T for each reacted fraction V/V^* . The results
360 obtained solving Eq. 11 are presented in Figure 6 together with the experimental measurements of the
361 pyrolysis process performed in the TGA under exponential temperature increases, for both the *C. vulgaris*
362 and the sewage sludge samples. A proper agreement between the numerical results obtained from Eq. 11
363 and the experimental measurements can be observed in Figure 6 for both samples.



364
 365 Figure 6: Comparison of experimental and numerical results obtained for the relation between the reacted
 366 fraction, V/V^* , and the temperature, T , during the pyrolysis process under exponential temperature
 367 increases. a) *C. vulgaris*, b) Sewage sludge.

368 The deviation between the numerical estimation of the temperature from Eq. 11 and the experimental
 369 measurement carried out in the TGA during the pyrolysis of the samples under exponential temperature
 370 increases is shown in Figure 7 for total reaction times around 70 and 210 min, depending on the different
 371 exponential temperature profiles used. Low deviations of less than 4 °C between the numerically obtained
 372 and the experimentally measured temperature are obtained for both the microalgae and the sewage sludge
 373 samples for both exponential temperature profiles, in a range of reacted fractions between 20% and 80%,
 374 when the pyrolysis process is faster. Higher deviations of less than 9 °C are obtained for lower (<20%) and
 375 higher (>80%) values of the reacted fraction, where the linearity of the Arrhenius plot was lower (see Figure
 376 3) and thus the uncertainties associated with the kinetic parameters of the pyrolysis reaction increased (see
 377 Figure 5). These low temperature deviations obtained for exponential temperature increases indicate that
 378 the activation energy E_a and the pre-exponential factor k_0 shown in Figure 4 for the *C. vulgaris* and the
 379 sewage sludge pyrolysis, and the Arrhenius equation (Eq. 11) derived by [34], could be employed to
 380 simulate the pyrolysis process occurring in these fuel particles when the Lumped Capacitance Method can
 381 be applied.



382

383 Figure 7: Deviations between the temperature estimated by the Arrhenius equation (Eq. 11) and the
 384 temperature measured in TGA for the pyrolysis under exponential temperature increases. a) *C. vulgaris*, b)

385

Sewage sludge.

386 4.5. Parabolic temperature increases

387 The parabolic temperature increases programmed in the TGA for the pyrolysis tests of the samples were in
 388 the form:

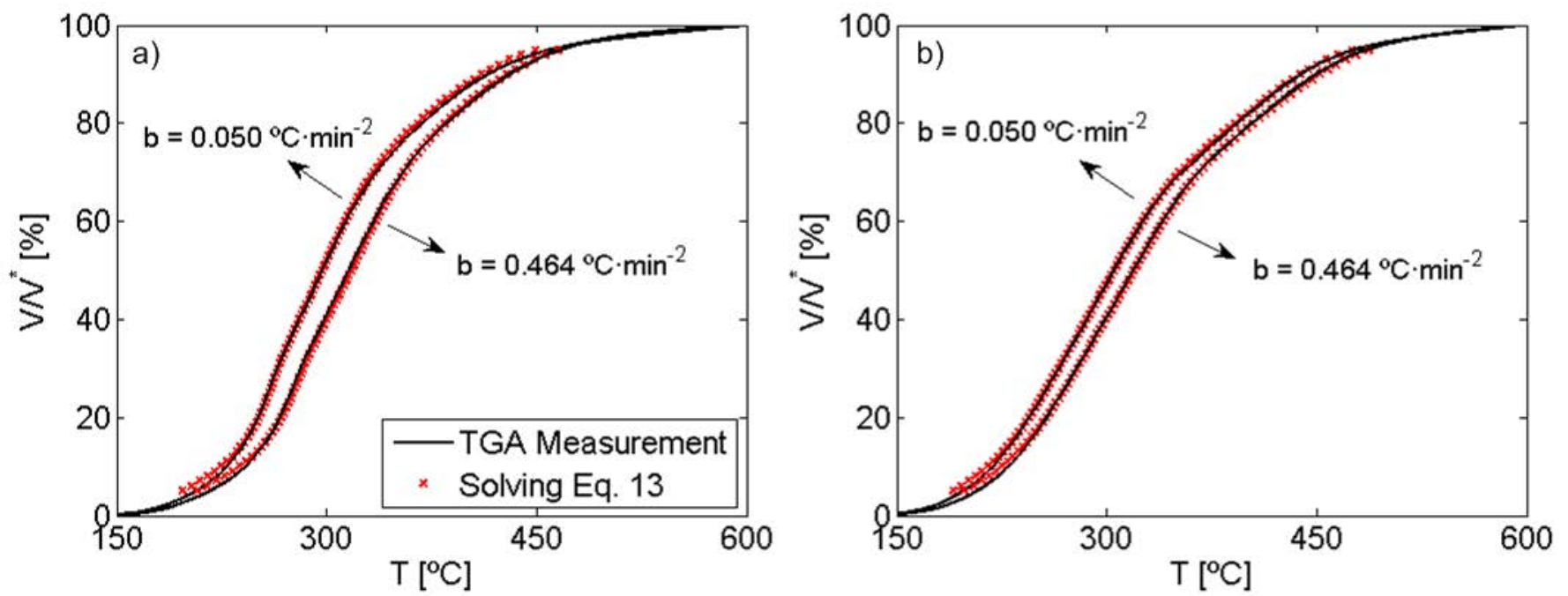
$$389 \quad T[^\circ\text{C}] = 150 + b \cdot t^2 \quad (12)$$

