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# Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment

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## Abstract

In recent years, sewage sludge management has been considered one of the biggest concerns in the wastewater industry for the environmental impacts linked to its high content of pollutants. Hydrothermal Treatments are a good option for converting wet biomass such as sewage sludge into high-value products. The digestate following anaerobic treatment of sewage sludge has high organic matter content despite initial conversion into biogas and is normally spread on land or composted; however, this does not fully harness its full potential. In fact, the digestate is a potential feedstock for hydrothermal processing and this route may produce higher value products. In this study, the potential of hydrothermal processing as a novel alternative to treat the digestate has been evaluated. The effect of temperatures is evaluated with respect to product yields, biomethane potential and solubilisation of organic carbon. Three different temperatures were evaluated: 160, 220 and 250°C at 30 minutes reaction time. The hydrochar yields obtained were 73.42% at 220°C, 68.79% at 250 °C and 56.75% at 160°C treatment. The solubilisation of carbon was increased from 4.62% in the raw feedstock to 31.68%, 32.56% and 30.48% after thermal treatments at 160, 220 and 250°C, respectively. The thermal treatment enhanced the potential methane production in all products up to 58% for both, the whole fraction (hydrochar + processed water) and processed waters. The Boyle's and Buswell's equation were used to calculate theoretical methane yields for all hydrothermal products. Theoretical methane yields were compared with experimental data from biomethane potential (BMP) tests and it was found that the Boyle's equation had closer agreement to BMP values.

**Keywords:** Digestate, Hydrochar, Hydrothermal process, Sewage sludge, Process waters.

## 39 1. Introduction

40 Over the past decade, sludge management at Waste Water Treatment Works  
41 (WWTWs) has been considered one of the biggest concerns for water companies  
42 and environment protection agencies. In the UK, over 16 billion litres of waste water  
43 per day are collected and treated in 9,000 WWTWs before they are discharged to  
44 inland waters, estuaries or the sea. As a result of that, around 1.4 million tonnes (dry  
45 weight) of sewage sludge are produced annually in the UK (DEFRA, 2012).

46 Sewage sludge can be used for the production of bioenergy due to its large organic  
47 matter content; in fact, nearly one half of the organic matter in sewage sludge is  
48 susceptible to anaerobic biodegradation, resulting in the formation of biogas (Kim et  
49 al., 2014, Hindle, 2013). In the UK for instance, the anaerobic digestion (AD) process  
50 has become the most common alternative for SS treatment with the added benefit of  
51 energy generation from methane, which has helped to reduce the net energy  
52 consumption from the national grid for sewage treatment. Despite the progress  
53 made with regard to the development and implementation of pre-treatment  
54 processes aimed at increasing the anaerobic biodegradability of sewage sludge  
55 (mainly for secondary sludge), the resulting digested sludge (digestate) still contains  
56 large amounts of non-biodegradable organic matter that can be harnessed for  
57 additional energy production, which makes it an interesting feedstock for  
58 thermochemical conversion (Mumme et al., 2015, Kim et al., 2014). Current  
59 practices for digestate disposal in the UK and across Europe include agricultural  
60 application, but upcoming changes in EU legislation would make digestate no longer  
61 suitable for this practice (Dichtl et al. (2007)). As a consequence, WWTWs will have  
62 to face the very difficult task of finding alternatives to current sewage sludge  
63 treatment and final disposal routes.

64 Hydrothermal treatments (HT) are considered an alternative technology to harness  
65 energy from SS in the presence of water and avoid the energy-intensive drying step  
66 required for other thermal processes (He *et al.*, 2013). The main aim of the  
67 hydrothermal processing routes is energy densification via hydrochar production,  
68 which is produced largely by the removal of oxygen. After HT, the resulting  
69 hydrochars show moderate calorific value and are biologically inert, so they can be  
70 co-fired with coal or safely disposed in agricultural land as soil amendment  
71 (Bargmann et al., 2014, He et al., 2013, Biller and Ross, 2012). Hydrothermal

72 processing also generates a by-product or “process water” rich in organic  
73 compounds that cannot be directly disposed into the environment, but has been  
74 proved to be suitable for methane production via anaerobic digestion (Almeida,  
75 2010, Becker et al., 2014, Kim et al., 2014, Stemann et al., 2013, Wirth et al., 2015,  
76 Zhao et al., 2014).

77 The integration of a hydrothermal treatment step into waste water systems has been  
78 suggested to be energy positive (Mumme et al., 2015, Sridhar Pilli et al., 2015). In  
79 fact, commercial high-temperature processes like CAMBI® and BIOTHELYS® have  
80 been successfully developed as pre-treatment steps for hydrothermal hydrolysis of  
81 SS, which has resulted in improving methane production to up to 43%, when  
82 compared with conventional AD processes without pre-treatment (Sridhar Pilli *et al.*,  
83 2015). Hydrothermal treatment as a post-treatment step after AD are still under  
84 research and development, but preliminary findings have shown that this approach  
85 could be even more effective with regard to overall biogas production from sewage  
86 sludge – i.e., thermal hydrolysis can help to produce as much as 36% more biogas  
87 when placed as a post-treatment step than when used as a pre-treatment step for  
88 AD (Shana et al. (2011). Therefore, further research on process conditions and  
89 overall benefits from hydrothermal processes as a post-treatment step after AD is  
90 still needed.

91 A range of different solid wastes have been studied for hydrothermal processing,  
92 including microalgae and manures (Ekpo *et al.*, 2015), municipal solid wastes (Berge  
93 *et al.*, 2011), sewage sludge (Danso-Boateng *et al.*, 2015), digestate (Kim *et al.*,  
94 2014), and wood chips (Stemann et al., 2013). Most of the studies regarding  
95 hydrothermal treatment of sewage digestate have focused either on the  
96 characterisation of the resulting products (Berge et al., 2011, Danso-Boateng et al.,  
97 2015, Escala et al., 2013, Kim et al., 2014, Nipattummakul et al., 2010) or on the  
98 anaerobic digestion of the liquid products following hydrothermal treatment (Wirth et  
99 al., 2015, Hübner and Mumme, 2015, Wirth et al., 2012, Mumme et al., 2014). Kim  
100 *et al.* (2014) demonstrated that hydrothermal carbonisation can be used to convert  
101 sewage digestate into a solid fuel by increasing the high heating value and carbon  
102 content in the resulting hydrochar. Danso-Boateng *et al.* (2015) reported the effect of  
103 process conditions in hydrochars and process waters characteristics and included  
104 data for theoretical biomethane potential in process waters from treated primary

105 sewage sludge. Hübner and Mumme (2015) showed that process waters from the  
106 pyrolysis of farm digestate can be converted into biogas without any additives or  
107 inoculum acclimation – i.e., COD removal rates of 63% and methane yields of up to  
108  $220 \text{ Lg}^{-1}_{\text{CODs}}$ . Mumme *et al.* (2014) showed the behaviour and biodegradability of  
109 biochars in anaerobic digestion and concluded that the addition of biochar to  
110 anaerobic digesters may contribute to reduce ammonia inhibition. However, there  
111 are no studies that integrate the influence of process conditions during hydrothermal  
112 treatments of sewage digestate on the characteristics of hydrochars and process  
113 waters, and the fate of nutrients like nitrogen and phosphorus.

114 This research is aimed at making a contribution in that regard and hence,  
115 investigates the effect of process temperature on the characteristics of hydrochars  
116 and process waters from hydrothermal processing of sewage digestate and  
117 compares the yields and characteristics of the different products including the fate of  
118 nitrogen and phosphorus species. In addition, experimental biomethane potential  
119 (BMP) tests were conducted on process waters on their own and in combination with  
120 hydrochars to assess the effect that hydrochars may have on AD processes. The  
121 results from experimental BMP tests were compared to theoretical predictive models.

## 122 **2. Methods**

### 123 *2.1. Digestate samples*

124 Digestate samples were collected from AD reactors processing sewage sludge at  
125 Yorkshire Water's Knostrop Wastewater Treatment Works in Leeds, West Yorkshire,  
126 UK. Digestate samples were stored at 4°C and then used for hydrothermal  
127 treatments.

128

### 129 *2.2. Hydrothermal experiments*

130 Hydrothermal experiments were conducted in a non-stirred 500mL stainless steel  
131 batch Parr reactor. In each batch experiment, 220mL of digestate (4.5% solids) were  
132 loaded in the reactor and sealed. The actual hydrothermal treatments were  
133 conducted at 160°C for 30min at 5 bar; 220°C for 30 min at 35 bar; and 250°C for 30  
134 min at 40 bar. After treatment, the reactor was cooled down to 25°C and the slurries

135 (hydrochar and process water) were collected for characterisation. The experiments  
136 were conducted in triplicate.

137

### 138 *2.3. Characterisation of products from hydrothermal processing*

139 The slurry following hydrothermal treatments was characterised according to  
140 standard analytical methods for Chemical Oxygen Demand (COD), Total Solids (TS),  
141 Suspended Solids (SS), Volatile Solids (VS), Volatile Fatty Acids (VFAs),  
142 Phosphorus (Total and Reactive), Total Kjeldahl Nitrogen (TKN), Ammonium and pH  
143 (APHA, 2005; He *et al.*, 2013).

144 Elemental analysis for Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) were  
145 performed using a CHNS elemental analyser (CE Instruments, Flash EA 1112  
146 Series) for dry digestate, hydrochar and process water samples. Proximate analyses  
147 were performed in a thermogravimetric analyser (Shimadzu, TGA-50) to determine  
148 moisture, ash and volatile matter. Total organic carbon (TOC) analyses were  
149 performed in a TOC analyser (HACH Lange, IL550 TOC/TIC Analyser).

