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

C. Aragon-Briceno[a], A. B. Ross[b] and M. A. Camargo-Valero[a,c]

[a] Institute for Public Health and Environmental Engineering (iPHEE), School of Civil Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom
[b] School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, Leeds, United Kingdom
[c] Departamento de Ingeniería Química, Universidad Nacional de Colombia, Campus La Nubia, Manizales, Colombia

Corresponding email: M.A.Camargo-Valero@leeds.ac.uk

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 be 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 compare 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.*

1. Introduction

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

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

Hydrothermal treatments (HT) are considered an alternative technology to harness energy from SS in the presence of water and avoid the energy-intensive drying step required for other thermal processes (He *et al.*, 2013). The main aim of the hydrothermal processing routes is energy densification via hydrochar production, which is produced largely by the removal of oxygen. After HT, the resulting hydrochars show moderate calorific value and are biologically inert, so they can be co-fired with coal or safely disposed in agricultural land as soil amendment (Bargmann et al., 2014, He et al., 2013, Biller and Ross, 2012). Hydrothermal processing also generates a by-product or “process water" rich in organic compounds that cannot be directly disposed into the environment, but has been proved to be suitable for methane production via anaerobic digestion (Almeida, 2010, Becker et al., 2014, Kim et al., 2014, Stemann et al., 2013, Wirth et al., 2015, Zhao et al., 2014).

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

A range of different solid wastes have been studied for hydrothermal processing, including microalgae and manures (Ekpo *et al.*, 2015), municipal solid wastes (Berge *et al.*, 2011), sewage sludge (Danso-Boateng *et al.*, 2015), digestate (Kim *et al.*, 2014), and wood chips (Stemann et al., 2013). Most of the studies regarding hydrothermal treatment of sewage digestate have focused either on the characterisation of the resulting products (Berge et al., 2011, Danso-Boateng et al., 2015, Escala et al., 2013, Kim et al., 2014, Nipattummakul et al., 2010) or on the anaerobic digestion of the liquid products following hydrothermal treatment (Wirth et al., 2015, Hübner and Mumme, 2015, Wirth et al., 2012, Mumme et al., 2014). Kim *et al*. (2014) demonstrated that hydrothermal carbonisation can be used to convert sewage digestate into a solid fuel by increasing the high heating value and carbon content in the resulting hydrochar. Danso-Boateng *et al*. (2015) reported the effect of process conditions in hydrochars and process waters characteristics and included data for theoretical biomethane potential in process waters from treated primary sewage sludge. Hübner and Mumme (2015) showed that process waters from the pyrolysis of farm digestate can be converted into biogas without any additives or inoculum acclimation – i.e., COD removal rates of 63% and methane yields of up to 220 Lg^{-1}_{CODs}. Mumme *et al.* (2014) showed the behaviour and biodegradability of biochars in anaerobic digestion and concluded that the addition of biochar to anaerobic digesters may contribute to reduce ammonia inhibition. However, there are no studies that integrate the influence of process conditions during hydrothermal treatments of sewage digestate on the characteristics of hydrochars and process waters, and the fate of nutrients like nitrogen and phosphorus.

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

2. Methods

2.1. Digestate samples

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

2.2. Hydrothermal experiments

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

2.3. Characterisation of products from hydrothermal processing

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

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

2.4. Biochemical methane potential (BMP) experimental tests

The Biochemical Methane Potential (BMP) tests followed the principles and methods described by Angelidaki et al. (2009) and Diaz-Baez et al. (2002). BMP tests were carried out for slurries and process waters following hydrothermal treatment. For slurries, the inoculum and slurry were mixed maintaining a solid ratio of 1:1 with a total concentration of volatile solids (VS) of 10 gVS/L for the slurry (feedstock) and 10g/L of volatile suspended solids (VSS) for the Inoculum. Process waters were used with the same concentration of soluble COD used in the slurries, but using the same amount of solids for the inoculum (10g VSS/L). The anaerobic digestion process for each batch was performed in 120mL bottles sealed with a rubber stopper and aluminium cap to avoid biogas leakage and incubated at 37°C. All BMP tests were carried out in duplicate and bottles containing only inoculum (blanks) were also incubated. Two control samples were tested using digestate (Control Slurry) and filtered digestate (Control Liquor). The headspace of each bottle was filled with nitrogen to keep anaerobic conditions and avoid leaching of oxygen into the reactor. Test bottles were kept undisturbed at all time, apart from the periods when mixing occurred during biogas production measurements. Methane production was monitored by using a volumetric method following the absorption of CO_2 in a solution of NaOH (3M) (Herrera and Niño, 2012).

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

2.5. Inoculum

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

2.6. Data processing and analysis

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

2.6.1. Hydrochar Yield

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

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

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

$$E_y(\%) = E_d \times Y \qquad (3)$$

where *HHV* is High Heating Value

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

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

$$(\%)Hy_{crec} = \frac{\frac{\%C_{Hydrochar}}{100}\ x\ char\ mass}{\frac{\%C_{feedstock}}{100}\ x\ mass\ of\ dry\ Digestate\ feedstock} * 100 \qquad (4)$$

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

2.6.3. High Heating Value (HHV)

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

$$HHV\ (MJxKg^{-1}) = 0.336\ (\ \%Carbon) + 1.433\ \left(\%Hydrogen - \left(\frac{\%Oxygen}{8}\right)\right) + 0.0942\ (\%\ Sulphur) \qquad (6)$$

2.6.4. Biochemical Methane Production (BMP)

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

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

where:

BMP = Biochemical Methane Potential (mL of CH_4/ g of COD added)

V_{CH4} = Volume of methane produced in bottle (mL)

$V_{CH4,\ blank}$ = Volume of methane produced in the blanks (mL)

Mass of substrate = Mass of substrate as g of COD

2.6.5. Theoretical BMP (BMP_{th})

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

Buswell's equation:

$$\mathrm{BMP}_{thBW} = \frac{22400\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right)}{12n+a+16b} \qquad (8)$$

Boyle's equation:

$$\mathrm{BMP}_{thBO} = \frac{22400\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}-\frac{3c}{8}\right)}{12n+a+16b+14c} \qquad (9)$$

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

2.6.6. Anaerobic biodegradability (BD)

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

$$BD_{CH4}(\%) = \frac{BMP_{exp}}{BMP_{Th}}\, x\, 100 \qquad (10)$$

3. Results and discussions

3.1. Chemical Oxygen Demand and nutrient balance of thermal products

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

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

Hydrothermal treatment at 220°C results in a decrease of organic P to 10.9%. On the other hand, the inorganic phosphorous content (PO_4^{3-}) initially at 13.9%, increased at 220°C to 51.3% whereas treatment at 160 and 250°C resulted in a decrease to less than 2.5%. Hydrothermal treatment at lower temperatures favours the extraction of organic P, which then releases inorganic P. As the temperature increases, further additional organic P can be released as more complex molecules start to hydrolyse. The fate of P during hydrothermal treatment is highly feedstock dependent and is linked to the levels of other metals present in the feedstock (Ekpo *et al*., 2015). The P associated with the hydrochar at 220°C is increased once more to 37%, maybe due to precipitation of some of the inorganic P with metals such as Al, Ca and Mg present in the hydrochar.

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

Hydrothermal treatment results in the solubilisation of organic matter from the digestate (Figure 1c). The raw digestate (Control) initially contained 4.6 wt% of solubilised COD in the liquid phase and this was increased to 31.7 wt%, 32.6 wt% and 30.5 wt% after hydrothermal treatment at 160, 220 and 250°C, respectively. The solubilisation of the organic matter into the aqueous phase is a result of hydrolysis releasing inorganic and organic compounds from carbohydrates, proteins and lipids (Danso-Boateng *et al*., 2015).