390 Two different values of b , $b = 0.050 \text{ }^\circ\text{C}\cdot\text{min}^{-2}$ and $b = 0.464 \text{ }^\circ\text{C}\cdot\text{min}^{-2}$, were employed during the tests to
 391 obtain two different parabolic temperature increases during the pyrolysis measurements in the TGA, these
 392 being the limit values studied in [34]. Additionally, [34] obtained the Arrhenius equation derived from the
 393 simplified Distributed Activation Energy Model for parabolic temperature increases:

$$394 \quad \ln\left(\frac{\sqrt{b}}{T^{1.5}}\right) = \ln\left(\frac{k_0 R}{2E_a}\right) + 1.0715 - \frac{E_a}{R T} \quad (13)$$

395 The values of the activation energy E_a and the pre-exponential factor k_0 of the samples, shown in Figure 4,
 396 were used to solve Eq. 13, determining the temperature T at which each reacted fraction V/V^* occurred. The
 397 results of the measurements during the pyrolysis process of the samples in the TGA under parabolic
 398 temperature increases are plotted, together with the numerical solution of Eq. 13, in Figure 8. A good
 399 agreement between the numerical estimation and the experimental measurements can be observed in
 400 Figure 8 both for the *C. vulgaris* and the sewage sludge pyrolysis processes. The pyrolysis processes with
 401 the lower value of b have a slower temperature rise with a more than 3 times longer reaction time (around
 402 95 min for complete pyrolysis) which results in a higher amount of reacted fraction at lower temperature than

403 during the pyrolysis processes with the higher value of b , which still needs more than 30 min for complete
 404 pyrolysis.