150

### 151 *2.4. Biochemical methane potential (BMP) experimental tests*

152 The Biochemical Methane Potential (BMP) tests followed the principles and methods  
153 described by Angelidaki *et al.* (2009) and Diaz-Baez *et al.* (2002). BMP tests were  
154 carried out for slurries and process waters following hydrothermal treatment. For  
155 slurries, the inoculum and slurry were mixed maintaining a solid ratio of 1:1 with a  
156 total concentration of volatile solids (VS) of 10 gVS/L for the slurry (feedstock) and  
157 10g/L of volatile suspended solids (VSS) for the Inoculum. Process waters were  
158 used with the same concentration of soluble COD used in the slurries, but using the  
159 same amount of solids for the inoculum (10g VSS/L). The anaerobic digestion  
160 process for each batch was performed in 120mL bottles sealed with a rubber stopper  
161 and aluminium cap to avoid biogas leakage and incubated at 37°C. All BMP tests  
162 were carried out in duplicate and bottles containing only inoculum (blanks) were also  
163 incubated. Two control samples were tested using digestate (Control Slurry) and  
164 filtered digestate (Control Liquor). The headspace of each bottle was filled with  
165 nitrogen to keep anaerobic conditions and avoid leaching of oxygen into the reactor.  
166 Test bottles were kept undisturbed at all time, apart from the periods when mixing

167 occurred during biogas production measurements. Methane production was  
168 monitored by using a volumetric method following the absorption of CO<sub>2</sub> in a solution  
169 of NaOH (3M) (Herrera and Niño, 2012).

170 The experimental period for each BMP test lasted for 21 days; monitoring  
171 measurements were performed during days 0, 2, 4, 7, 10, 14, 18 and 21. For every  
172 measurement, a bottle was removed from incubation and sacrificed for the  
173 corresponding analyses. During each measurement, the following parameters were  
174 monitored: pH, TS, VS, COD and VFAs. TKN, Ammonium and Phosphorus (Total  
175 and reactive) were measured from samples collected at day 0 and 21. All the  
176 analyses were carried out in duplicate.

177

## 178 2.5. Inoculum

179 The inoculum used for BMP tests was obtained from the outlet of an anaerobic  
180 reactor used for sewage sludge digestion at Yorkshire Water's Esholt WWTW in  
181 Bradford, UK. The inoculum was incubated at 37°C in sealed bottles and fed every  
182 week with sewage sludge to keep it active.

183

## 184 2.6. Data processing and analysis

185 Data processing from hydrochar analyses was made using the following equations  
186 reported by Danso-Boateng *et al.* (2015):

187

### 188 2.6.1. Hydrochar Yield

189 Hydrochar yield ( $Y$ ), energy densification ( $E_d$ ) and energy yield ( $E_y$ ) were determined  
190 as follows:

191

$$192 \quad Y (\%) = \frac{\text{mass of dry hydrochar}}{\text{mass of dry Substrate feedstock}} * 100 \quad (1)$$

$$193 \quad E_d = \frac{HHV_{char}}{HHV_{feedstock}} \quad (2)$$

$$194 \quad E_y(\%) = E_d \times Y \quad (3)$$

195 where  $HHV$  is High Heating Value

196

### 197 2.6.2. Carbon recovery in solid and liquid fractions after HT processing

198 Carbon recovery in hydrochar ( $Hy_{crec}$ ) and liquid phase ( $Lq_{crec}$ ) were calculated as  
199 follows:

200

$$201 \quad (\%)Hy_{crec} = \frac{\frac{\%C_{Hydrochar}}{100} \times \text{char mass}}{\frac{\%C_{feedstock}}{100} \times \text{mass of dry Digestate feedstock}} * 100 \quad (4)$$

202

$$203 \quad (\%)Lq_{crec} = \frac{\text{Total organic Carbon} \times \text{volume of filtrate}}{\frac{\%C_{feedstock}}{100} \times \text{mass of dry Digestate feedstock}} * 100 \quad (5)$$

204

### 205 2.6.3. High Heating Value (HHV)

206 In order to know the theoretical calorific value of the hydrochar, the Dulong equation  
207 reported by Channiwala and Parikh (2002) was used.

$$208 \quad HHV (MJ \times Kg^{-1}) = 0.336 (\%Carbon) + 1.433 \left( \%Hydrogen - \left( \frac{\%Oxygen}{8} \right) \right) + \\ 209 \quad 0.0942 (\%Sulphur) \quad (6)$$

210

### 211 2.6.4. Biochemical Methane Production (BMP)

212 In order to assess the performance of methane production by gram of organic matter  
213 added (measured as chemical oxygen demand – COD), the following formula was  
214 used:

215

$$216 \quad BMP = \frac{V_{CH_4} - V_{CH_4,blank}}{(\text{Mass of substrate fed in biodigester})} \quad (7)$$

217 where:

218 BMP = Biochemical Methane Potential (mL of CH<sub>4</sub>/ g of COD added)

219 V<sub>CH<sub>4</sub></sub> = Volume of methane produced in bottle (mL)

220 V<sub>CH<sub>4</sub>, blank</sub> = Volume of methane produced in the blanks (mL)

221 Mass of substrate = Mass of substrate as g of COD

222

### 223 2.6.5. Theoretical BMP ( $BMP_{th}$ )

224 The calculation of theoretical BMP values, which are based on the elemental  
225 composition (C, H, N and O) of the samples, was made by using stoichiometric  
226 equations for maximum biogas production. Both the Buswell's equation and the  
227 Boyle's equation were used to calculate the theoretical BMP values for each tested  
228 sample (Tarvin and Buswell, 1934, Raposo et al., 2011). The difference between  
229 them is that the Boyle's equation does consider the presence of proteins and  
230 ammonia in the reaction (Nielfa et al., 2015).

231

232 Buswell's equation:

$$233 \quad BMP_{thBW} = \frac{22400 \left( \frac{n}{2} + \frac{a}{8} - \frac{b}{4} \right)}{12n+a+16b} \quad (8)$$

234

235 Boyle's equation:

$$236 \quad BMP_{thBO} = \frac{22400 \left( \frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} \right)}{12n+a+16b+14c} \quad (9)$$

237 where  $n$ ,  $a$ ,  $b$  and  $c$  represent the molar fraction of C, H, O and N, respectively.

238

### 239 2.6.6. Anaerobic biodegradability (BD)

240 The anaerobic biodegradability of each sample can be calculated from the values  
241 reported from the experimental BMP ( $BMP_{exp}$ ) and the theoretical BMP ( $BMP_{Th}$ ),  
242 and gives an idea of the level of biodegradability of the slurries and process waters  
243 under anaerobic conditions (Raposo et al., 2011):

244

$$245 \quad BD_{CH_4}(\%) = \frac{BMP_{exp}}{BMP_{Th}} \times 100 \quad (10)$$

### 246 3. Results and discussions

#### 247 3.1. Chemical Oxygen Demand and nutrient balance of thermal products

248 The COD, nitrogen and phosphorus content of the feedstock (Control) and their fate  
249 after hydrothermal processing are shown in Figure 1. The contribution of the gas was  
250 not considered because in all the cases the gas fraction was lower than 0.5%.

251 The fate of phosphorous following hydrothermal treatment is shown in Figure 1a.  
252 The results indicate that the organic phosphorus fraction in the aqueous phase,  
253 initially reported as 64.4% of the total P present in the digestate, increases after  
254 hydrothermal treatment at 160°C and 250°C to 79.7% and 86.6%, respectively. This  
255 is accompanied by a reduction in P content in the solid fraction from 21.7% in the  
256 raw feedstock (Control) to 19.4 and 11% in the hydrochar after treatment at 160 and  
257 250°C, respectively.

258 Hydrothermal treatment at 220°C results in a decrease of organic P to 10.9%. On the  
259 other hand, the inorganic phosphorous content ( $\text{PO}_4^{3-}$ ) initially at 13.9%, increased at  
260 220°C to 51.3% whereas treatment at 160 and 250°C resulted in a decrease to less  
261 than 2.5%. Hydrothermal treatment at lower temperatures favours the extraction of  
262 organic P, which then releases inorganic P. As the temperature increases, further  
263 additional organic P can be released as more complex molecules start to hydrolyse.  
264 The fate of P during hydrothermal treatment is highly feedstock dependent and is  
265 linked to the levels of other metals present in the feedstock (Ekpo *et al.*, 2015). The  
266 P associated with the hydrochar at 220°C is increased once more to 37%, maybe  
267 due to precipitation of some of the inorganic P with metals such as Al, Ca and Mg  
268 present in the hydrochar.

269 The fate of nitrogen following hydrothermal treatment is shown in Figure 1b. The  
270 solubilisation of nitrogen is increased at higher temperature. The initial levels of  
271 nitrogen in the solid fraction decreased from 58.3% to 42.4%, 38.9% and 34.3% for  
272 the treatments at 160, 220 and 250°C, respectively.

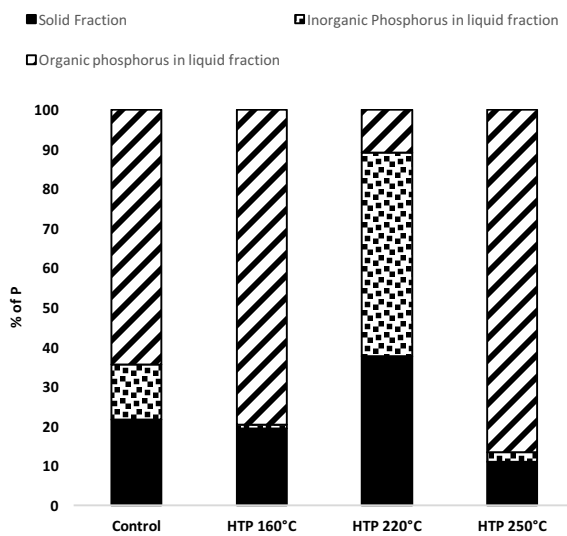
273 Hydrothermal treatment results in the solubilisation of organic matter from the  
274 digestate (Figure 1c). The raw digestate (Control) initially contained 4.6 wt% of  
275 solubilised COD in the liquid phase and this was increased to 31.7 wt%, 32.6 wt%  
276 and 30.5 wt% after hydrothermal treatment at 160, 220 and 250°C, respectively. The  
277 solubilisation of the organic matter into the aqueous phase is a result of hydrolysis

278 releasing inorganic and organic compounds from carbohydrates, proteins and lipids  
 279 (Danso-Boateng *et al.*, 2015).