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

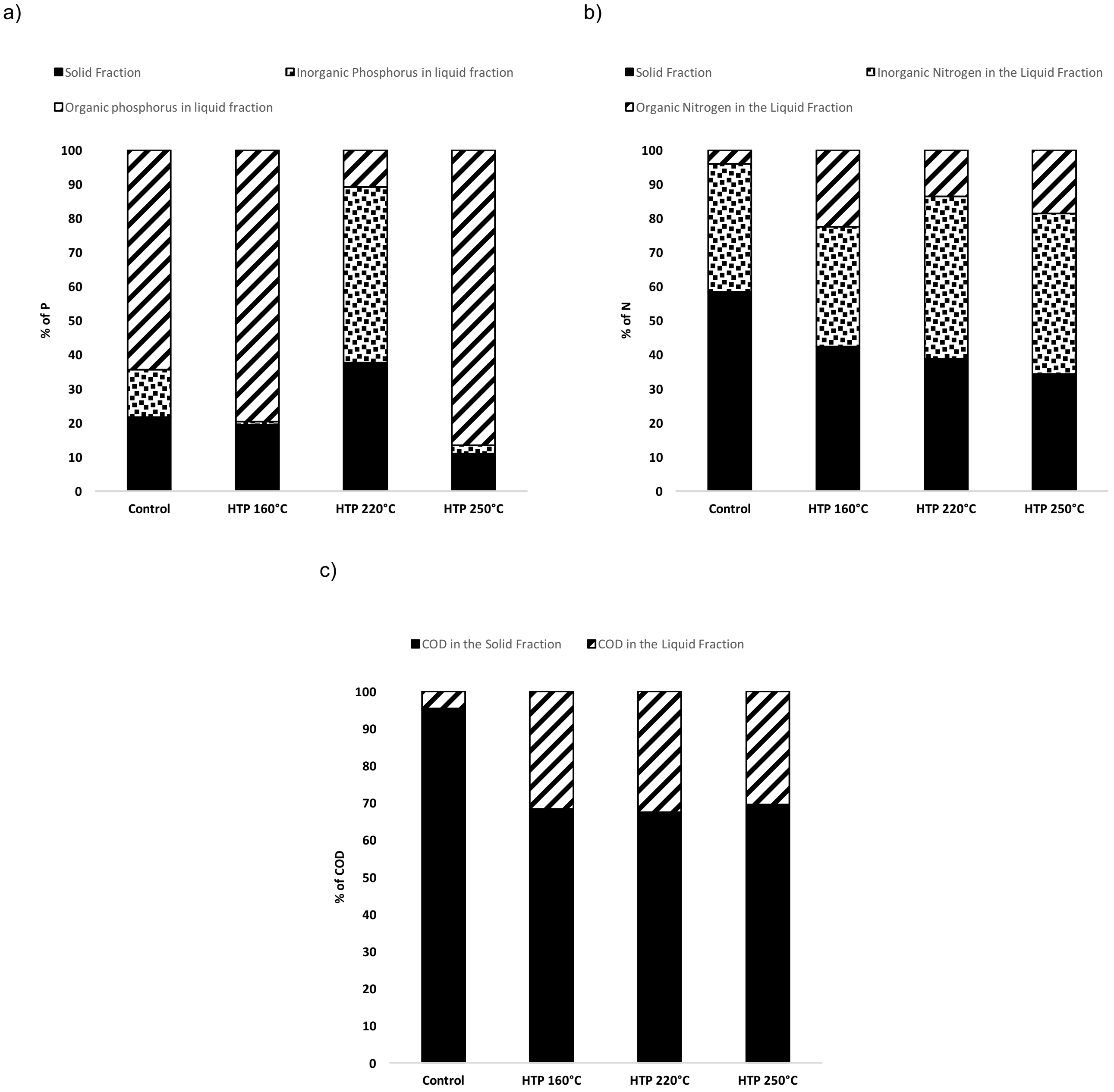


Figure 1. Fate of Phosphorus (a), Nitrogen (b) and organic matter (c) after hydrothermal processing of digestate samples (Control) for 30 min and at 160°C (5bar), 220°C (35bar) and 250°C (40bar)

3.2. Hydrochar Characteristics

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

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

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

3.2.1. Elemental composition in Hydrochar

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

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

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[a] (%db)	C (%)	H (%)	N (%)	O[b] (%)	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

[a] 100 - (moisture + ash + volatile matter).

[b] Calculated as difference between sum of C,H,N,S, ash.

3.2.2. Energy characteristics of Hydrochar

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

The calculation of energy yield provides a means of quantifying the energy remaining within the hydrochars from the original feedstock (Digestate), and is defined as the energy densification ratio multiplied by the mass yield of the hydrochar (Danso-Boateng *et al.*, 2013). The energy yield decreases with increasing temperature agreeing with the results from Danso-Boateng et al. (2015). The energy yields in our hydrochars ranged from 61.22% at 250°C to 70.05% at 160°C, but these values are significantly higher than the energy yield obtained by Berge et al. (2011) for digestate (41.5%) and more similar to the results by Danso-Boateng et al. (2015) for sewage sludge (68 - 89%). Energy densification takes place when the solid mass decreases as a result of dehydration and decarboxylation reactions; that means the carbon content increases and the hydrogen and oxygen content decrease. Therefore, temperature and reaction time have significant influence on the energy densification of the hydrochar (Danso-Boateng et al., 2015, Danso-Boateng et al., 2013). The energy densification values for the hydrochars obtained herein were 1.02 (for carbonisation at 160°C), 0.96 (for carbonisation at 220°C) and 1.08 (for carbonisation at 250°C). The values in our study were lower when compared with values obtained from primary sewage sludge by Danso-Boateng *et al.* (2015), which ranged from 1.02 to 1.28 at temperatures between 140 and 200°C and reaction times between 15 - 240min. However, it has to be taken into account that digestates have a lower carbon content compared with primary sewage sludges due to anaerobic digestion in which organic carbon is released during its conversion into biogas (CH_4 and CO_2).

Table 2.- Energy characteristics of hydrochar.

Hydrochar	HHV (Mj/Kg)	Energy densification (Mj/Kg)	Energy Yield (%)	H_{yCrec} (%)	L_{yCrec} (%)	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

HHV: High heating value
H_{yCrec}: Carbon recovered in the solid fraction
L_{yCrec}: Carbon recovered in the liquid fraction
CSF: Carbon Storage Factor

3.2.3. Carbon balance in the Hydrochar

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

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

The carbon storage factor (CSF) is the mass of carbon remaining (stored) in the solid following the biological decomposition in a dry mass of feedstock (Barlaz, 1998) and a similar approach can be applied to the remaining carbon in hydrochars after HT processes. Berge *et al.* (2011) have shown some evidence that after the HTC process (of municipal solids wastes) more carbon is stored within the hydrochar than if the waste material had been disposed uncarbonised. The CSFs of the digestate following hydrothermal treatment were 0.26, 0.26 and 0.23 for the treatments at 160°C, 220°C and 250°C respectively. Therefore, CSF values decreased as the carbonisation temperature increased, in agreement with the results reported by Danso-Boateng et al. (2015). Indeed, higher levels of CSF were obtained in our study at lower temperatures from sewage sludge digestate ranging from 0.30 (at 140°C) to 0.28-0.33 (at 160°C) and slightly lower values of CSF (0.26 to 0.28) at the highest temperature tested (200°C). (Berge et al., 2011) obtained lower values of CSF (0.14) from digestate after carbonisation at 250°C. This assessment is potentially useful in understanding the behaviour of hydrochars if used as a carbon source for soil amendment.

3.3. Characteristics of process waters

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

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

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

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

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

In addition to carbon, the levels of hydrogen and nitrogen increase after hydrothermal treatment. Moreover, the sulphur content in the liquid fractions increased from 0.74% up to 2.81% after hydrothermal treatment; that may have implications for levels of H_2S in the final biogas (or precipitation of metal sulphides), if process waters are recycled back into anaerobic digesters.

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 (%)[a]	54.11	34.50	29.75	10.92

[a] Calculated as a difference from the sum of C, H, N and S.

