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1 **Title Page**

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34 **Integrating anaerobic digestion and pyrolysis for treating digestates derived from sewage sludge and**
35 **fat wastes**

36

37

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45

46 **Abstract**

47 The coupling of biological and thermal technologies allows for the complete conversion of wastes into
48 energy and biochar eliminating the problem of sludge disposal. The valorisation of fatty residues as co-
49 substrate in a mesophilic digester of a wastewater treatment plant was studied considering an integrated
50 approach of co-digestion and pyrolysis. Four digested samples obtained from co-digestion of sewage
51 sludge and butcher's fat waste were studied by thermogravimetric analysis. The activation energy
52 corresponding to the sludge pyrolysis was calculated by a non-isothermal kinetic. Arrhenius activation
53 energy was lower for the pyrolysis of digested grease sample (92 kJ mol⁻¹ obtained by OFW and 86 kJ
54 mol⁻¹ obtained by Vyazovkin) than for the pyrolysis of sewage sludge and its blends (164-190 kJ mol⁻¹
55 obtained by OFW and 162-190 kJ mol⁻¹ obtained by Vyazovkin). The analysis of the integrated approach
56 of anaerobic co-digestion and pyrolysis of digestates demonstrated that the addition of 3% (w/v) of fat to
57 the feeding sludge results in a 25% increase in the electricity obtained from biogas (if a combined heat
58 and power unit is considered for biogas valorisation) and increasing the fat content to 15% allows for
59 covering all thermal needs for drying of digestate and more than doubles (2.4 times) the electricity
60 production when the scenario of digestion and pyrolysis is contemplated.

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61

62 *Keywords:* Butcher's fat waste; Thermal analysis; Kinetics; Energy balance; Heat integration; Process
63 efficiency

64

65 **Introduction**

66 Sewage sludge is the main by-product of wastewater treatment and its volumetric production is expected
67 to increase in future years due to the fast growth of the world population. As such, there is an increasing
68 concern with regards to conventional sludge disposal. Sewage sludge is a biosolid that could be used as a
69 green biofertiliser, should it be processed and improved from an ecological standpoint.

70 However, land application of this material still presents challenges due to its content in organic pollutants
71 that can impact the dynamic equilibrium of biological systems (Mohapatra et al. 2016). When properly
72 processed, sewage sludge can serve as a renewable energy source, due to its high-volume production and
73 energy content, that renders it a suitable material for energy valorisation. It is therefore important to
74 develop cleaner technologies for sludge disposal that allows for a holistic valorisation of waste materials.

75 To date, several thermal technologies, such as pyrolysis, gasification, combustion, and co-combustion
76 processes have been proposed for valorising sewage sludge for obtaining useful forms of energy (Agar et
77 al. 2018; Werle and Sobek 2019).

78

79 Pyrolysis is a thermo-chemical process that occurs in an inert atmosphere. In this process, organic matter
80 undergoes a series of complex reactions generating volatile products and condensed molecules, which
81 finally leads to char formation. Pyrolysis is vastly used in organic mass conversion industries; thus it
82 holds promise for sewage sludge treatment since it can transform it into valuable fuel. The process can be
83 optimised to produce fuels of different nature, such as gases and oils. Moreover, this technique appears to
84 be less contaminant than combustion, since most of the hazardous trace elements are partially retained in
85 the char (Folgueras et al. 2013). The combination of anaerobic digestion followed by thermal valorisation
86 processes could be an alternative for achieving higher energy efficiency to that from a single anaerobic
87 digestion treatment (Dussan and Monaghan 2018); especially when poor quality effluents, with high
88 volatile fatty acids (VFA) content, are obtained from the digestion process. The co-digestion of different
89 wastes has traditionally been used for improving digester performance *via* increased biogas production.

90 However, the addition of a high organic content co-substrate in a digester treating either sewage sludge or
91 manures can lead to a not-fully stabilised organic material causing detrimental effects if land application
92 of these digestates is the final disposal option (Albuquerque et al. 2012; Fierro et al. 2016)

93

94 The kinetic behaviour of the pyrolysis process needs to be better understood when sewage sludge is
95 aimed to be treated by pyrolysis or co-pyrolysis with other materials in existing infrastructures. For this
96 task, thermogravimetric analysis (TGA) has been widely applied to study the behaviour of carbonaceous
97 materials during pyrolysis/combustion treatments (Khiari et al. 2019; Martínez et al. 2016). The pyrolysis
98 process is primarily intended for energy valorisation, but it has the added benefit of biochar production as
99 a valuable carbon product. In recent years, the interest in biochar production and applications has grown
100 significantly with several works published in scientific literature regarding its characterisation, effect of
101 different process parameters on their main relevant qualities and the evaluation of different biomass
102 feedstocks including sewage sludge as well (Li et al. 2019). Other studies have examined the co-pyrolysis
103 process of sewage sludge with different types of wastes such as sawdust, cattle manure, poultry litter
104 among others for producing bio-oils and biochar (Pituello et al. 2015; Zhu et al. 2015).

105

106 Pyrolysis and gasification are technologies that promote the utilisation of biomass for energy harvesting
107 and commercially appeal for use in future energy systems, where modern integrated biorefinery concepts
108 and combinations of different technologies are required to maximise product yield and value (Hassen-
109 Trabelsi et al. 2018). This work aimed to study the feasibility of thermal valorisation of digestate obtained
110 from the co-digestion of sewage sludge with grease waste. In previous work, anaerobic co-digestion of
111 sewage sludge with grease waste discarded from butcheries was performed under both mesophilic and
112 thermophilic conditions in an attempt to increase biogas productivity of the digester. The results from
113 these experiments suggested that the obtained digestates were characterised by the accumulation of fat,
114 indicating incomplete degradation of substrates during the anaerobic treatment (Martínez et al. 2016).

115 This weighting factor made them unsuitable for agronomic valorisation, therefore, other alternatives need
116 to be explored. Hence, this work proposes the use of pyrolysis as a feasible option for recovering energy
117 from these digestates.

118

119 An evaluation of the process was performed to establish the conditions required for meeting the thermal
120 demands of the proposed methodology. In the present work, non-isothermal thermogravimetric analysis
121 was used for calculating the activation energy of digested samples. To this extent, the Ozawa-Flynn-Wall
122 (Ozawa 1965; Flynn and Wall 1966) and the Vyazovkin (Vyazovkin 1997) kinetic methods were used.
123 Energy evaluation was performed considering the co-digestion of fat with sewage sludge and the
124 subsequent pyrolysis of digestates by assessing the energy demand of the processes and the suitability of
125 different fat content proportions in the co-digestion mixture.