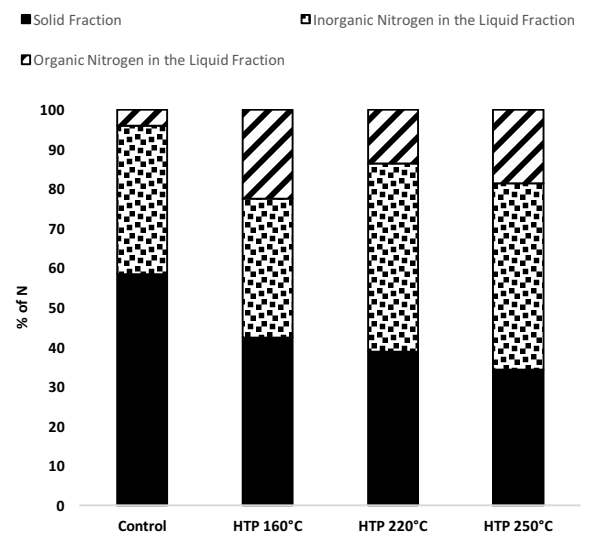
280 The composition of carbon and the nutrient species in hydrothermal products will  
 281 depend mainly on the nature of the feedstock and process temperature (Ekpo *et al.*,  
 282 2015, Toor *et al.*, 2011). During hydrothermal treatment, the levels of water soluble  
 283 products generally increase with reaction severity due to the combination of  
 284 solubilisation of inorganics and increase in production of soluble organics  
 285 hydrocarbons (Ekpo *et al.*, 2015, Keymer *et al.*, 2013, Qiao *et al.*, 2011).

286

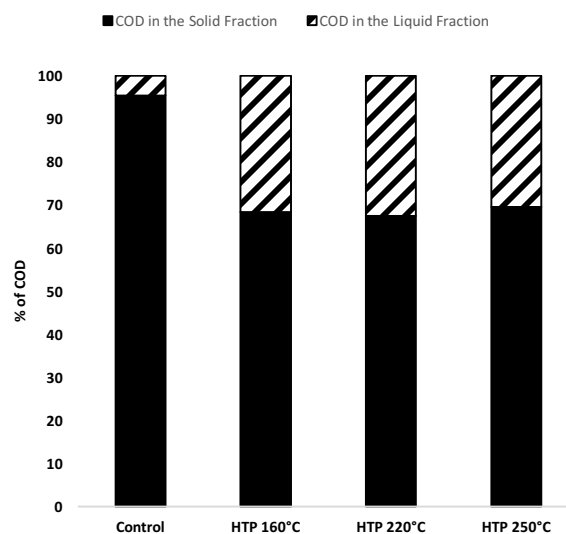
a)



b)



c)



287 **Figure 1.** Fate of Phosphorus (a), Nitrogen (b) and organic matter (c) after hydrothermal processing  
288 of digestate samples (Control) for 30 min and at 160°C (5bar), 220°C (35bar) and 250°C (40bar)

289

### 290 3.2. Hydrochar Characteristics

291 The volatiles, ash content, elemental composition and yields of the hydrochars are  
292 presented in Table 1. According to Danso-Boateng *et al.* (2015) and Ekpo *et al.*  
293 (2015), hydrochar yields are influenced by reaction temperature and time. Hydrochar  
294 yields decrease with increasing temperature and reaction time. In the work reported  
295 herein, the highest yield of hydrochar was obtained at 220°C (73.4%), followed by  
296 the yields reported at 160°C (68.8%) and at 250°C (56.8%) (Table 1).

297 The ash content increases after hydrothermal carbonisation as shown in Table 1,  
298 from 31.77% in the feedstock to 45.11%. These levels of ash content from  
299 anaerobically digested sewage sludge were similar to the results that Ekpo *et al.*  
300 (2015), Danso-Boateng *et al.* (2015) and Berge *et al.* (2011) reported (33.03 -  
301 38.94%; 78.3 - 81.4%; and 58.8% dry basis, respectively).

302 The volatile matter content of the hydrochar decreases after thermal treatment,  
303 having the lowest value at 220°C (43.82%) followed by the results found at 160°C  
304 (49.65%) and at 250°C (51.11%); our figures are below the reported values by  
305 Danso-Boateng *et al.* (2015) for anaerobically digested sewage sludge after  
306 carbonisation (55.33 - 66.17%). The reduction of volatile matter is due to chemical  
307 dehydration and decarboxylation and the increase in fixed carbon (FC).

308

#### 309 3.2.1. Elemental composition in Hydrochar

310 The nitrogen content in the original digestate samples (5.04 wt%) is higher than the  
311 figures found in the hydrochar after hydrothermal treatment at 160, 220 and 250°C  
312 (i.e., 4.19, 2.01 and 4.23 wt%, respectively). This suggests there is a 'sweet spot'  
313 where the nitrogen content is minimised. Reincorporation of nitrogen into the  
314 hydrochar may occur at higher temperatures as carbonisation reactions proceed  
315 more rapidly. A reduction in nitrogen content in the hydrochar corresponds to an  
316 increase in solubilised nitrogen. The oxygen content of the hydrochars is lower to the  
317 initial digestate. The initial oxygen content was 20.32 wt% and after hydrothermal  
318 treatment at 220°C and 160°C is observed to decrease slightly to 14.66 and 15.46

319 wt% respectively; oxygen then reduces slightly to 14.78 wt% at 250°C. The hydrogen  
 320 content of the hydrochar increases after treatment at 160°C and 250°C from 3.93%  
 321 to 4.19 and 4.89% respectively, but reduces after 220°C treatment to 3.91 wt%.

322  
 323 **Table 1.-** Proximate and ultimate analyses of the feedstock (digestate) and hydrochar.

Sample	Proximate Analyses				Ultimate analysis					Yield (%)
	Moisture (%)	Ash (% dry base -db)	Volatile matter (%db)	Fixed carbon <sup>a</sup> (%db)	C (%)	H (%)	N (%)	O <sup>b</sup> (%)	S (%)	
Digestate (Control)	4.66	31.77	55.81	7.76	34.78	3.93	5.04	20.32	1.15	
Hydrochar										
160 °C - 30 min	2.56	38.63	49.65	9.16	35.53	4.19	5.11	15.46	1.07	68.8
220 °C - 30 min	2.02	45.11	43.82	9.05	33.21	3.91	2.01	14.66	1.09	73.4
250 °C - 30 min	2.81	36.88	51.11	9.21	38.03	4.89	4.23	14.78	1.19	56.8

<sup>a</sup> 100 - (moisture + ash + volatile matter).

<sup>b</sup> Calculated as difference between sum of C,H,N,S, ash.

324  
 325  
 326  
 327 **3.2.2. Energy characteristics of Hydrochar**

328 High heating values (HHV) of the hydrochars produced at different process  
 329 temperatures are presented in Table 2. Temperature is reported to have a major  
 330 influence on heating values improving HHV with increasing temperature (Danso-  
 331 Boateng *et al.*, 2015); however, this is feedstock dependent and not true for all  
 332 feedstocks (Smith *et al.*, 2016). Many authors have shown a reduced heating value  
 333 for hydrochars produced from certain feedstocks compared to the original feedstocks  
 334 (Berge *et al.*, 2011a; Zhang *et al.*, 2014). In this case, the HHV of the hydrochars  
 335 generally increase but only slightly. The HHV of the original digestate is increased  
 336 from 16.61 Mj kg<sup>-1</sup> to a maximum of 17.80 Mj kg<sup>-1</sup> representing only a marginal  
 337 energy densification. Assessment of the combustion behaviour of this fuel has not  
 338 been performed. The hydrochar contains 36.88% ash and 4.2 wt% N and so it would  
 339 still be classified as a low-quality fuel. Despite that, the HHV of the hydrochars  
 340 produced are within a similar range to those reported by Danso-Boateng *et al.* (2015)  
 341 for digestate and for wastewater solids and sludge (17.2 - 18.4 Mj kg<sup>-1</sup>). This  
 342 indicates that for sewage derived solids and digestates, the energy densification is  
 343 quite low compared to other feedstocks and indicates that a significant amount of the  
 344 energy in the original feedstock is in the soluble water fraction (process waters),  
 345 which may be recovered via anaerobic digestion.