3.4. Anaerobic digestion of HT Slurries and Process waters

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

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

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

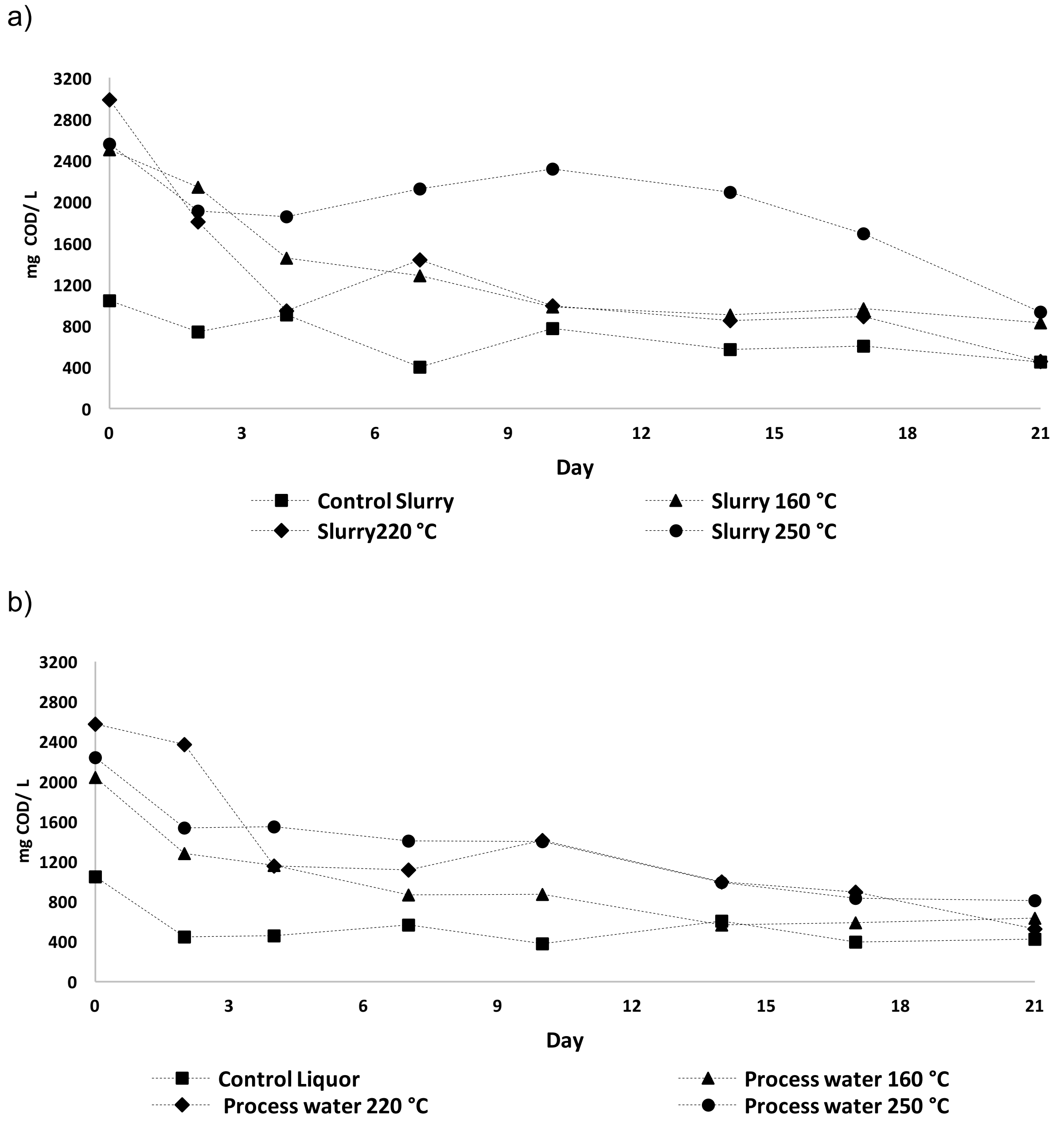


Figure 2.- Changes in soluble COD of Slurries (a) and Process Waters (b) during BMP tests.

During the anaerobic digestion process, substrate constituents are hydrolysed by bacterial action into soluble COD. The soluble COD is fermented and turned into VFAs and eventually converted into biogas by methanogenic bacteria. Yields of VFAs produced per mg soluble COD added (mg of VFAs/ mg of COD_{sol} added) during the anaerobic digestion process of Slurries and Process Waters are shown in Figure 3. The 160°C HTP treatment did not improve the contribution to VFA formation from the hydrochar as the maximum VFA/COD concentration found from the slurry sample (0.15 mg of VFAs/ mg of COD_{sol} added, at day 2) was lower than the corresponding figures found in its process water (0.22 at day 2 and a maximum of 0.24 mg of VFAs/ mg of COD_{sol} added, at day 4). That may suggest potential inhibitory effects on VFA production caused by the actual nature of the hydrochar produced at 160°C. For the HTP treatments at 220°C and 250°C, the resulting hydrochar made a substantial net contribution towards VFA formation with an increment of 13.3% at 220°C and 16.1% at 250°C, with regard to the highest figures found from process waters. For the 220°C slurry, the maximum yield found was 0.17 mg of VFAs/ mg of COD_{sol} added at day 2 and the corresponding figure found in its process water was 0.15 mg of VFAs/ mg of COD_{sol} added, also at day 2. The 250°C slurry produced 0.30 mg of VFAs/ mg of COD_{sol} added after 7 days, while the corresponding process water reported a maximum of 0.31 mg of VFAs/ mg of COD_{sol} added within the same period; the maximum yield of VFA production was found from the slurry at day 14 (0.36 mg of VFAs/ mg of COD_{sol} added).