126

127 **Experimental**

128 **Materials**

129 The samples of digested sludge used in pyrolysis were obtained from on-site laboratory operating
130 anaerobic digestion reactors. Sludge was obtained from the wastewater treatment plant (WWTP) of
131 Cáceres (Spain). Sewage sludge was composed of a mixture of waste activated sludge and primary
132 sludge. Due to operating constraints associated with the size and capacity of this plant, waste activated
133 sludge had a high recycling ratio. Grease waste (excessive fat content of veal meat) was added as co-
134 substrate, and sourced from a local meat market (León, Spain). The addition of this co-substrate has
135 shown to improve the stability of digestion and biogas yield. The anaerobic digestion of sewage sludge
136 and its blends with fat was carried out using both mesophilic and thermophilic regimens. Mesophilic
137 digestion was evaluated at a temperature of 35 °C and a hydraulic retention time of 40 d. thermophilic
138 reactors operated at a temperature of 55 °C and a retention time of 30 d. Reactors were provided with
139 mechanical stirrers Heidolph RZR 1 at 200 rpm. Detailed explanation of the anaerobic co-digestion
140 process is given elsewhere, where the addition of fat to the sludge mixture was 5% (w/v) (Martínez et al.
141 2016).

142

143 Four different samples were obtained from all tested regimes; thermophilic co-digestion of sewage sludge
144 and grease (TSSG), mesophilic co-digestion of the same mixture (MSSG) and thermophilic digestion of
145 sewage sludge (TSS). A sample was also obtained from the fat aggregates derived from the thermophilic
146 co-digestion system which was denoted as T_{Grease}.

147 Samples were analysed by proximate and ultimate analyses, and the calorific value was also measured.
148 Proximate and ultimate analyses were realised according to the methodology described by López et al.
149 (2013). Higher heating value (HHV) at a constant volume was measured using an adiabatic oxygen bomb
150 calorimeter.

151

152 **Pyrolysis process**

153 Pyrolysis of the digested samples was carried out by thermogravimetric analysis. Digested sludge samples
154 were first oven-dried at 105 °C and later ground in a ball mill. Following that, they were sieved so the
155 particle diameter of materials used for this study was from 0.105 to 0.210 mm. Thermogravimetric
156 analysis was carried out using a TA Instruments equipment, model SDT Q600. Pyrolysis of the samples
157 was performed at atmospheric pressure in the furnace of the thermobalance at a controlled temperature
158 under a nitrogen atmosphere (continuous flow rate of 100 mL min⁻¹). Samples of 5.0 ± 0.1 mg were
159 submitted to dynamic runs up to 1073 K at four different heating rates (β): 5, 10, 20 and 40 K min⁻¹.
160 Duplicate experiments for each test were performed to confirm the reproducibility of the results.

161

162 **Kinetic analysis**

163 A kinetic study was conducted using the rate of conversion, x , as a function of the pyrolysis time, t . The
164 apparent reaction rate is dependent on the temperature, T , and can be expressed using the Arrhenius
165 equation. In the case of dynamic data which are obtained at a constant heating rate, $\beta = dT/dt$, the
166 conversion can be expressed by Eq. (1):

167

$$168 \quad \frac{dx}{dT} = \frac{1}{\beta} A e^{-E/RT} f(x) \quad (1)$$

169

170 where, x is the mass conversion ratio estimated using the ratio between the mass variation at any time t
171 and total mass variation experienced by the sample.

$$172 \quad x = (m_0 - m_t)/(m_0 - m_f) \quad (2)$$

173 where m_0 is the initial mass of the sample, m_t is the mass at time t and m_f is the final mass.

174 $f(x)$, represents the reaction model., A is the pre-exponential factor, E is the activation energy and R is the
175 gas constant. Integrating Eq. (1) gives:

176

$$177 \quad g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT \quad (3)$$

178

179 where $g(x)$ is the integral function of conversion. The experimental approaches for the analysis of solid-
180 state kinetics are either isothermal or non-isothermal. Moreover, regarding the mathematical analysis, two
181 kinds of methods can be used: model-fitting and isoconversional (free model). Isoconversional methods
182 have been used mainly because they can compute kinetic parameters without modelling assumptions.
183 Moreover, thermal decomposition is a particularly complicated process which involves hundreds of
184 complex components and their parallel and/or consecutive reactions, so the isoconversional methods are
185 highly recommended to evaluate apparent activation energy for their reliability and objectiveness (Lin et
186 al. 2016; Otero et al. 2008).

187

188 In the present work, once the temperatures corresponding to fixed values of x for different heating rates
189 were measured, activation energy was calculated by the non-isothermal isoconversional method
190 according to Flynn, Wall and Ozawa (Ozawa 1965; Flynn and Wall 1966) using Doyle's approximation
191 of $p(x)$ (Doyle 1962). This involves measuring the temperatures corresponding to fixed values of
192 conversion from experiments at different heating rates.

$$193 \quad \ln \beta = \ln \left[\frac{AE}{Rg(x)} \right] - 5.331 - 1.052 \frac{E}{RT} \quad (4)$$

194 Thus, the activation energy, E , is estimated by linear regression analysis from the slope of the straight line
195 obtained by plotting $\ln \beta$ vs. $1/T$. Likewise, the Vyazovkin isoconversional kinetic method was also used
196 (Vyazovkin 1997). According to this method, from Eq. (1), and since $E/2RT \gg 1$, the temperature integral
197 can be approximated by:

$$198 \quad \int_{T_0}^T e^{-E/RT} dT \approx \frac{R}{E} T^2 e^{-E/RT} \quad (5)$$

199 Substituting the temperature integral and taking the logarithm, Eq. (5) is obtained:

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{RA}{Eg(x)} \right] - \frac{E}{R} \frac{1}{T} \quad (6)$$

For each x value, a data set is obtained representing a straight line when $\ln\beta/T^2$ plotted vs. $1/T$. Applying linear regression analysis the value of the slope thus obtained represents $-E/R$ and therefore, the activation energy may be estimated.