346 The calculation of energy yield provides a means of quantifying the energy remaining  
 347 within the hydrochars from the original feedstock (Digestate), and is defined as the  
 348 energy densification ratio multiplied by the mass yield of the hydrochar (Danso-  
 349 Boateng *et al.*, 2013). The energy yield decreases with increasing temperature  
 350 agreeing with the results from Danso-Boateng *et al.* (2015). The energy yields in  
 351 our hydrochars ranged from 61.22% at 250°C to 70.05% at 160°C, but these values  
 352 are significantly higher than the energy yield obtained by Berge *et al.* (2011) for  
 353 digestate (41.5%) and more similar to the results by Danso-Boateng *et al.* (2015) for  
 354 sewage sludge (68 - 89%). Energy densification takes place when the solid mass  
 355 decreases as a result of dehydration and decarboxylation reactions; that means the  
 356 carbon content increases and the hydrogen and oxygen content decrease.  
 357 Therefore, temperature and reaction time have significant influence on the energy  
 358 densification of the hydrochar (Danso-Boateng *et al.*, 2015, Danso-Boateng *et al.*,  
 359 2013). The energy densification values for the hydrochars obtained herein were 1.02  
 360 (for carbonisation at 160°C), 0.96 (for carbonisation at 220°C) and 1.08 (for  
 361 carbonisation at 250°C). The values in our study were lower when compared with  
 362 values obtained from primary sewage sludge by Danso-Boateng *et al.* (2015), which  
 363 ranged from 1.02 to 1.28 at temperatures between 140 and 200°C and reaction  
 364 times between 15 - 240min. However, it has to be taken into account that digestates  
 365 have a lower carbon content compared with primary sewage sludges due to  
 366 anaerobic digestion in which organic carbon is released during its conversion into  
 367 biogas (CH<sub>4</sub> and CO<sub>2</sub>).

368

369 **Table 2.-** Energy characteristics of hydrochar.

Hydrochar	HHV (Mj/Kg)	Energy densification (Mj/Kg)	Energy Yield (%)	H <sub>yCrec</sub> (%)	L <sub>yCrec</sub> (%)	CSF
Digestate (Control)	16.61	-	-	-	-	-
160 °C - 30 min	16.97	1.02	70.05	70.28	32.65	0.26
220 °C - 30 min	14.33	0.96	70.62	70.11	31.93	0.26
250 °C - 30 min	17.80	1.08	61.22	62.04	33.99	0.23

370

371

HHV: High heating value

L<sub>yCrec</sub>: Carbon recovered in the liquid fraction

H<sub>yCrec</sub>: Carbon recovered in the solid fraction

CSF: Carbon Storage Factor

372

### 373 3.2.3. Carbon balance in the Hydrochar

374 The carbon content of the hydrochars obtained after hydrothermal treatment are  
375 similar to those reported by Danso-Boateng et al. (2015) (36.63-39.24%) and Berge  
376 et al. (2011) (32.6%). It is important to highlight that it is sometimes challenging to  
377 make direct comparisons between hydrothermal treatments conducted by different  
378 researchers due to differences in reactor configurations, reaction conditions and  
379 solid loadings, all of which have a large influence on the characteristics of the  
380 products during carbonisation (Berge et al., 2011).

381 The carbon balance across solid and liquid products is presented in Table 2. The  
382 fraction of carbon recovered in the biochar ( $H_{yCrec}$ ) as a percentage of initial  
383 feedstock carbon, indicates that the carbon in the solid fraction gradually reduces  
384 with increasing temperature. The lower value of the carbon recovery in the  
385 carbonisation at 250°C (62.04%) was due to a lower hydrochar yield. Nevertheless,  
386 the carbon recovery in the hydrochar increased to more than 70% after treatment at  
387 220°C. The carbon recovery in the liquid fraction ( $L_{yCrec}$ ) is related to the Total  
388 Organic Carbon (TOC) obtained in the liquid fraction after carbonisation (see Table  
389 3). Table 2 also indicates that a similar fraction of Carbon in the liquid was recovered  
390 after hydrothermal treatment at each temperature. The carbon fraction that was  
391 transferred from the feedstock into the liquid phase ranged from 32.7% at 160°C to  
392 31.9% at 220°C and 34.0% at 250°C, indicating that there was carbon solubilisation  
393 after hydrothermal treatment in agreement with (Danso-Boateng et al., 2015).

394 The carbon storage factor (CSF) is the mass of carbon remaining (stored) in the  
395 solid following the biological decomposition in a dry mass of feedstock (Barlaz, 1998)  
396 and a similar approach can be applied to the remaining carbon in hydrochars after  
397 HT processes. Berge *et al.* (2011) have shown some evidence that after the HTC  
398 process (of municipal solids wastes) more carbon is stored within the hydrochar than  
399 if the waste material had been disposed uncarbonised. The CSFs of the digestate  
400 following hydrothermal treatment were 0.26, 0.26 and 0.23 for the treatments at  
401 160°C, 220°C and 250°C respectively. Therefore, CSF values decreased as the  
402 carbonisation temperature increased, in agreement with the results reported by  
403 Danso-Boateng et al. (2015). Indeed, higher levels of CSF were obtained in our  
404 study at lower temperatures from sewage sludge digestate ranging from 0.30 (at  
405 140°C) to 0.28-0.33 (at 160°C) and slightly lower values of CSF (0.26 to 0.28) at the

406 highest temperature tested (200°C). (Berge et al., 2011) obtained lower values of  
407 CSF (0.14) from digestate after carbonisation at 250°C. This assessment is  
408 potentially useful in understanding the behaviour of hydrochars if used as a carbon  
409 source for soil amendment.

### 410 3.3. Characteristics of process waters

411 The characterisation of the feedstock's liquid fraction (Control liquor) and the process  
412 waters after hydrothermal treatment is shown in Table 3. The results show that the  
413 pH in the aqueous phase is influenced by temperature and is generally alkaline. The  
414 highest pH of 9.15 was observed after treatment at 160°C, this reduces to 7.14 as  
415 the temperature increases to 220°C but then increases to 8.08 as the temperature  
416 increases to 250°C. The changes in pH are related to the presence of VFAs, amino  
417 acids and ammonia nitrogen that are generated during hydrothermal treatment (Qiao  
418 *et al.*, 2011). The hydrolysis of organic material results in a significant increase in  
419 soluble carbon (Wirth *et al.*, 2015). In this case, the concentration of soluble  
420 Chemical Oxygen Demand (COD) increases 7-fold after hydrothermal treatment,  
421 increasing from 1,843 mg/L in the initial digestate, to 12,992 mg/L after 220°C  
422 treatment; 12,642 mg/L after 160°C treatment; and 12,164 mg/L after 250°C  
423 treatment. The same trend is observed for Total Organic Carbon (TOC)  
424 concentrations which shows a 10-fold increase from 461 to 4,879 mg of TOC per  
425 litre.

426 The total soluble phosphorus concentration increases after 160°C and 250°C  
427 treatments (3% and 13.8% of P concentration, respectively) and decreases after  
428 220°C treatment (21.5% of P). The concentration of reactive phosphorus decreased  
429 with respect of the feedstock between 32.7 y 25.3% after hydrothermal treatment.

430 There are many proteins in the digestate because of the large amount of organic  
431 matter from bacterial biomass. During hydrothermal treatment, the proteins  
432 hydrolyse and ammonium is released increasing the nitrogen concentration in the  
433 process waters (Keymer et al., 2013, Wilson and Novak, 2009). The soluble nitrogen  
434 concentration increased with temperature from an initial concentration of 1,493  
435 mgN/l to 2,066, 2,191 and 2,354 mgN/L for the treatments at 160°C, 220°C and  
436 250°C, respectively. The concentration of ammonium nitrogen was lower although  
437 gradually increased with temperature.

438 The concentration of Volatile Fatty Acids (VFAs) increased with temperature and  
 439 corresponded to 191, 406 and 715 mg/L of COD for 160°C, 220°C and 250°C  
 440 treatments respectively (see Table 3). Acetic acid makes the highest contribution to  
 441 VFAs produced in all the treatments.

442 Following hydrothermal treatment, the level of carbon in the aqueous phase is higher  
 443 than in the hydrochars for all treatments, as shown in tables 2 and 3. The carbon  
 444 composition in the hydrochar ranges between 33 and 38%, whereas in evaporated  
 445 residues of process waters, the carbon content ranges from 30 to 68%. The carbon  
 446 content increases at higher temperature agreeing with the results obtained from TOC  
 447 analysis. This demonstrates that for this type of feedstock, a large degree of  
 448 solubilisation occurs following hydrothermal treatment, in agreement with previous  
 449 reports from similar treatments (Ekpo et al., 2015, López Barreiro et al., 2015).

450 In addition to carbon, the levels of hydrogen and nitrogen increase after  
 451 hydrothermal treatment. Moreover, the sulphur content in the liquid fractions  
 452 increased from 0.74% up to 2.81% after hydrothermal treatment; that may have  
 453 implications for levels of H<sub>2</sub>S in the final biogas (or precipitation of metal sulphides),  
 454 if process waters are recycled back into anaerobic digesters.

455 **Table 3.-** Characterization of filtered digestate (Control liquor) and process waters after HTP.

Parameter	Control liquor	160°C, 5bar, 30min	220°C, 35bar, 30min	250°C, 40bar, 30min
Soluble COD (mg/L)	1,843	12,642	12,992	12,164
pH	7.78	9.15	7.14	8.08
TKN (mg N/L)	1,493	2,066	2,191	2,354
Ammonium (mg-N/L)	1,344	1,258	1,704	1,685
Total Soluble Phosphorus (mg-P/L)	91.27	94.03	72.60	103.83
Reactive Phosphorus (mg-P/L)	80.12	53.88	59.84	56.84
VFAs (mg COD/L)	4.8	191.1	406.0	715.7
TOC (mg-C/L)	461.56	4,686.77	4,583.71	4,879.33
C (%)	30.53	45.77	49.21	67.97
H (%)	4.44	6.77	6.32	6.56
N (%)	10.19	11.11	12.31	6.56
S (%)	0.74	1.85	2.41	1.82
O (%) <sup>a</sup>	54.11	34.50	29.75	10.92

456 <sup>a</sup> Calculated as a difference from the sum of C, H, N and S.