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

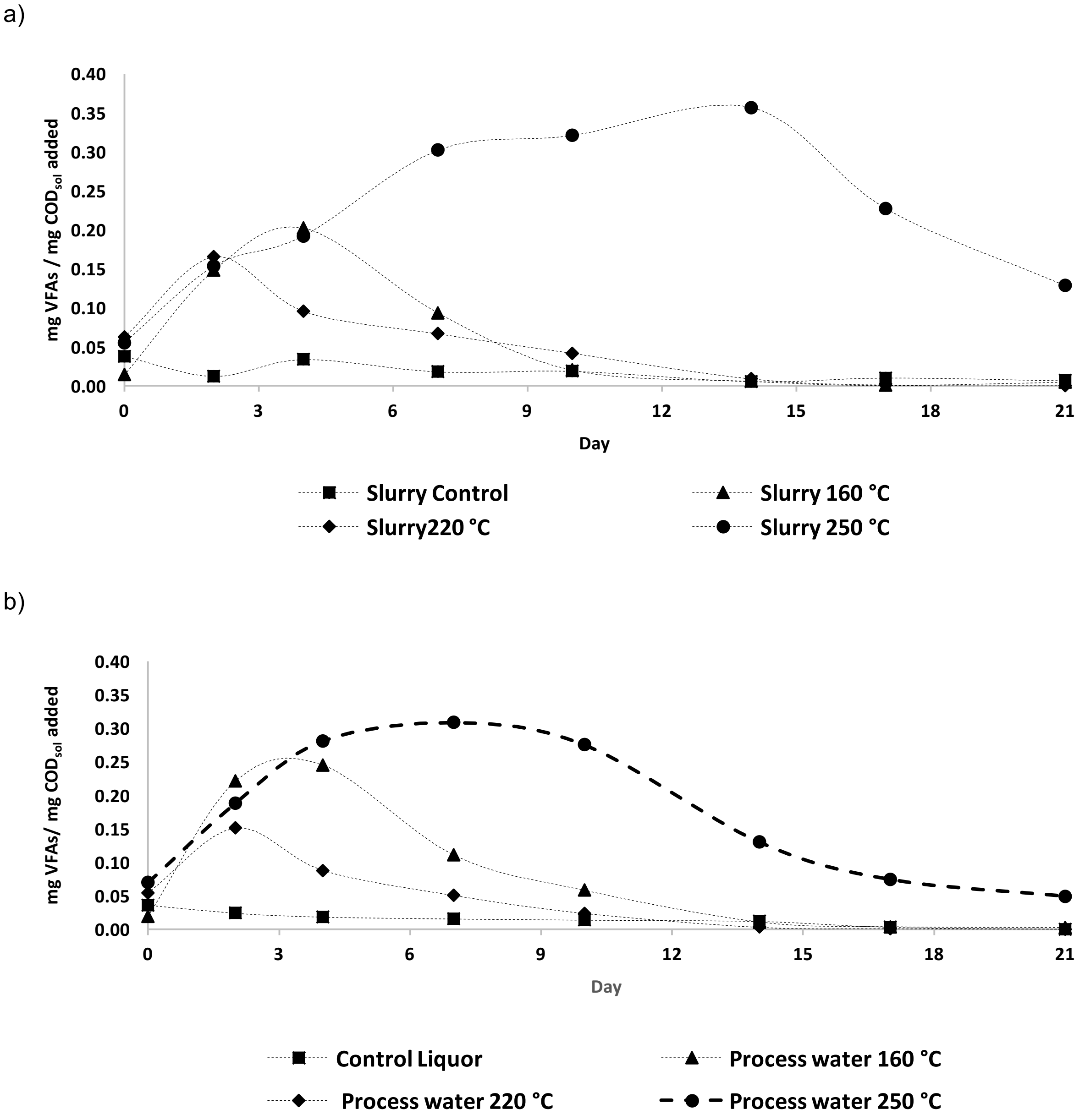


Figure 3.- Normalised VFA production from Slurries (a) and Process Waters (b) during BMP tests