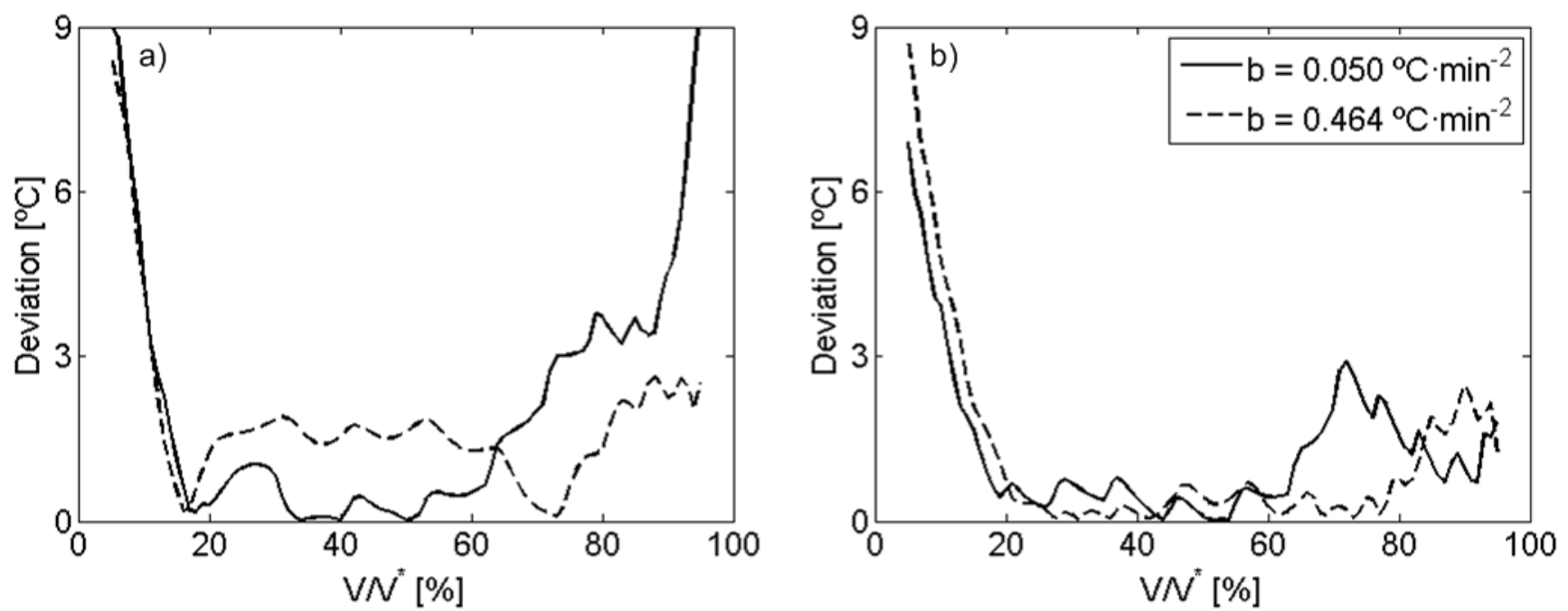


405

406 Figure 8: Comparison of experimental and numerical results obtained for the relation between the reacted
 407 fraction, V/V^* , and the temperature, T , during the pyrolysis process under parabolic temperature increases.

408 a) *C. vulgaris*, b) Sewage sludge.

409 The deviations between the temperatures estimated solving Eq. 13 and the TGA measurements during the
 410 pyrolysis process of the samples under parabolic temperature increases can be observed in Figure 9. The
 411 deviations between the numerical and the experimental temperature are again lower than 4 °C for a wide
 412 range of reacted fractions, between 20% and 80%. As for the case of the pyrolysis under exponential
 413 temperature increases, the temperature deviations for the pyrolysis under parabolic temperature increases
 414 are slightly higher for reacted fractions lower than 20% and higher than 80%, where the uncertainties
 415 associated with the activation energy and the pre-exponential factor are higher (Figure 5). In view of the low
 416 deviations obtained between the numerical and the experimental temperatures, shown in Figure 9, the
 417 kinetic parameters of the pyrolysis reaction, E_a and k_0 , for the *C. vulgaris* and the sewage sludge shown in
 418 Figure 4, and the Arrhenius equation (Eq. 13) derived by [34], could be employed to simulate the pyrolysis
 419 process occurring in these fuel particles subjected to parabolic temperature increases.



420

421 Figure 9: Deviations between the temperature estimated by the Arrhenius equation (Eq. 13) and the
 422 temperature measured in TGA for the pyrolysis under parabolic temperature increases. a) *C. vulgaris*, b)
 423 Sewage sludge.

424 **5. Conclusions**

425 Non-isothermal thermogravimetric analysis was employed to characterize the pyrolysis of *C. vulgaris* and
 426 sewage sludge. The simplified Distributed Activation Energy Model was applied to simulate the pyrolysis of
 427 the samples, obtaining the activation energy and the pre-exponential factor of *C. vulgaris* and sewage
 428 sludge, together with their associated uncertainties. The activation energies of *C. vulgaris* are in the range of
 429 150 – 250 kJ/mol and its pre-exponential factor varies between 10^{10} and 10^{15} s⁻¹, whereas for the sewage
 430 sludge the activation energies range between 200 and 400 kJ/mol and pre-exponential factors vary from
 431 10^{15} to 10^{20} s⁻¹.

432 Experimental measurements of the pyrolysis process of the samples under exponential and parabolic
 433 temperature increases were conducted in the TGA, and the corresponding Arrhenius equations for these
 434 temperature increases were solved using the values obtained for the pyrolysis kinetic parameters. The
 435 comparison of the experimental and numerical data resulted in excellent agreement, confirming the
 436 accuracy of the values reported for E_a and k_0 . Thus, the values reported for the activation energy and the
 437 pre-exponential factor for the *C. vulgaris* can be employed as reference values in numerical studies of the
 438 pyrolysis of this biofuel due to its homogeneity of chemical and biological composition. However, for sewage
 439 sludge pyrolysis the situation is quite different due to its variable composition. Therefore, the pyrolysis kinetic
 440 parameters obtained for our sewage sludge sample can be only used for modelling the pyrolysis of sewage
 441 sludge with a similar composition, or in cases where no better data are available.

442

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602 2016; 30, 4869-4878.

603 **List of figures**

604 Figure 1: Evolution of the reacted fraction, V/V^* , with temperature, T , during the pyrolysis process at
605 constant heating rates. a) *C. vulgaris*, b) Sewage sludge.

606 Figure 2: Arrhenius plot obtained using conversion rate intervals of 5%. a) *C. Vulgaris*, b) Sewage sludge.

607 Figure 3: Determination coefficient of the linear fitting of the Arrhenius plot.

608 Figure 4: Kinetic parameters of the pyrolysis process: a) activation energy and b) pre-exponential factor.

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