#### 457 3.4. Anaerobic digestion of HT Slurries and Process waters

458 The experimental determination of Biomethane Potential was performed for a period  
459 of 21 days and deemed to have completed once the daily production of biogas was  
460 less than 1% (Nielfa *et al.*, 2015). During all the assays, soluble COD, VFAs,  
461 methane potential (BMP), and phosphorus and nitrogen species were measured.  
462 The organic composition of the substrates has a big impact on the performance of  
463 anaerobic digestion (AD) processes with regard to methane production and  
464 stabilisation of organic matter (Nielfa *et al.*, 2015). Figure 2 presents the changes in  
465 soluble COD concentration during anaerobic digestion of the different substrates.  
466 The results indicate that the soluble COD was consumed by the consortium of  
467 anaerobic bacteria in most of the resulting slurries and their process waters to  
468 produce biogas. For the 250°C slurry, from the 4<sup>th</sup> to the 10<sup>th</sup> day there was a COD  
469 solubilisation that may have come from the hydrochar (see Figure 2a). The presence  
470 of hydrochar seems to affect the consumption of organic matter by anaerobic  
471 bacteria.

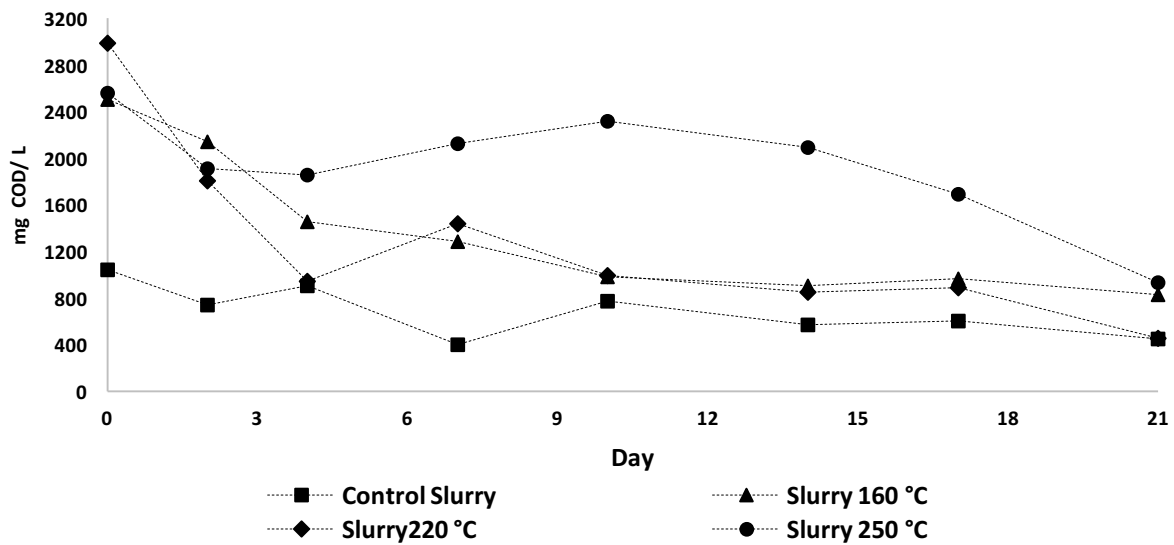
472 The raw digestate (Control Slurry) and filtered digestate (Control Liquor) did not  
473 produce big changes in soluble COD consumption. That may be because the  
474 digestate and its filtered fraction has previously been treated by anaerobic digestion  
475 and only a small amount of organic matter is available for further biodegradation;  
476 however, that still represents a matter of concern for fugitive methane emissions if  
477 untreated digestate is disposed on land (see Figure 4a).

478 The COD degradation efficiency of the Slurries and Process Waters within 21 days  
479 were 56.6% for the raw digestate, 66.9% for the 160°C slurry, 84.6% for the 220°C  
480 slurry and 63.6% for the 250°C slurry. Process waters had similar degradation  
481 efficiency as the slurries where the filtered digestate had 59.4%, and 69.1%, 79.6%  
482 and 63.8% for the 160°C, 220°C and 250°C process waters respectively. These  
483 figures are lower than the results obtained by Wirth *et al.* (2015), who reported COD  
484 degradation efficiencies between 84 and 107% in process waters from anaerobically  
485 digested sewage sludge after HTC at 200°C for 6 hours.

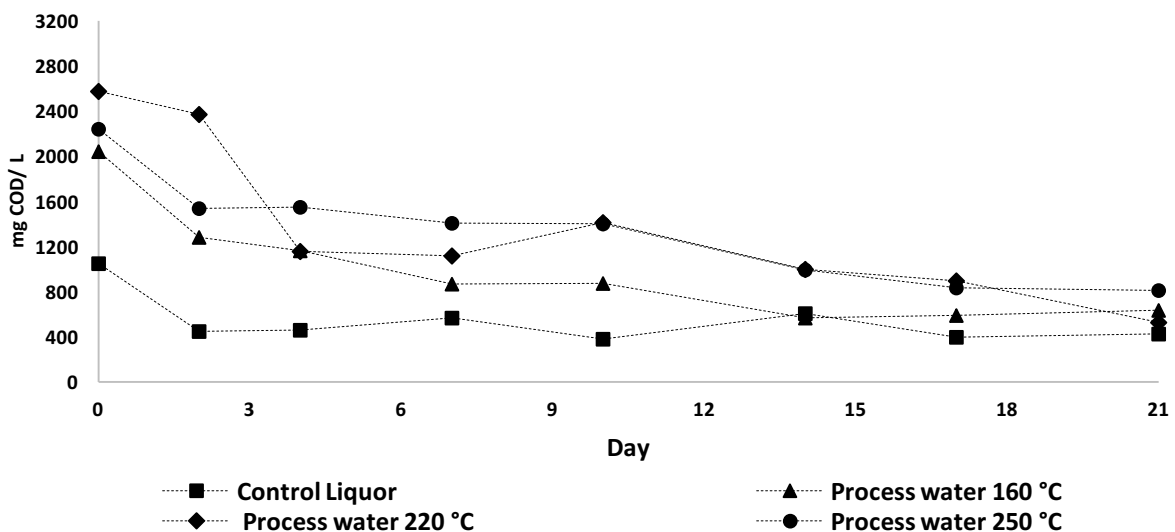
486

487

a)



b)



488 **Figure 2.-** Changes in soluble COD of Slurries (a) and Process Waters (b) during BMP tests.

489

490 During the anaerobic digestion process, substrate constituents are hydrolysed by  
 491 bacterial action into soluble COD. The soluble COD is fermented and turned into  
 492 VFAs and eventually converted into biogas by methanogenic bacteria. Yields of  
 493 VFAs produced per mg soluble COD added (mg of VFAs/ mg of COD<sub>sol</sub> added)  
 494 during the anaerobic digestion process of Slurries and Process Waters are shown in  
 495 Figure 3. The 160°C HTP treatment did not improve the contribution to VFA  
 496 formation from the hydrochar as the maximum VFA/COD concentration found from

497 the slurry sample (0.15 mg of VFAs/ mg of COD<sub>sol</sub> added, at day 2) was lower than  
498 the corresponding figures found in its process water (0.22 at day 2 and a maximum  
499 of 0.24 mg of VFAs/ mg of COD<sub>sol</sub> added, at day 4). That may suggest potential  
500 inhibitory effects on VFA production caused by the actual nature of the hydrochar  
501 produced at 160°C. For the HTP treatments at 220°C and 250°C, the resulting  
502 hydrochar made a substantial net contribution towards VFA formation with an  
503 increment of 13.3% at 220°C and 16.1% at 250°C, with regard to the highest figures  
504 found from process waters. For the 220°C slurry, the maximum yield found was 0.17  
505 mg of VFAs/ mg of COD<sub>sol</sub> added at day 2 and the corresponding figure found in its  
506 process water was 0.15 mg of VFAs/ mg of COD<sub>sol</sub> added, also at day 2. The 250°C  
507 slurry produced 0.30 mg of VFAs/ mg of COD<sub>sol</sub> added after 7 days, while the  
508 corresponding process water reported a maximum of 0.31 mg of VFAs/ mg of COD<sub>sol</sub>  
509 added within the same period; the maximum yield of VFA production was found  
510 from the slurry at day 14 (0.36 mg of VFAs/ mg of COD<sub>sol</sub> added).

511 After reaching their maxima, VFA concentrations would decrease until they will be  
512 totally consumed by methanogenic bacteria; therefore, biogas production rates (see  
513 figures 4a and 4b) are intrinsically related to VFA concentrations and based on our  
514 findings, it seems that HTC treatments at 220°C and 250°C produce a hydrochar that  
515 enhance VFA production and hence, they would potentially contribute to higher  
516 methane yields. However, it seems that the net accumulation of VFAs reported from  
517 products obtained at 250°C (Figure 3) is the result of less VFA transformation into  
518 methane (Figure 4), which raises questions over the inhibitory effect that the  
519 hydrochar and the process water at 250°C may have over methanogenic bacteria.