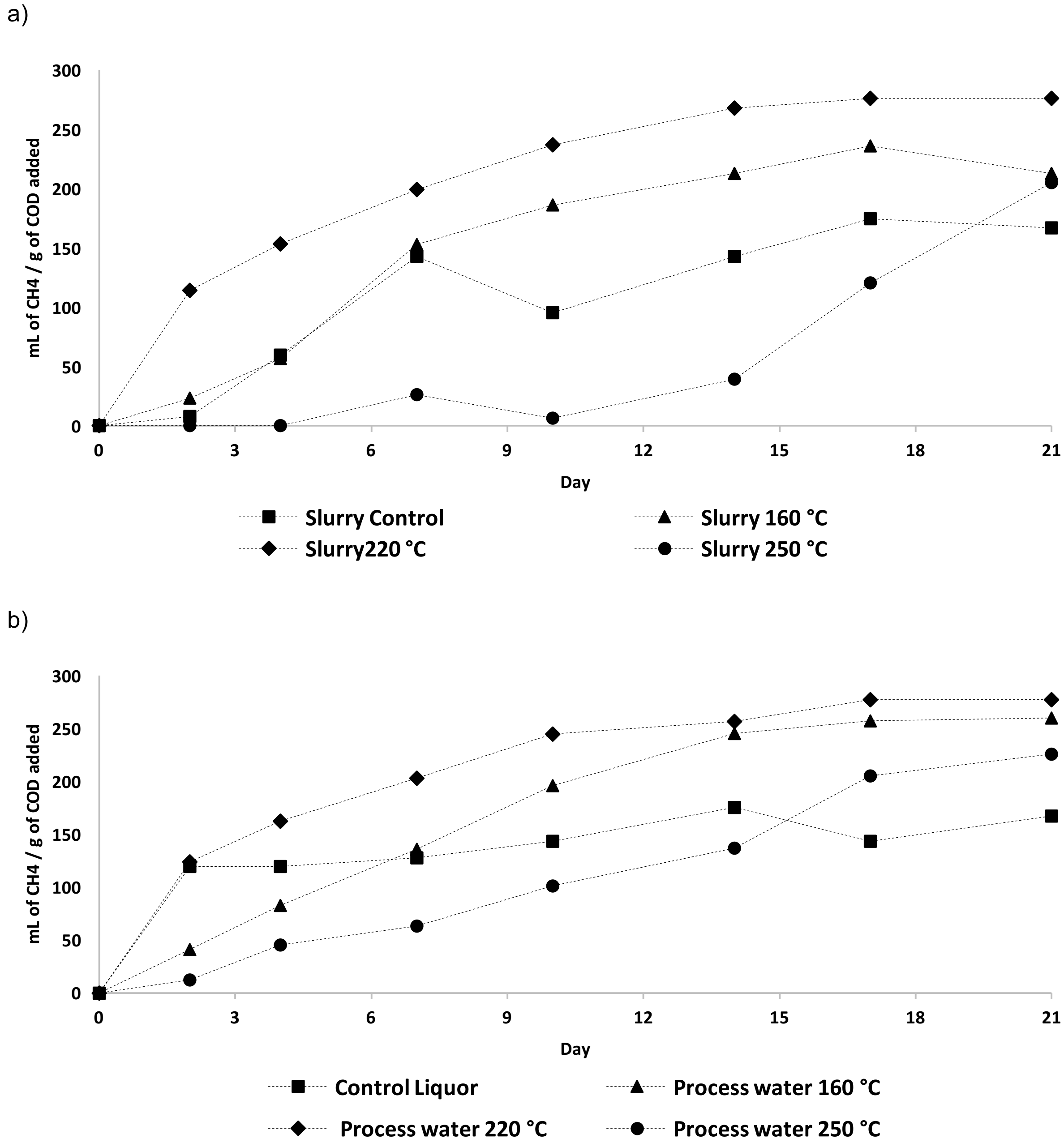


Figure 4.- Normalised methane production from Slurries (a) and Process Waters (b) during BMP tests.

Previous studies using hydrothermal processes as a pre-treatment for anaerobic digestion have shown an increase in methane yields in BMP tests, due to the additional solubilisation of organic matter achieved via thermal hydrolysis (Keymer *et al.*, 2013). After hydrothermal treatment, the BMP increases between 17% and 58% compared with the control (175 mL of CH_4/ g of COD). It is shown in Figure 4 that the BMP values for the slurries following hydrothermal treatment were 236 at

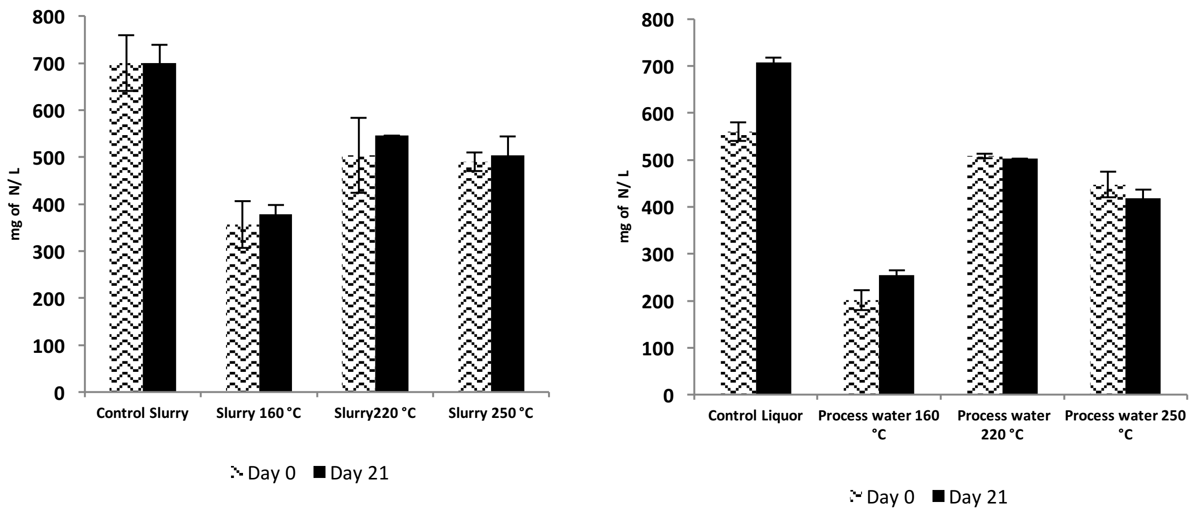
160°C, 276 at 220°C and 205 at 250°C, all reported in mL of CH_4/ g of COD. Nevertheless, it is worth to provide further discussion to the results from the BMP test of the digestate treated at 250°C, as it seems that the methane production could have continued after the 21 days of the BMP test, considering the remaining VFA concentration (Figure 3). Therefore, the methane potential of the digestate treated at 250°C has been underestimated and it is inferred that the net methane production should have been higher than the results obtained at 220°C after 21 days. The presence of hydrochar affects the production of biogas which is reflected in the delay of VFA production (Figure 3) and the subsequent delay in the production of methane (Figure 4). Also it was observed that an additional solubilisation of COD (Figure 2a) occurs after the VFAs reached the highest concentration. Although other factor that might influence is the presence of less digestible higher molecular weight organic compounds formed during the thermal process at that temperature (Danso-Boateng et al., 2015), or other compounds that could delay methane production.