In order to determine the reaction order, Avrami's theory was extended to describe non-isothermal cases, where variation of the degree of conversion with temperature and heating rate can be described as:

$$x(T) = 1 - \exp\left(\frac{-k(T)}{\beta^n}\right) \quad (7)$$

Taking the double logarithm of both sides of Eq. (8), with $k(T)=Ae^{-E/RT}$, gives:

$$\ln[-\ln(1-x(T))] = \ln A - \frac{E}{RT} - n \ln \beta \quad (8)$$

Hence, a plot of $\ln[-\ln(1-x(T))]$ vs. $\ln\beta$, which is obtained at the same temperature from a number of isotherms taken at different heating rates, should yield straight lines whose slope will have the value of the reaction order or the Flynn-Wall-Ozawa exponent n (Flynn and Wall 1966; Ozawa 1965).

212

213 **Energy evaluation of the thermal valorisation of digestates**

The evaluation of the energy produced was carried out assuming an integral approach of anaerobic digestion of sludge and fat as co-substrate followed by the thermal valorisation of digestates. The assumptions were based on an average WWTP for 100,000 equivalent inhabitants (Eq. Inh.). The water line of the base scenario was composed of a conventional waste activated system and an air flotation unit for concentrating the secondary sludge. The sludge line consisted of the primary settler and the gravity thickener. The primary sludge was assumed to be concentrated and subsequently mixed with secondary sludge from the air flotation units. The anaerobic digester treating this mixture was assumed to be operating at a hydraulic retention time (HRT) of 25 d. The energy evaluation was performed assuming different ratios of fat addition as co-substrate. The volumetric sludge flow was considered as constant and different scenarios were evaluated increasing fat content from 3 to 15% (w/v) in the mixture. The volumetric production of biogas B (expressed in $\text{m}^3 \text{h}^{-1}$) was calculated using Eq. 3

225

$$B = \frac{F_{sludge} * [VS]_{sludge} * SMP}{\%CH_4} \quad (9)$$

227

228 where F_{sludge} is the volumetric flow of sludge ($m^3 h^{-1}$), $[VS]_{sludge}$ is the content of volatile solids in the
 229 sludge mixture (considering primary and secondary sludge), SMP is the specific methane production of
 230 the sludge and $\%CH_4$ is the methane content in biogas which was assumed as 60%.

231

232 Thermal energy needs for the digester were taken into account for an average temperature of the influent
 233 sludge of 15 ± 1 °C. It was assumed that the amount of inorganic solids was not affected during digestion
 234 and biogas produced was derived from the conversion of volatile solids. Heating needs of the digester
 235 were calculated based on

$$Th_{dig} = m * c_p * (T_{dig} - T_{slurry}) \quad (10)$$

237 where Th_{dig} is the thermal energy needed for increasing the slurry temperature from a value of 15 (T_{slurry})
 238 to 37 °C (temperature of the mesophilic digester, T_{dig}). The mass of the slurry to be heated is m , and for
 239 simplicity the heat capacity was assumed to be that of water (c_p , $4.2176 \text{ kJ (kg K)}^{-1}$). To account for
 240 thermal losses, this value was increased by 8%.

241 The valorisation of biogas was assumed to be performed by a combined heat and power (CHP) unit. The
 242 theoretical calculation of the energy demand for drying the digested sludge was estimated by assuming
 243 dehydration at 25% solid content (Neyens et al. 2004) and drying until a value of 90% was achieved.
 244 Energy demand for sludge drying was calculated considering a thermal efficiency of 75% and the heat of
 245 vaporisation of water was $2345.4 \text{ kJ kg}^{-1}$ at 65 °C. This stage was considered as part of the conventional
 246 WWTP scenario since a drying unit is frequently available for reducing transportation costs associated
 247 with the final disposal of sludge.

248 The integration of a pyrolysis unit for the conversion of digestates into bio-oil and pyrolysis gases was
 249 evaluated taking into account the energy produced from the valorisation of biogas obtained from the
 250 digester, as well as that produced from pyrolysis gases and bio-oil obtained from the pyrolysis unit. There
 251 exist several reports in literature regarding pyrolysis performance of sewage sludge. Table 1 reports on

252 different studies where yields of pyrolysis products are indicated for pyrolysis processes taking place at
253 temperatures between 400 – 650 °C

254

255 Table 1

256

257 In the present study the pyrolysis process was assumed to yield 34.2% of char, 55.7% of bio-oil and
258 10.1% of pyrolysis gas based on average values reported by Monlau et al. (2015) and Titiladunayo et al.
259 (2012). It was also considered that the water content of bio-oils was 52%, which reduces the bio-oil yield
260 to a value of 37.6%. This assumption was based on characteristics reported by Abnisa et al. (2013) and
261 Mullen and Boateng (2011) regarding the expected amount of water in pyrolysis bio-oils. The high
262 heating value of pyrolysis bio-oil was assumed to be 32.1 ± 4 MJ/kg for bio-oil free of the aqueous phase.
263 Energy requirements for maintaining thermal demands of the pyrolysis process were assumed as 1.8
264 MJ/kg feed (Salman et al. 2017).

265 The presence of lipidic residue in solid digestates was assumed to affect the yields of pyrolysis products.
266 Ito et al. (2012) reported on the production of pyrolysis oils from animal fats, indicating a greater yield in
267 bio-oils with low water content. Similar results were reported by Wiggers and co-workers (2009) when
268 evaluating the pyrolysis of waste fish oil. The latter yielded 72.8% of bio-oil, and 15.8 and 11.3% of gas
269 and coke fractions using these values estimating energy production. These oils were characterised by
270 having greater HHV. In this line, a conservative value of 38 ± 1.4 MJ kg⁻¹ was set as an average of those
271 reported by different authors when studying pyrolysis products derived from animal fats and waste frying
272 oils (Adebanjo e al. 2005; Kraiem et al. 2017; Trabelsi et al. 2018). Based on these assumptions the
273 energy contained in gas and oil pyrolysis products is shown in Fig. 3c.

274

275 **Results and discussion**

276 **Characterisation of samples**

277 Results from proximate and ultimate analyses, as well as the calorific values, of sludge and digested
278 samples are shown in Table 2. Sludge sample shows high volatile matter content and relatively high ash
279 content. However these valued are within the range of those reported for other authors for similar samples
280 (Grigante et al. 2010; Zuo et al. 2014). As it can be seen, the TSS sample (derived from thermophilic

281 digestion) displayed the highest ash content. This value highlights the capacity of mesophilic systems for
282 achieving higher mineralisation of the organic content compared to the other samples obtained from
283 digesters operating under thermophilic regime, explaining thus the lower values obtained for the ash
284 content from thermophilic digesters treating the mixture of fat and sludge. Besides, it was observed that
285 the thermophilic digester formed aggregates which were separately and analysed, hence the denomination
286 T_{Grease} sample as mentioned above.