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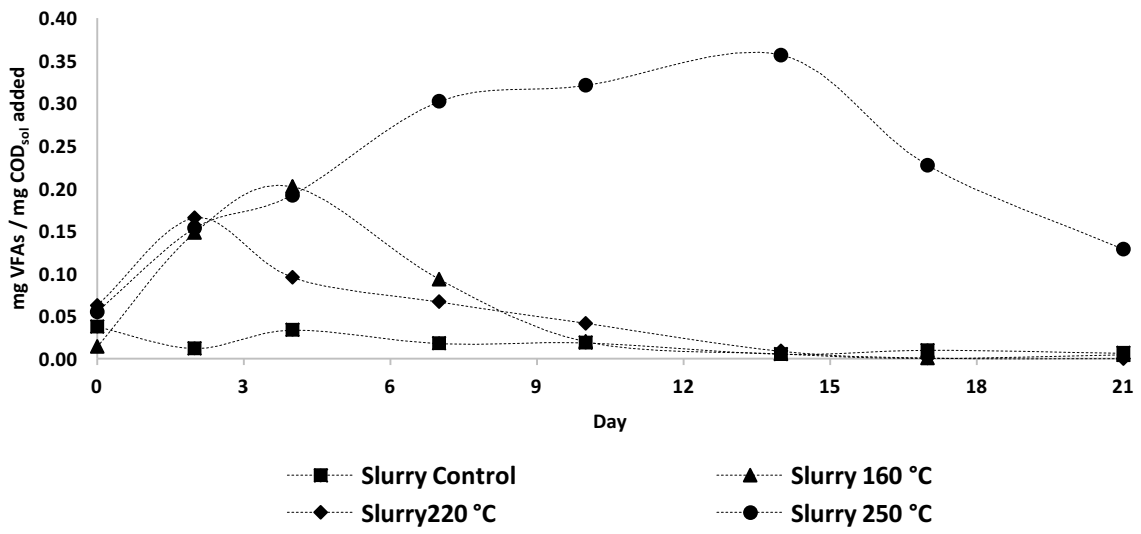
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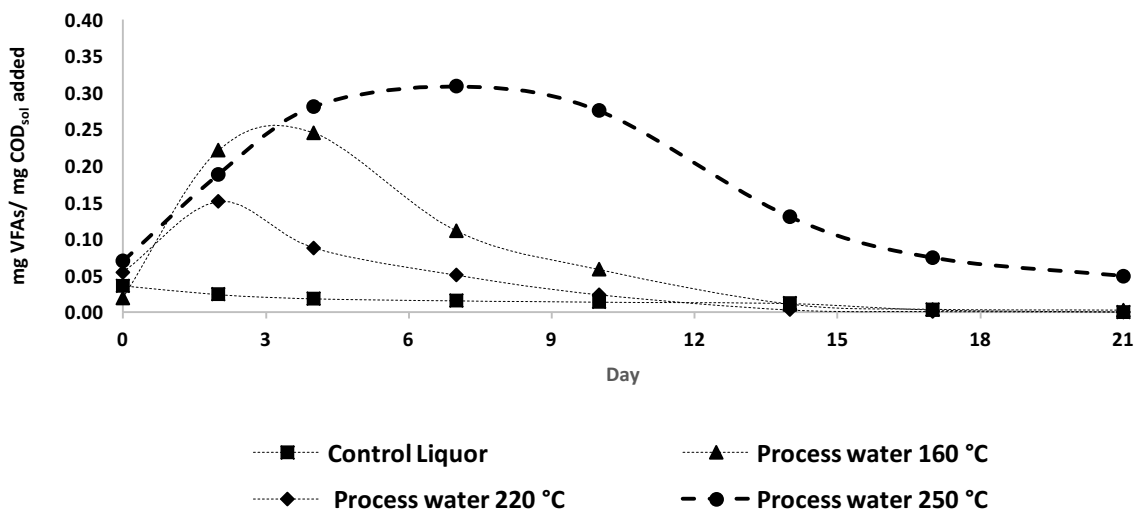
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a)



b)



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530

**Figure 3.-** Normalised VFA production from Slurries (a) and Process Waters (b) during BMP tests

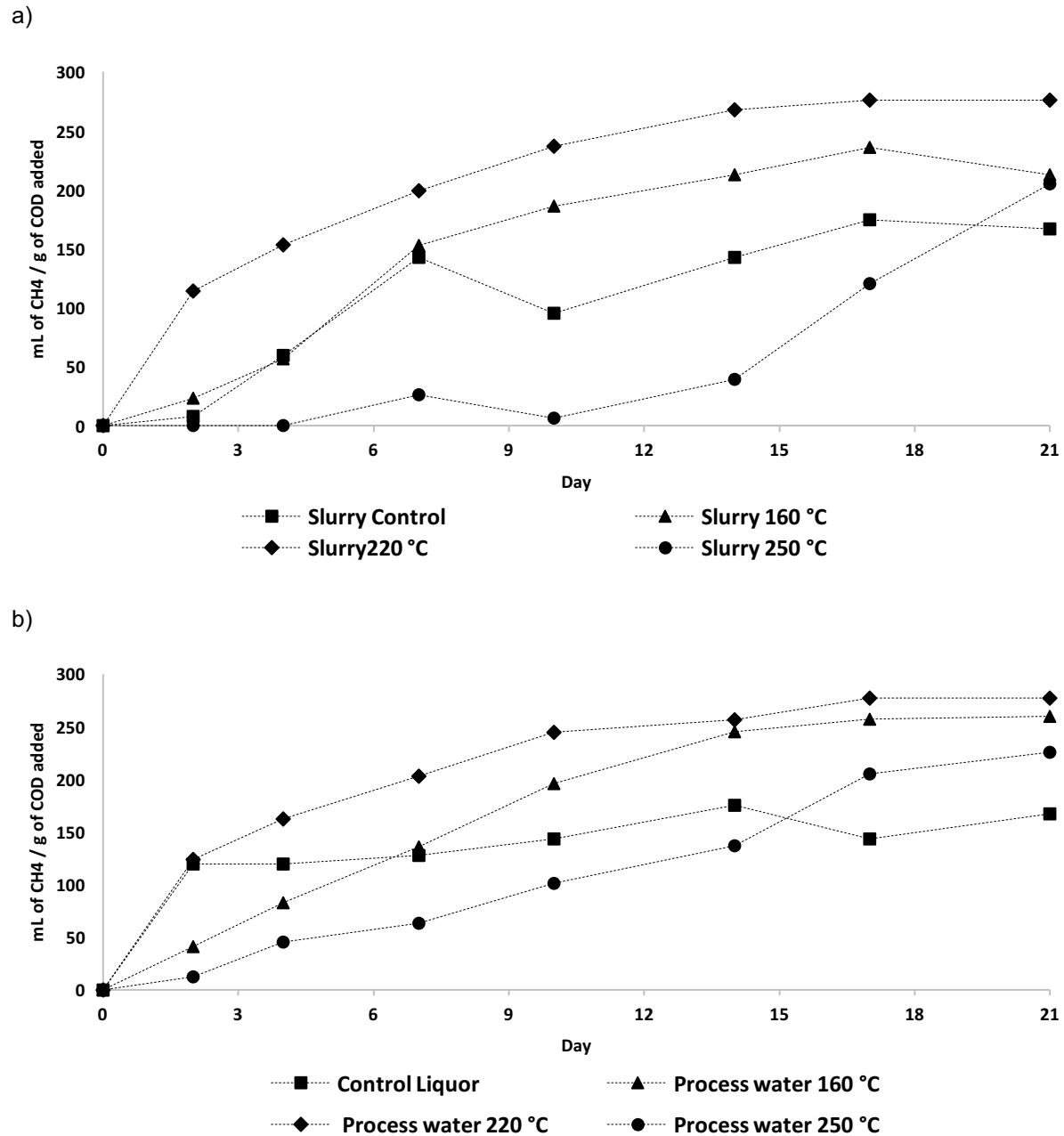
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536 **Figure 4.-** Normalised methane production from Slurries (a) and Process Waters (b) during BMP  
 537 tests.

538

539 Previous studies using hydrothermal processes as a pre-treatment for anaerobic  
 540 digestion have shown an increase in methane yields in BMP tests, due to the  
 541 additional solubilisation of organic matter achieved via thermal hydrolysis (Keymer  
 542 *et al.*, 2013). After hydrothermal treatment, the BMP increases between 17% and  
 543 58% compared with the control (175 mL of CH<sub>4</sub>/ g of COD). It is shown in Figure 4  
 544 that the BMP values for the slurries following hydrothermal treatment were 236 at

545 160°C, 276 at 220°C and 205 at 250°C, all reported in mL of CH<sub>4</sub>/ g of COD.  
546 Nevertheless, it is worth to provide further discussion to the results from the BMP  
547 test of the digestate treated at 250°C, as it seems that the methane production could  
548 have continued after the 21 days of the BMP test, considering the remaining VFA  
549 concentration (Figure 3). Therefore, the methane potential of the digestate treated at  
550 250°C has been underestimated and it is inferred that the net methane production  
551 should have been higher than the results obtained at 220°C after 21 days. The  
552 presence of hydrochar affects the production of biogas which is reflected in the delay  
553 of VFA production (Figure 3) and the subsequent delay in the production of methane  
554 (Figure 4). Also it was observed that an additional solubilisation of COD (Figure 2a)  
555 occurs after the VFAs reached the highest concentration. Although other factor that  
556 might influence is the presence of less digestible higher molecular weight organic  
557 compounds formed during the thermal process at that temperature (Danso-Boateng  
558 et al., 2015), or other compounds that could delay methane production.

559 The BMP values for process waters following hydrothermal treatment increased  
560 between 29% and 58% compared with the control sample (175 mL of CH<sub>4</sub>/ g of  
561 COD). The highest value was for the processed water of 220°C treatment (277 mL of  
562 CH<sub>4</sub>/ g of COD) followed by 160°C treatment (260 mL of CH<sub>4</sub>/ g of COD) and 250°C  
563 treatment (225.8 mL of CH<sub>4</sub>/ g of COD). The BMP values of process waters were  
564 similar to the slurries of the digestate after hydrothermal treatment for the treatments  
565 at 160 and 220°C and the hydrochars did not affect the anaerobic process unlike the  
566 250°C slurry and its process water.