The BMP values for process waters following hydrothermal treatment increased between 29% and 58% compared with the control sample (175 mL of CH_4/ g of COD). The highest value was for the processed water of 220°C treatment (277 mL of CH_4/ g of COD) followed by 160°C treatment (260 mL of CH_4/ g of COD) and 250°C treatment (225.8 mL of CH_4/ g of COD). The BMP values of process waters were similar to the slurries of the digestate after hydrothermal treatment for the treatments at 160 and 220°C and the hydrochars did not affect the anaerobic process unlike the 250°C slurry and its process water.

A similar study was carried out by Qiao et al. (2011) in which they use sewage sludge treated at 170°C for 1 hour; they also performed BMP tests on the slurry and the processed water. The results showed an improvement of 65.5% in methane production from the slurry (257 mL of CH_4/ g of VS) and 147.5% (385 mL of CH_4/ g of VS) of methane production of the process water with respect the raw sewage sludge (155 mL of CH_4/ g of VS).

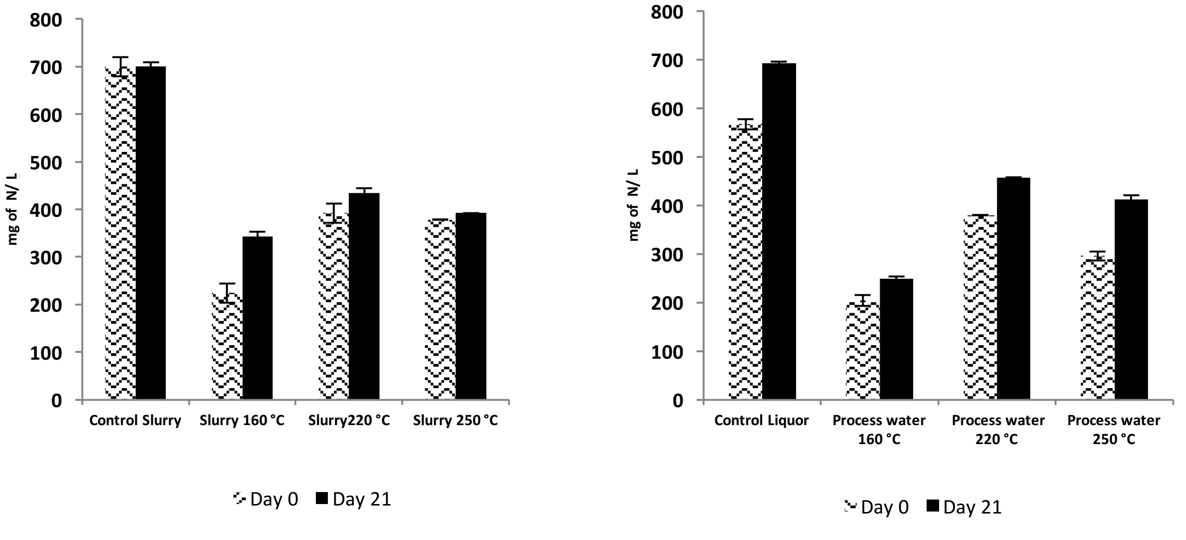
3.4.1. Nutrient solubilisation during the BMP test

Figure 5 shows the soluble nitrogen fraction (soluble TKN and ammonium) before and after anaerobic digestion (i.e., at Day 0 and Day 21 of the BMP tests). It can be seen that after anaerobic digestion, with the exception of the slurry control and the processed water at 220 and 250°C treatment, the soluble TKN concentration increased from 3 to 26% in all the other substrates. Also, the ammonium concentration increases in all substrates after the anaerobic digestion between 4 and 39%. As a result, the nitrogen solubilised during the anaerobic digestion was mostly ammonium coming from the hydrolysis step of proteins and bacterial biomass. As a consequence, an increase in the nitrogen concentration, especially in ammonium is observed (Münch and Barr, 2001, Wilson and Novak, 2009). These findings match with previous studies of substrates such as algae after hydrothermal and anaerobic treatments, in which the soluble nitrogen concentration increased after anaerobic digestion (Keymer et al., 2013, Ras et al., 2011).