287

288 The thermophilic digested solids exhibited (samples TSSG and T_{Grease}) higher volatile matter values (69.2
289 and 76.0 wt.%, respectively), whereas the volatile content in MSSG and TSS were 54.4 and 51.1 wt.%,
290 respectively. The lower values of these two samples were associated with an improved performance of
291 the mesophilic reactor in the first case. However, in the latter case the low valued reported for the
292 thermophilic reactor was associated with the low organic load added to this digestion system, since this
293 thermophilic reactor was not supplied with co-substrate. Because of the different performance of
294 digestion systems, that is grease accumulation was observed during the thermophilic of the sludge and fat
295 mixtures but not in the mesophilic ones, samples TSSG and T_{Grease} also exhibited the highest carbon
296 content (47.4 and 51.3 wt.%, respectively), as well as the highest HHV value (22.7 and 24.6 MJ kg⁻¹,
297 respectively). Furthermore, both samples showed higher H and lower N contents than the MSSG and TSS
298 samples, which was again associated with the grease accumulation phenomenon.

299

300 Table 2

301

302 **Pyrolysis process**

303 The thermogravimetric data (TG curves) for pyrolysis obtained at heating rates of 5, 10, 20 and 40 K min⁻¹
304 for the studied samples are presented in Fig. 1. The thermal behaviour of these samples aligns with the
305 performance of the different digestion processes. The accumulation of fatty material found in TSSG
306 sample becomes evident through the faster mass loss rate (Fig. 1a) observed in the graph, compared to the
307 profile from the MSSG and TSS samples (Fig. 1b and Fig. 1c respectively). Additionally, the fatty
308 agglomerate separated from the thermophilic liquor of the digester treating the mixture of fat and sludge

309 (i.e., sample T_{Grease}) showed the highest loss in mass, (Fig. 1d) indicating the great lability of their organic
310 components, which was on par with its high volatile content and low ash content reported in Table 2.

311

312 Figure 1

313

314 It was observed that for all samples the increase of the applied heating rate caused a shift towards higher
315 temperature for the initiation of mass loss, which started at slightly higher temperatures. This happens
316 because the heat transfer among particles experiences a delay due to the increase in the heating rate, as
317 also reported by Xu et al. (2018). On the other hand, higher temperatures were needed for pyrolysis to
318 start in the case of the MSSG and TSS samples (around 525 K) possibly related to the higher
319 mineralisation obtained from the digestion of these substrates. When compared with the performance of
320 samples TSSG and T_{Grease}, both presented lower temperatures for pyrolysis (taking place around 475 K)
321 which can be attributed to poor microbial degradation and interpreted as an underperforming digester.

322

323 The first derivative of the thermogravimetric data (DTG curves) obtained from the temperature
324 programmed pyrolysis using a heating rate of 20 K min⁻¹ are shown in Fig. 2. Two differentiated zones or
325 pyrolysis stages can be observed. The first one in the temperature range of 473-673 K, corresponding to
326 the decomposition of easily-degradable and volatile compounds. The second one in the temperature range
327 of 673-800 K, usually related to the decomposition of more complex and higher molecular weight
328 materials, mainly matter of bacterial origin (Folgueras et al. 2013). It is noteworthy that during the first
329 stage, the DTG curves for the TSSG and T_{Grease} samples showed two different peaks: between 473 and
330 573 K for the first one, and between 573 and 673 K for the second one.

331

332 Lipids have been reported to be highly reactive in the temperature range of 423-513 K by Lin et al.
333 (2016), linking their degradation to mass loss occurring during pyrolysis at these temperatures. Between
334 513 and 673 K, the loss in mass experienced in this temperature range has been associated by these
335 authors with the degradation of cellulose, whilst between 673 and 857 K was ascribed to proteins
336 decomposing reactions. Accordingly, the first peak (473-573 K) observed in the present work for samples
337 TSSG and T_{Grease} was due to higher amount of non-degraded grease present in those samples. This high

338 organic content of the digested material may cause rampant degradation problems should their
339 valorisation in terms of land application be attempted. This is supported by the fact that digestates rich in
340 readily degradable material could cause a high release of CO₂ and N-immobilisation and/or denitrification
341 after their application to soil (Albuquerque et al. 2012b).

342

343 Regarding the DTG curves corresponding to the second stage (673-800 K) for the TSSG and T_{Grease}
344 samples, the peak intensities in this range were much higher than those of the other samples (Fig. 2). This
345 may be indicative of condensation reactions of long chain hydrocarbon molecules which were
346 subsequently degraded at higher temperatures. Thus, thermophilic digestion was attained, but
347 agglomeration of the fatty material combined with the poor performance of the digestion system at this
348 temperature prevented the complete conversion of the supplied organic load in the reactor.

349

350 Figure 2

351

352 **Kinetic analysis**

353 Several percentages of mass loss along the pyrolysis process have been marked in Fig. 1. These lines
354 cross the curves corresponding to each heating rate. As mentioned above, based on these points activation
355 energy, E , can be calculated using the Ozawa-Flynn-Wall and the Vyazovkin kinetic methods. The slopes
356 derived from the linear fittings and the corresponding correlation coefficients (R^2) are shown in Table 3.
357 As it can be seen, correlation coefficients for the Ozawa-Flynn-Wall method are slightly higher than those
358 obtained from the Vyazovkin method. Most of the correlation coefficients were greater than 0.96,
359 showing a good accuracy of results.

360

361 Table 3

362

363 The activation energy of all the samples increased with the conversion value selected as shown in Table
364 3. This table also shows the average values of E estimated for the pyrolysis of the four studied samples.
365 The Ozawa-Flynn-Wall method gave slightly higher E values compared to the Vyazovkin method,
366 although the differences between both values were negligible. Sample TSSG showed the highest

367 activation energy (190 kJ mol^{-1}), followed by sample TSS (172 kJ mol^{-1}) and sample MSSG (164 kJ mol^{-1})
368 ¹) whereas T_{Grease} sample (92 kJ mol^{-1}) presented the lowest value. These results indicated that samples
369 derived from thermophilic digestion showed higher values of activation energy than those from
370 mesophilic systems, even though the thermophilic digester was underperforming because of grease
371 accumulation. Besides, the evaluation of the fatty aggregate reported a value for the activation energy
372 significantly lower than the other samples containing sewage sludge. The E values obtained from these
373 samples were in the same range of those previously reported for thermal kinetic analysis of anaerobically
374 digested sludge (Folgueras et al. 2013; Sánchez et al. 2009). In the case of the fatty aggregate, this low
375 value of the activation energy signifies the reactive nature of the lipid material in the aggregate.