567 A similar study was carried out by Qiao et al. (2011) in which they use sewage  
568 sludge treated at 170°C for 1 hour; they also performed BMP tests on the slurry and  
569 the processed water. The results showed an improvement of 65.5% in methane  
570 production from the slurry (257 mL of CH<sub>4</sub>/ g of VS) and 147.5% (385 mL of CH<sub>4</sub>/ g  
571 of VS) of methane production of the process water with respect the raw sewage  
572 sludge (155 mL of CH<sub>4</sub>/ g of VS).

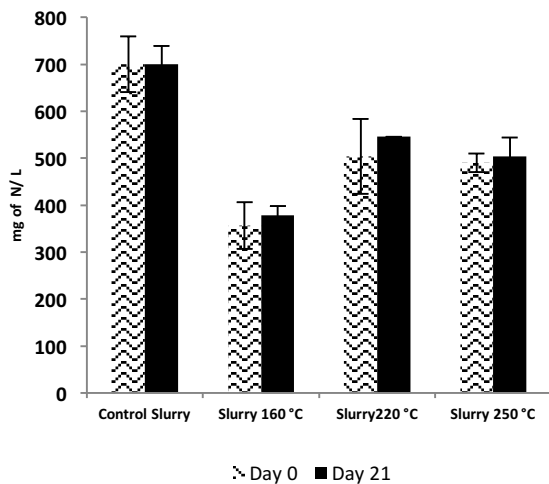
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#### 574 3.4.1. Nutrient solubilisation during the BMP test

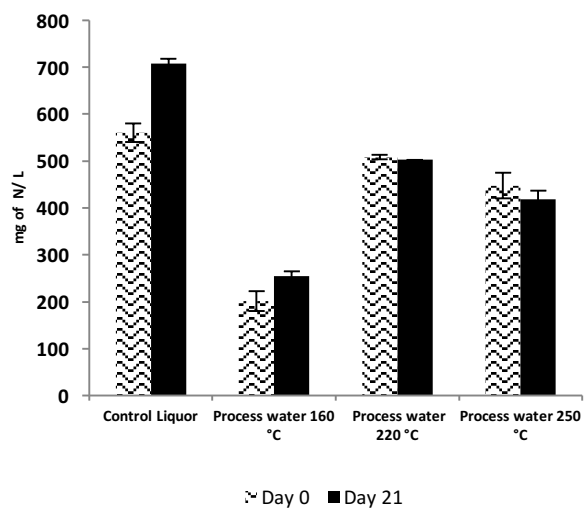
575 Figure 5 shows the soluble nitrogen fraction (soluble TKN and ammonium) before  
576 and after anaerobic digestion (i.e., at Day 0 and Day 21 of the BMP tests). It can be

577 seen that after anaerobic digestion, with the exception of the slurry control and the  
 578 processed water at 220 and 250°C treatment, the soluble TKN concentration  
 579 increased from 3 to 26% in all the other substrates. Also, the ammonium  
 580 concentration increases in all substrates after the anaerobic digestion between 4 and  
 581 39%. As a result, the nitrogen solubilised during the anaerobic digestion was mostly  
 582 ammonium coming from the hydrolysis step of proteins and bacterial biomass. As a  
 583 consequence, an increase in the nitrogen concentration, especially in ammonium is  
 584 observed (Münch and Barr, 2001, Wilson and Novak, 2009). These findings match  
 585 with previous studies of substrates such as algae after hydrothermal and anaerobic  
 586 treatments, in which the soluble nitrogen concentration increased after anaerobic  
 587 digestion (Keymer et al., 2013, Ras et al., 2011).

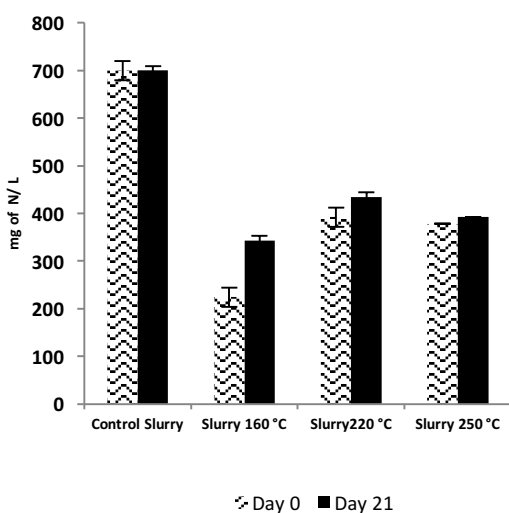
a) Soluble TKN in slurries



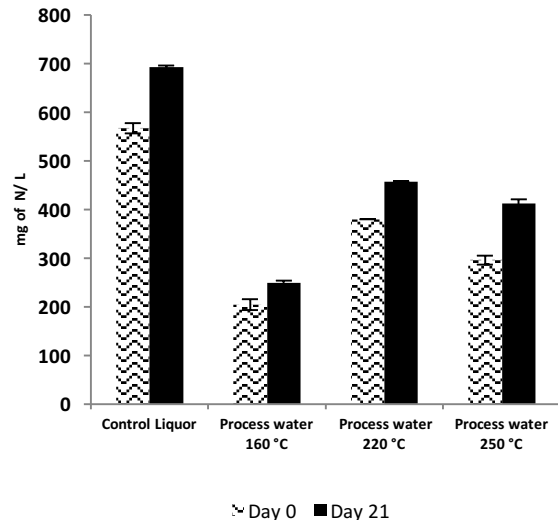
b) Soluble TKN in process waters



c) Ammonium in slurry



d) Ammonium in process waters



588 **Figure 5.** Changes in the concentrations of soluble TKN and ammonium in slurries (a and c) and  
589 process waters (b and d) before (Day 0) and after (Day 21) BMP tests

590

591 The total soluble phosphorus concentration after anaerobic digestion tends to  
592 increase. Figure 6 indicates that there is a solubilisation of phosphorus for all the  
593 substrates after anaerobic digestion ranging between 2 to 242% over the starting  
594 concentration, which is in agreement with the work conducted by Münch and Barr  
595 (2001). Most of the phosphorus solubilised was reactive phosphorus as shown in  
596 figures 6c and 6d, where the concentration increased after anaerobic digestion. All  
597 the slurries had good solubilisation of reactive phosphorous. The highest  
598 solubilisation was for the 160°C slurry with almost a 9-fold increase over the starting  
599 concentration. The level of P solubilisation from the slurry produced at 160°C (242%)  
600 is comparable with that for the control slurry (236%); whereas for the slurries  
601 produced at higher temperature, the solubilisation of P is much lower (26-54%),  
602 which may be due to interaction with the hydrochar.

603 Those results represent an improvement in nutrient retention when compared with  
604 figures found in digestate cake (sewage sludge digestate after dewatering); that  
605 characteristic may also improve the release rate of P in the hydrochar when spread  
606 on land. Hydrothermal treatment of the process waters alone results in significantly  
607 less solubilisation of phosphorous (2 - 33%), with the majority of P coming from the  
608 biomass in the inoculum. The process waters did not experience major changes with  
609 regard to the concentration of reactive phosphorus probably due to the small amount  
610 of solids presented in the mixtures, which may indicate a high adsorption capacity of  
611 the hydrochar for phosphate species.

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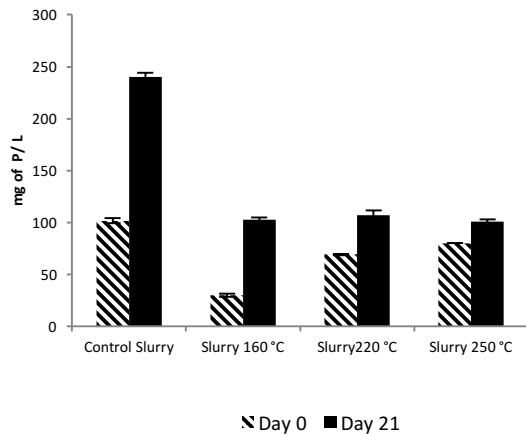
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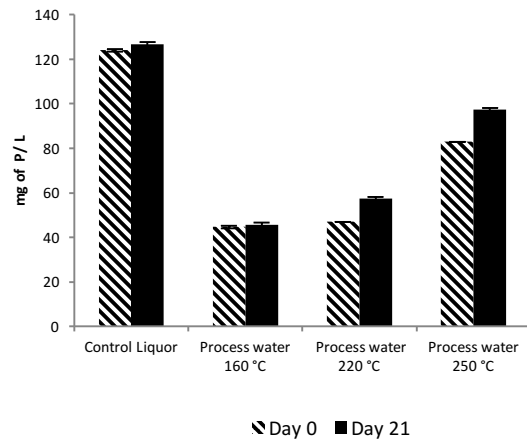
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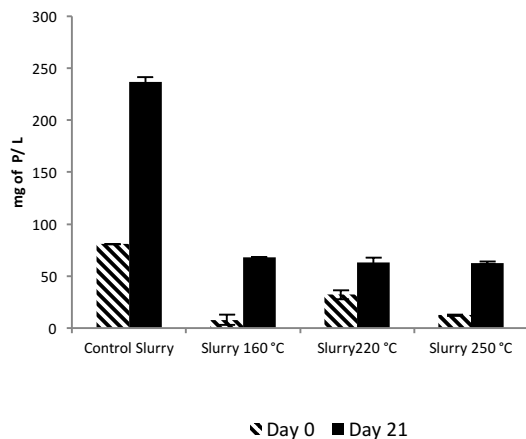
a) Total soluble phosphorus in slurries



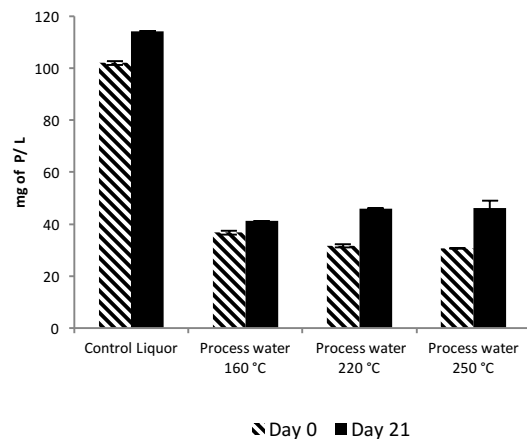
b) Total soluble phosphorus in process waters



c) Reactive phosphorus in slurries



d) Reactive phosphorus in process waters



619 **Figure 6.** Changes in Total Soluble Phosphorus and Reactive Phosphorus concentrations in slurries  
 620 (a and c) and in process waters (b and d) before (Day 0) and after (Day 21) BMP tests.