a) Soluble TKN in slurries

b) Soluble TKN in process waters



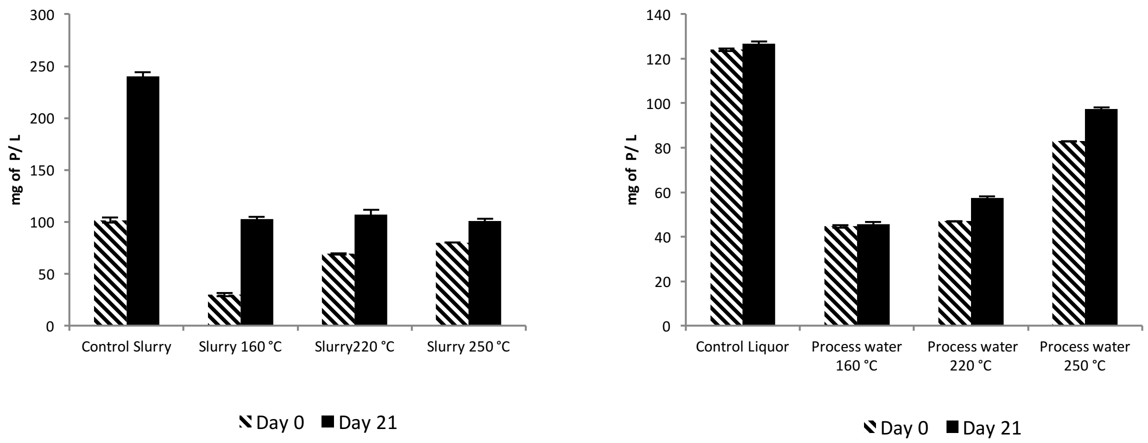
c) Ammonium in slurry

d) Ammonium in process waters

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

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

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



a) Total soluble phosporus in slurries

b) Total soluble phosphorus in process waters

c) Reactive phosphorus in slurries

d) Reactive phosphorus in process waters

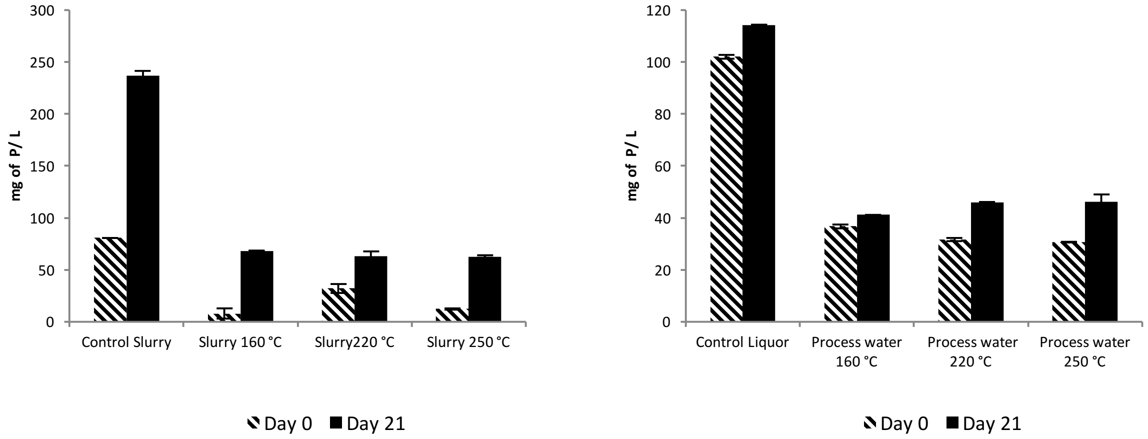


Figure 6. Changes in Total Soluble Phosphorus and Reactive Phosphorus concentrations in slurries (a and c) and in process waters (b and d) before (Day 0) and after (Day 21) BMP tests.

3.5. Theoretical BMP v. Experimental BMP

The use of empirical formulas to predict the potential production of methane is widely accepted, due largely in part to being relatively fast, reliable and economical. Nevertheless these equations do not differentiate between biodegradable and non-biodegradable organic matter (Lesteur et al., 2010, Nielfa et al., 2015). According to Labatut *et al.* (2011) the values of the theoretical formulas are always higher than the experimental ones because they do not account for the substrate biodegradability or metabolic processes. For example, the Buswell's equation does not count the carbon that is locked in the cell protoplasm of new anaerobic bacteria (nearly 12%) (Labatut *et al.*, 2011). Therefore, not all the biodegradable organic matter used by the bacteria contributes to the production of methane.

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

The Buswell's equation predicts higher values than the Boyle's equation. However, the BMPth values in both cases are higher than the experimental values. The Boyle's equation has the closest match to the experimental values and that may be due to the fact that the model considers the presence of proteins and ammonia whereas the Buswell's equation does not consider the presence of nitrogen (Nielfa *et al.*, 2015).

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

The experimental BMP tests show that the lower temperature hydrothermal treatments produce higher BMP than the higher temperature processing. This is probably due to inhibitory effects increasing with process temperatures. The control shows the lowest BMP as expected. Comparison between the theoretical prediction and experimental figures generally indicates that for lower temperature processing (160 - 220°C), the equations provide a reasonable match. The experimental BMP is 96% of the theoretical BMPth determined by the Boyle equation and 70% of the BMPth determined by the Buswell equation. As the temperature rises to 250°C, the experimental BMP drops significantly to 44% of BMPth, however this still represents a significant enhanced biogas formation. The value of biodegradability in the digestate treated at 250°C does not represent the complete potential as this test was still generating methane after 21 days so this result may underestimate the true BMP. The biodegradability values provide more robust data for predicting overall enhanced energy recovery, which can be used to better calculate and assess energy balances for integrating AD and HTC at WWTWs. Based on the results in this study, it is likely that lower temperature hydrothermal treatment is more advantageous than higher temperature for processing sewage sludge digestate.

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

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

Sample	BMPexp (mL of CH_4 /g of COD added)	BMPth Boyle's Equation (mL CH_4 / g COD)	BMP Buswell's eq. (mL CH_4 / 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%

BD: Biodegradability; DT: Digestate treated;
BMP_{exp}: Experimental Biomethane Potential; BMPth: Theoretical Biomethane Potential.

3.6. Energy production of the hydrothermal treatments.

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

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

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

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

	Energy produced from CH_4 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

BMP of Mix sludge = 226 of CH4 /g of COD added (experimental value)
*BMP of THP Mix sludge = 323.2 of CH4 /g of COD added (assuming 43% additional production) (Sridhar Pilli et al., 2015)
HHV of methane, 1m3 = 35.8Mj

4. Conclusions

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

5. Acknowledgments

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