376

377 The values of reaction order (n) as a function of temperature for the different samples are shown in
378 Table 4. There is a similar variance in temperature for all the samples, with a maximum value at 573 K,
379 indicating a dependence on the extent of the reaction, i.e., they are not constant during the reaction, which
380 is evidence of a multiple-step process (Otero et al. 2008). The average values of n ranged from close to
381 zero (pseudo-zero-order reaction) for TSSG, TSS and MSSG, with maximum of 0.28 for the T_{Grease}
382 sample. The values obtained for the reaction order were in the same range with the ones reported in
383 literature (Sánchez et al. 2009).

384

385 Table 4

386

387 **Energy evaluation**

388 Based on the results derived from the kinetic evaluation and thermal degradation analysis, it can be
389 proposed that digestates obtained from sources whereby fat is used as co-substrate may be considered
390 insufficiently stabilised, because of the low mineralisation and the accumulation of fatty material in the
391 digested solids. The recovery of energy using a pyrolysis unit was proposed as alternative to their land
392 application. In terms of real-world scale, a feasibility scenario consisting of a conventional WWTP and
393 the potential of analysis using a pyrolysis unit that is integrated into the WWTP are further evaluated.

394

395 The main characteristics of the base scenario are shown in Table 5. It was assumed a specific methane
396 production (SMP) of $240 \pm 24 \text{ mL CH}_4 \text{ g}^{-1} \text{ VS}$ for the mixture of primary and secondary sludge based on
397 data reported by Martínez et al. (2016) under batch mesophilic conditions, taking into consideration a
398 20% reduction in methane production due to the extrapolation of data to continuous operation. The
399 production of sludge was estimated based on the operating conditions described by García-Cascallana et
400 al. (2019). The energy content in biogas was calculated considering a low heating value (LHV) for
401 methane of 35.8 MJ m^{-3} . The valorisation of biogas was assumed to be performed by the use of a CHP
402 unit with an electrical efficiency of 40% and a thermal efficiency of 48% (Dressler et al. 2012). Under
403 these assumptions the available heat recovered from the CHP unit was 1015 MJ h^{-1} capable of meeting
404 thermal digester needs but insufficient to cover the thermal drying of sludge to 10% water content.

405

406 The introduction of a fatty co-substrate allows for a significant improvement in biogas yields. The value
407 reported by Martínez et al. (2016) was on average close to $400 \text{ mL CH}_4 \text{ g}^{-1} \text{ VS}$ based on the addition of
408 fat as a co-substrate at 5% (w/v) in the mixture. The evaluation of digestates reported in previous sections
409 demonstrated the accumulation of fatty aggregates of high energy content that refrained the reactor from
410 reaching a steady state. In the present study this value was estimated taking into account the Buswell
411 equation for fat and considering that 20% of this material was not degraded by the microbial microflora.
412 This led to the estimation that SMP is $302 \text{ mL CH}_4 \text{ g}^{-1} \text{ VS}$. Even though this value represents a significant
413 increase in the recovery of heat and the production of electricity, there is still a need of an added fuel for
414 covering the high heat demand in the conventional process of sludge drying, which is usually natural gas
415 externally supplied.

416

417 Table 5

418

419 The integration of a pyrolysis unit into a conventional WWTP would allow for recovering extra energy
420 needed in this process. There are different approaches for reducing the volume of sludge but they may
421 also increase the electrical and heat demand in a conventional WWTPs. Many industrial applications
422 require an extra demand of energy when introducing a pre-treatment stage for sludge, as it would be the
423 case of thermal pre-treatments for reducing sludge volume and increasing biogas yield (García-Cascallana

424 et al. 2019). On the other hand, new alternatives as it is the introduction of bioelectrochemical systems
425 allow for a decrease in the electricity demand but also decrease the biogas obtained because of the lower
426 generation of microbial sludge to be treated in an anaerobic digester, thus resulting in a negative energy
427 balance (Martínez et al. 2019).

428

429 This study showcases the possibility of introducing a pyrolysis unit for producing fuels thermally
430 valorised for optimising heat generation during the sludge drying process. This hypothesis aims to
431 address the reduction of the overall disposal of sludge, whilst converting dried sludge into a stable organic
432 product commercially meaningful to the energy market. Based on the projected yields from the pyrolysis
433 unit, the recovery of thermal energy from this process accounts for 1611 MJ h⁻¹. This value stands for
434 sewage sludge being served as the sole substrate for the anaerobic digester and pyrolysis gas with oil
435 being used for producing heat in a conventional burner operating at an efficiency of 90%. However,
436 should the thermal demand of this unit be considered, the recovery of energy is reduced by 25.7% (1197
437 MJ h⁻¹). The total amount of heat that can be recuperated, including both digestion and pyrolysis
438 processes, sum up to 2212 MJ h⁻¹. Ergo, this fails to satisfy both the thermal needs of the digester (614 MJ
439 h⁻¹) and for the sludge drying process (2858 MJ h⁻¹).

440

441 The addition of fat as co-substrate has a dual advantage as it increases the SMP of the feeding mixture
442 and enhances heat recovery from the pyrolysis unit. It was assumed that this fatty material was partially
443 converted into biogas due to constraints associated with the hydraulic dynamic of the digester, by which
444 20% of the feeding co-substrate ends up accumulating in the solid fraction of the digestate. Fig. 3a depicts
445 the SMP expected values as increasing amounts of fat are added as co-substrate in the feeding mixture.
446 The increase in SMP is linearly correlated to the increase in the content of fat resulting in higher biogas
447 production and as a consequence in the amount of electricity by the CHP unit (Fig. 3b).

448

449 The addition of co-substrate seemed to have little influence on the total amount of sludge derived from
450 the digester since most of this material is converted into biogas, and its accumulation in the digester
451 liquor can be neglected based on the total volume of biosolids generated from the digestion of sludge.
452 Therefore, the amount of heat needed for drying the sludge down to 10% moisture content was not

453 significantly affected by the addition of fat. Nevertheless, its composition was considered to be
454 characterised by a higher lipid content that maintained a linear correlation with the initial amount added
455 to the digestion process.