621

622 **3.5. Theoretical BMP v. Experimental BMP**

623 The use of empirical formulas to predict the potential production of methane is widely  
 624 accepted, due largely in part to being relatively fast, reliable and economical.  
 625 Nevertheless these equations do not differentiate between biodegradable and non-  
 626 biodegradable organic matter (Lesteur et al., 2010, Nielfa et al., 2015). According to  
 627 Labatut *et al.* (2011) the values of the theoretical formulas are always higher than the  
 628 experimental ones because they do not account for the substrate biodegradability or  
 629 metabolic processes. For example, the Buswell's equation does not count the

630 carbon that is locked in the cell protoplasm of new anaerobic bacteria (nearly 12%)  
631 (Labatut *et al.*, 2011). Therefore, not all the biodegradable organic matter used by  
632 the bacteria contributes to the production of methane.

633 To define how accurate Buswell's and Boyle's equations are in order to determine  
634 the methane yields in the hydrothermally treated substrates, a comparison between  
635 the experimental and theoretical BMP was carried out as shown in Table 4. The  
636 values of theoretical BMPs (BMP<sub>th</sub>) were calculated based on the elemental  
637 composition of the process waters with and without the presence of hydrochars.  
638 Previously, authors have reported that the theoretical productivity decreases in  
639 substrates containing higher nitrogen, hydrogen and sulphur content, which can  
640 produce toxic concentration of ammonia and hydrogen sulphide (Denis and Burke,  
641 2001).

642 The Buswell's equation predicts higher values than the Boyle's equation. However,  
643 the BMP<sub>th</sub> values in both cases are higher than the experimental values. The  
644 Boyle's equation has the closest match to the experimental values and that may be  
645 due to the fact that the model considers the presence of proteins and ammonia  
646 whereas the Buswell's equation does not consider the presence of nitrogen (Nielfa *et*  
647 *al.*, 2015).

648 Some researchers have proposed that the theoretical methane yields are affected by  
649 reaction temperature and time during hydrothermal treatment (Danso-Boateng *et al.*,  
650 2015). The predictive equations both show similar trends, with the highest  
651 temperature for hydrothermal processing resulting in the highest BMP<sub>th</sub>. As the  
652 predictive calculations are based on elemental content, the control samples have a  
653 higher predicted BMP<sub>th</sub> than the hydrothermally treated samples. The  
654 biodegradability and methane yields of the substrates can also be determined by  
655 using values of BMP<sub>exp</sub> and BMP<sub>th</sub> (Raposo *et al.*, 2011). The biodegradability  
656 represents the amount of organic material that is degraded during the anaerobic  
657 process. Table 4 presents the biodegradability of the substrates based on both the  
658 Boyle's and Buswell's equations.

659 The experimental BMP tests show that the lower temperature hydrothermal  
660 treatments produce higher BMP than the higher temperature processing. This is  
661 probably due to inhibitory effects increasing with process temperatures. The control  
662 shows the lowest BMP as expected. Comparison between the theoretical prediction

663 and experimental figures generally indicates that for lower temperature processing  
 664 (160 - 220°C), the equations provide a reasonable match. The experimental BMP is  
 665 96% of the theoretical BMP<sub>th</sub> determined by the Boyle equation and 70% of the  
 666 BMP<sub>th</sub> determined by the Buswell equation. As the temperature rises to 250°C, the  
 667 experimental BMP drops significantly to 44% of BMP<sub>th</sub>, however this still represents  
 668 a significant enhanced biogas formation. The value of biodegradability in the  
 669 digestate treated at 250°C does not represent the complete potential as this test was  
 670 still generating methane after 21 days so this result may underestimate the true  
 671 BMP. The biodegradability values provide more robust data for predicting overall  
 672 enhanced energy recovery, which can be used to better calculate and assess energy  
 673 balances for integrating AD and HTC at WWTWs. Based on the results in this study,  
 674 it is likely that lower temperature hydrothermal treatment is more advantageous than  
 675 higher temperature for processing sewage sludge digestate.

676 For lower temperature hydrothermal treatment, slurry samples had similar  
 677 biodegradability as process waters and the presence of hydrochars did not affect the  
 678 biodegradation of the organic matter present in process waters. Biodegradability  
 679 dropped for both process water and slurry following higher temperature processing  
 680 indicating that inhibitory effects may occur.

681 **Table 4.-** Comparisons between experimental BMP and theoretical BMP.

Sample	BMP <sub>exp</sub> (mL of CH <sub>4</sub> /g of COD added)	BMP <sub>th</sub> Boyle's Equation (mL CH <sub>4</sub> / g COD)	BMP Buswell's eq. (mL CH <sub>4</sub> / g COD)	BD Boyle's Equation	BD Buswell's Equation
Control Slurry	174.6	251.0	303.7	70%	57%
160° Slurry	235.9	271.6	353.9	87%	67%
220° Slurry	276.1	289.3	384.4	95%	72%
250° Slurry	205.0	403.0	513.2	51%	40%
Control Liquor	175.4	251.0	303.7	70%	58%
160°C Process Water	260.0	271.6	353.9	96%	73%
220°C Process Water	277.2	289.3	384.4	96%	72%
250°C Process Water	225.8	403.0	513.2	56%	44%

682 BD: Biodegradability; DT: Digestate treated;  
 683 BMP<sub>exp</sub>: Experimental Biomethane Potential; BMP<sub>th</sub>: Theoretical Biomethane Potential.

684

685

686 3.6. Energy production of the hydrothermal treatments.

687 The energy production of the conventional AD is limited by the production of  
 688 methane from sewage sludge in which 35 to 45% of the organic fraction is  
 689 biodegradable (Shana *et al.*, 2011). Thermal hydrolysis as a pre-treatment helps to  
 690 improve biogas production up to 43% and COD removal up to 75% (Sridhar Pilli *et*  
 691 *al.*, 2015). However, the integration of thermal treatments following anaerobic  
 692 digestion, not only improves digestate dewaterability by reducing moisture in the  
 693 solid fraction, but also it was found that the solid fraction has the potential to be used  
 694 either as a solid fuel or as a carbon source for soil amendment.

695 Table 5 shows the energy production per kg of sewage sludge from different process  
 696 configurations including conventional AD, thermal hydrolysis (TH) as a pre-treatment  
 697 of AD processing (TH + AD) and different hydrothermal treatments as post-treatment  
 698 steps following AD.

699 The biogas production following thermal hydrolysis as pretreatment is better than the  
 700 conventional AD and the hydrothermal treatments. However, the use of hydrochars  
 701 as an energy source gives an added value to the hydrothermal treatments favouring  
 702 the energy production. The additional energy that can be obtained from hydrothermal  
 703 treatments comes from the hydrochar that can be used as a solid fuel and ranges  
 704 from 153 to 179% in comparison with the thermal hydrolysis that is just 43%. The  
 705 results suggest a better use of the sewage sludge when hydrothermal treatment is  
 706 used after AD.

707 **Table 5.-** Energy production of different thermal treatment configurations for a 15% solids sewage  
 708 sludge.

	Energy produced from CH <sub>4</sub> per kg of feedstock (Mj)	Energy produced in char per kg of feedstock (Mj)	Overall energy produced per Kg of feedstock (Mj)
Conventional AD	7.08	-	7.08
*TH + AD	10.13	-	10.13
AD + 160T + AD	8.09	11.68	19.77
AD + 220T + AD	8.36	10.52	18.88
AD + 250T + AD	7.86	10.10	17.96

710  
711  
712

BMP of Mix sludge = 226 of CH<sub>4</sub> /g of COD added (experimental value)  
 \*BMP of THP Mix sludge = 323.2 of CH<sub>4</sub> /g of COD added (assuming 43% additional production) (Sridhar Pilli *et al.*, 2015)  
 HHV of methane, 1m<sup>3</sup> = 35.8Mj

#### 713 **4. Conclusions**

714 Hydrothermal treatments improved the characteristics of the sewage digestate  
715 producing hydrochars and process waters rich in organic matter and nutrients.  
716 Anaerobic digestion was demonstrated to be a suitable option to treat process  
717 waters from hydrothermal treatments for further biomethane production. Processing  
718 of digestate at 250°C resulted in a hydrochar that enhanced the net production of  
719 VFAs, although delayed methane production (longer lag phase) and hence, higher  
720 methane production would be expected. The addition of hydrochar (250°C) to the  
721 process water delayed VFA production during anaerobic digestion. Hydrothermal  
722 processing of process water and slurries at lower temperature (160-220°C) produced  
723 high levels of biogas, with no detrimental effect due to the presence of hydrochar.  
724 The Boyle's equation had a closer match to the values provided by experimental  
725 biomethane potential (BMP) tests at lower temperature. Further studies are needed  
726 to understand the influence of adding hydrochar on the quality and safety of the  
727 digestate for final disposal, as well as the impacts on AD processes due to process  
728 water recycling.

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