456

457 The presence of a co-substrate affects the characteristics of the organic matter contained in the digested
458 solids. When high organic content co-substrates are added to conventional digesters, sludge stabilisation
459 may be deteriorated, which eventually has a negative impact on its agronomic quality. The increase in
460 biogas compensates for the lower quality of organic matter deriving from the digestion process as
461 reported by Fierro et al. (2016) and González et al. (2019). It is therefore reasonable to suggest that the
462 valorisation of this type of material will be best to pursue the thermal payoff aspect rather than land
463 application of digestates.

464

465 The presence of lipidic residue in solid digestates was assumed to affect the performance of pyrolysis.
466 Based on these assumptions the energy contained in gas and oil pyrolysis products is shown in Fig. 3c.
467 The increase in energy due to pyrolysis products is different in comparison to the increase in electricity
468 from biogas. Adding just 3% (w/v) of fat to the feeding substrate results in a 25% increase in the
469 electricity obtained from biogas, but pyrolysis products only report 6% increase in the energy contained.
470 This was due to the small amount of fatty material remaining in the digested solids, thus the scenario
471 containing the higher values of fat addition (15% fat) reports an increase of 34% with respect to the
472 scenario of sludge pyrolysis, whereas the electricity production doubles (2.4 times).

473

474 Figure 3

475

476 The recovery of thermal energy from biogas valorisation (in CHP unit) and pyrolysis products (gas and
477 oil in a conventional burner) was also estimated for different contents of fat in the feeding mixture to the
478 digester. Fig. 4 depicts the thermal energy necessary for performing the drying of sludge from 75% to
479 10% humidity. This heat demand is maintained almost constant for the different percentages of fat added
480 to the sludge, because the increasing content of this material to the mixture fed into the anaerobic
481 digestion process results in a small increase of solids in the digested sludge. Therefore, small modification

482 in the concentration of solids does not significantly affect the total amount of water to be removed by
483 thermal drying. The sum of heat recovered from the CHP unit (with this value having an increasing trend
484 with the increase in fat addition) and from combustion of pyrolysis fractions (gas and oil) can address the
485 demands in thermal energy only for the two last evaluated scenario (12 and 15% fat content).

486

487 Figure 4

488

489 **Conclusions**

490 Non-isothermal isoconversional methods by Ozawa-Flynn-Wall and Vyazovkin were used for estimating
491 the activation energy for the pyrolysis process of digested sewage sludge and butcher's fats from
492 thermogravimetric analysis. Arrhenius activation energy was lower for the digested grease sample ($E \sim 92$
493 kJ mol^{-1}) than it was for sewage sludge and its blends with fat ($E \sim 164\text{-}190 \text{ kJ mol}^{-1}$). The thermal analysis
494 of digested samples demonstrated the suitability of valorising high organic content digestates. Thermophilic
495 samples showed accumulation of organic material and poor stabilisation thus indicating that direct
496 agronomic valorisation should be averted. The valorisation by means of a pyrolysis unit integrated in a
497 conventional wastewater treatment plant (WWTP) may be a feasible option covering completely the
498 thermal needs for sludge drying when the content in fat co-substrate is greater than 12% (w/v) in the feeding
499 mixture of the anaerobic digester.

500

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508

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510

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679 **Figure caption**

680 **Fig. 1** TG curves at different heating rates obtained during pyrolysis of samples **a** TSSG **b** MSSG **c** TSS

681 and **d** T_{Grease}

682 **Fig. 2** DTG curve for the pyrolysis of the studied samples at a heating rate (β) of 20 K min^{-1}

683 **Fig. 3** Schematic description of the integrated approach for digestion and pyrolysis of sludge and fat. **a**

684 Specific methane production of sludge as a function of the percentage ($w \text{ v}^{-1}$) of fat added **b** Electricity

685 production and **c** Energy contained in gas and oil derived from pyrolysis of digestate

686 **Fig. 4** Heat demand associated with thermal drying of digested sludge and heat recovery from biogas

687 valorisation by means of CHP and combustion of pyrolysis products (gas and oil)

688

689

690

Fig. 1

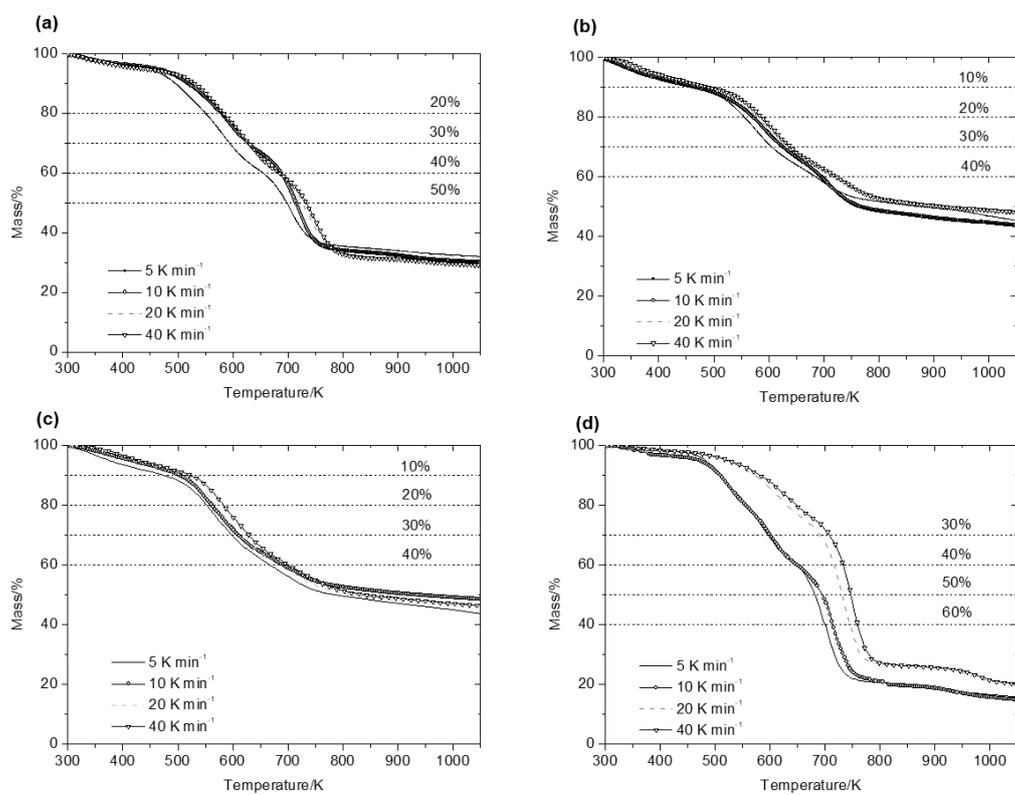


Fig. 2

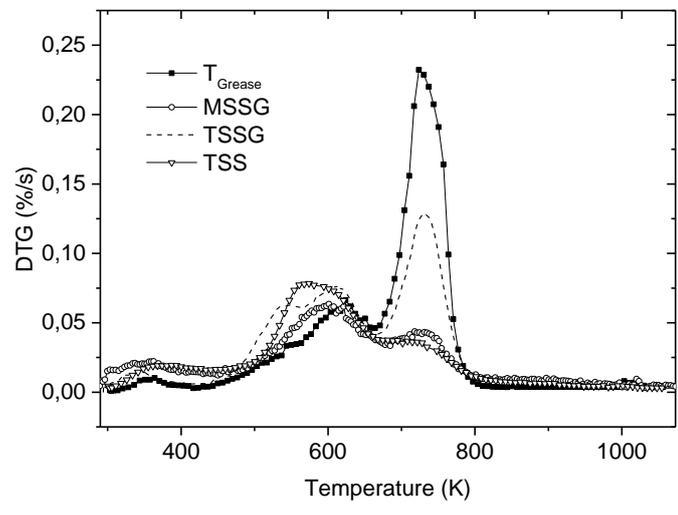


Figure 3

Fig 3

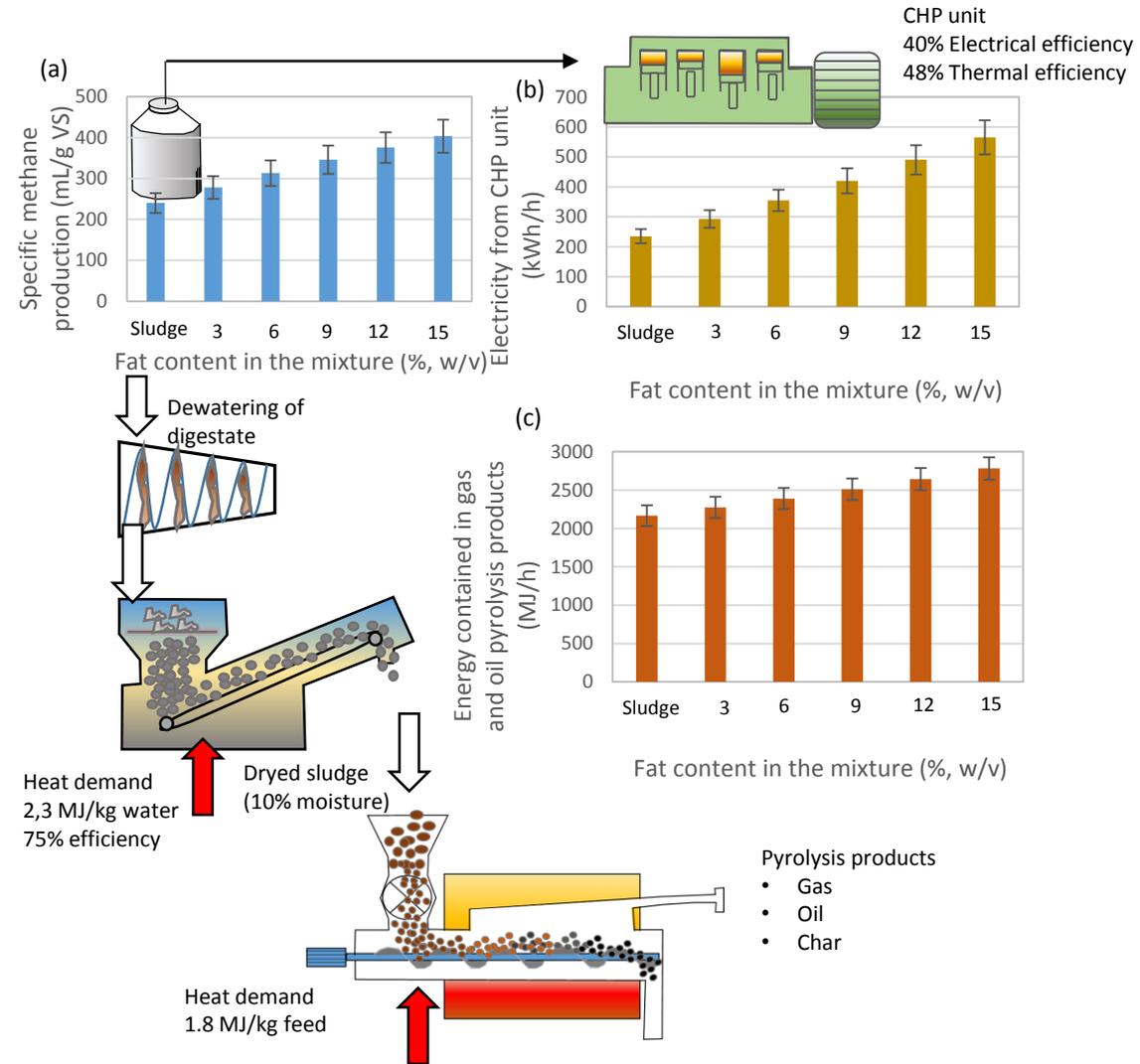


Fig. 4

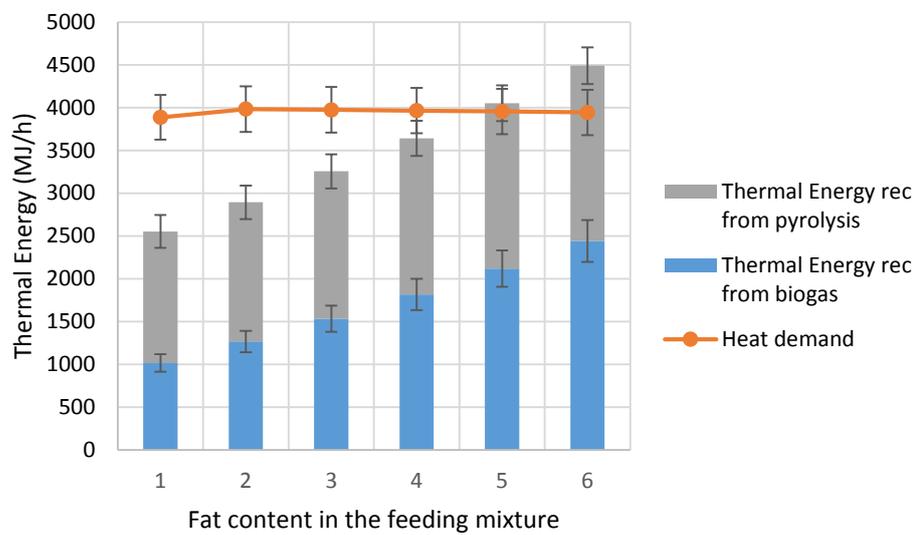


Table 1 Yields of pyrolysis products reported in literature for sewage sludge and digested sludge

Bio-oil (%)	HHV (MJ kg ⁻¹)	Gas (%)	HHV (MJ m ⁻³)	Reference
24 - 36	30.6 – 32.1	22 – 35	8.1 – 11.4	Fonts et al. 2009
37 - 50	35 – 30	10.8 – 23.5	N.A.	Tian et al. 2011
25 - 32	N.A.	19 - 29	18 – 21	Agar et al. 2018
28.6	36.2	11.3	N.A.	Viana et al. 2016
23.2*	42	21.4	10.5	Pánek et al. 2014
30 – 40**	22 - 28	N.A.	12 - 13	Inguanzo et al. 2002
27 - 44	14 – 38.4	N.A.	N.A.	Leng et al. 2015

* Data calculated without the water fraction, **Bio-oil content in aqueous fraction, N.A.: not available

Table 2 Proximate and ultimate analyses, and calorific values for sludge and digested sludge samples

Sample	Moisture (%)	Volatile (%) ^a	Ash (%) ^a	C (%) ^b	H (%) ^b	N (%) ^b	S (%) ^b	HHV (MJ kg ⁻¹)
Sludge	4.8	59.2	35.4	32.9	4.74	4.47	0.9	16.2
TSSG	3.7	69.2	26.5	47.4	7.0	2.5	0.7	22.7
MSSG	5.8	54.4	36.7	32.7	4.6	4.2	1.0	14.0
TSS	6.0	51.1	41.6	30.1	4.4	4.1	1.1	13.2
T _{Grease}	4.3	76.0	22.2	51.3	7.7	1.3	0.3	24.6

^a Dry basis; ^b Dry ash free basis

TSSG: Thermophilic co-digestion of sewage sludge and grease waste; MSSG: Mesophilic co-digestion of sewage sludge and grease waste; TSS: Thermophilic digestion of sewage sludge; T_{Grease}: Fatty aggregate from thermophilic co-digestion of sewage sludge and grease waste

Table 3 Slopes, correlation coefficients (R^2) and values of activation energy, E , obtained by the Ozawa-Flynn-Wall and Vyazovkin kinetic methods for the studied samples

Sample	Mass loss (%)	Ozawa-Flynn-Wall			Vyazovkin		
		Slope	R^2	E (kJ mol ⁻¹)	Slope	R^2	E (kJ mol ⁻¹)
TSSG	20	-8.56	0.9759	155.8	-18.59	0.9731	154.5
	30	-8.84	0.9668	160.8	-19.13	0.9628	159.1
	40	-11.98	0.9614	218.0	-26.25	0.9567	218.2
	50	-12.43	0.9655	226.2	-31.14	0.9621	226.1
<i>Average E^a</i>		<i>190.2 ± 37.0</i>			<i>189.5 ± 37.9</i>		
MSSG	10	-7.25	0.9762	132.0	-15.72	0.9731	130.7
	20	-8.72	0.9837	158.7	-18.94	0.9818	157.5
	30	-9.02	0.9842	164.2	-19.54	0.9823	162.5
	40	-10.99	0.9871	199.9	-23.89	0.9854	198.7
<i>Average E^a</i>		<i>163.7 ± 27.9</i>			<i>162.3 ± 28.0</i>		
TSS	10	-4.94	0.9855	89.9	-10.38	0.9830	86.3
	20	-9.47	0.9706	172.4	-20.68	0.9673	171.9
	30	-10.94	0.9756	199.1	-23.97	0.9731	199.3
	40	-12.50	0.9859	227.4	-27.41	0.9845	227.9
<i>Average E^a</i>		<i>172.2 ± 59.3</i>			<i>171.4 ± 61.1</i>		
T _{Grease}	30	-2.56	0.8863	47.2	-4.68	0.8274	38.9
	40	-3.84	0.8743	69.8	-7.46	0.8326	62.0
	50	-6.30	0.9699	114.6	-13.08	0.9632	108.7
	60	-7.57	0.9773	137.8	-15.98	0.9731	132.8
<i>Average E^a</i>		<i>92.3 ± 41.3</i>			<i>85.6 ± 42.8</i>		

^a Average E was calculated as the arithmetic average of the E values obtained for the different conversion values considered

Table 4 Reaction order, n , as a function of temperature obtained by the Ozawa-Flynn-Wall kinetic method

Temperature (K)	TSSG		MSSG		TSS		T _{Grease}	
	n	R ²	n	R ²	n	R ²	n	R ²
473	0.11	0.977	0.07	0.989	0.16	0.923	0.34	0.938
573	0.20	0.960	0.14	0.947	0.18	0.968	0.56	0.861
673	0.11	0.977	0.08	0.947	0.06	0.941	0.46	0.897
773	0.05	0.968	0.04	0.977	0.03	0.924	0.16	0.939
<i>Average n</i>	<i>0.12±0.06</i>		<i>0.08±0.04</i>		<i>0.11±0.07</i>		<i>0.28±0.17</i>	

Table 5 Main characteristics of the evaluated scenario considering a conventional WWTP

Parameter	Value	Unit
WWTP capacity	100 000	Eq. Inh
Wastewater quantity	350	L (Eq. inh. d) ⁻¹
<i>Characteristics of conventional WWTP (base scenario)</i>		
Energy demand [30]	1.1	kWh m ⁻³
Sludge flow	6.1	m ³ h ⁻¹
Digester working volume	3600	m ³
HRT	25	d
Biogas production	93	m ³ h ⁻¹
Energy contained in biogas produced per hour	2114	MJ
Digester thermal needs	614	MJ h ⁻¹
Electrical energy hourly produced	235	kWh
Heat recovery	1015	MJ h ⁻¹
Digested sludge flow at 25% TS	0.827	m ³ h ⁻¹
Thermal drying of sludge	3063	MJ h ⁻¹
<i>Biogas improvement thanks to the addition of co-substrate (5% fat in the mixture. (w/v))</i>		
Biogas production	134	m ³ h ⁻¹
Electrical energy hourly produced	334	kWh
Heat recovery	1440	MJ h ⁻¹
Thermal drying of sludge	2858	MJ h ⁻¹