Anaerobic Digestion of Liquid Products following Hydrothermal Carbonisation of Sewage Sludge with different reaction conditions

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Abstract

The Hydrothermal Carbonisation (HTC) conversion of wet wastes, such as sewage sludge, generates a carbon- rich material (called 'hydrochar'), and an aqueous fraction with a small release of gas. The liquid fraction is high in soluble COD, from 10-50g/L, and could not be reused or discharged to the natural environment without treatment. This study investigates the anaerobic digestability (AD) of this HTC liquid stream from different HTC temperatures and retention times (140–200^{o}C for 30-240 minutes).It is focused on biogas production in order to improve the energy input of the HTC process and to render the entire process sustainable.The results demonstrated that the lower HTC temperatures gave better biogas production. The biogas yield from the 140°C HTC filtrate digestion was 0.51-0.84 L/L $_{reactor}$ /d, 0.37 L/L $_{reactor}$ /d from 170°C and 0.35-0.51 L/L $_{reactor}$ /d from 180°C. The lowest AD efficiency was recorded for the treatment from 200°C when the biogas yield was 0.08 L/L $_{reactor}$ /d. The best quality of hydrochar, on the other hand, has been shown to be produced by the highest temperatures. The data also shows that low AD hydraulic retention time (HRT), typical of high rate fixed biomass digesters can be used to treat the HTC filtrate. Halving the AD HRT to 0.9 days resulted in 1.8 to 6.8 times greater biogas yield.

Keywords: Hydrothermal carbonisation, anaerobic digestion, sludge treatment, liquid, filtrate

1-INTRODUCTION

There is renewed interest in thermal sewage sludge treatment due to the successful commercialization of Hydrothermal carbonisation (HTC), both to increase biogas yields in anaerobic digestion (AD) but also (> 160 0C) to generate a carbon-enriched char (Libra et al., 2011). The products are stable and sanitised compared to traditional sludge and sewage treatment. Most studies have focused on the energy value of hydrochar, its use for soil improvement or as an adsorbent for soil remediation. However, when HTC is to be used to produce char at the higher temperature range a high concentration soluble organic compounds leachate is generated which requires further treatment (COD >20g/L) and this has received comparatively little research attention. Water plays an important role in HTC reaction as a solvent and 22-24% of the carbon remains in the liquid fraction increasing with temperature (E.Danso-Boateng,2013).Previous work on AD thermal pre-treatment indicates dewaterability and soluble organic matter increase as the HTC temperature increases (above 150°C) (Fisher et al., 1971). Some literature, also suggests concurrent formation of refractory COD (Penaud et al., 1999) at higher temperatures, mainly through Maillard reactions, reducing digestibility. Compounds such as furans, phenols, acetic acid, levulinic acid, and other persistent coloured soluble organic compounds has been reported in previous works (Goto et al., 2004; Berge et al., 2011; Wang et al., 2012). Maillard reactions depend on conditions and this study investigates the anaerobic treatment of the HTC liquid stream from sewage sludge for the common temperatures ranges 140-160oC and 160-200oC and retention times (30-240 minutes) for either extra anaerobic biogas or biochar production for smaller wastewater treatment plants.

Figure 1 shows a hypothetical combined HTC-AD process as a suggestion for a combined resource recovery/wastewater process. The main steps are the HTC process followed by the separation of the products using a pressure filter. The liquid is digested anaerobically producing biogas which is combusted to heat the HTC reactor. Regarding the solids there are different options depending on the energy and environmental needs that a community has. Drying the solids produces a hydrochar which can be a fuel for combustion, or it can be used with fermentation to produce bioethanol. The third option is to use the solids as a soil conditioner. Using the hydrochar for soil improvement has recently been reported to increase soil fertility while providing a long-term carbon sink (Titirici, 2007). Energy is also recovered from the steam released in the flash tank (Figure 1), after the reactor, which can be used to improve the energy balance of the proposed process.

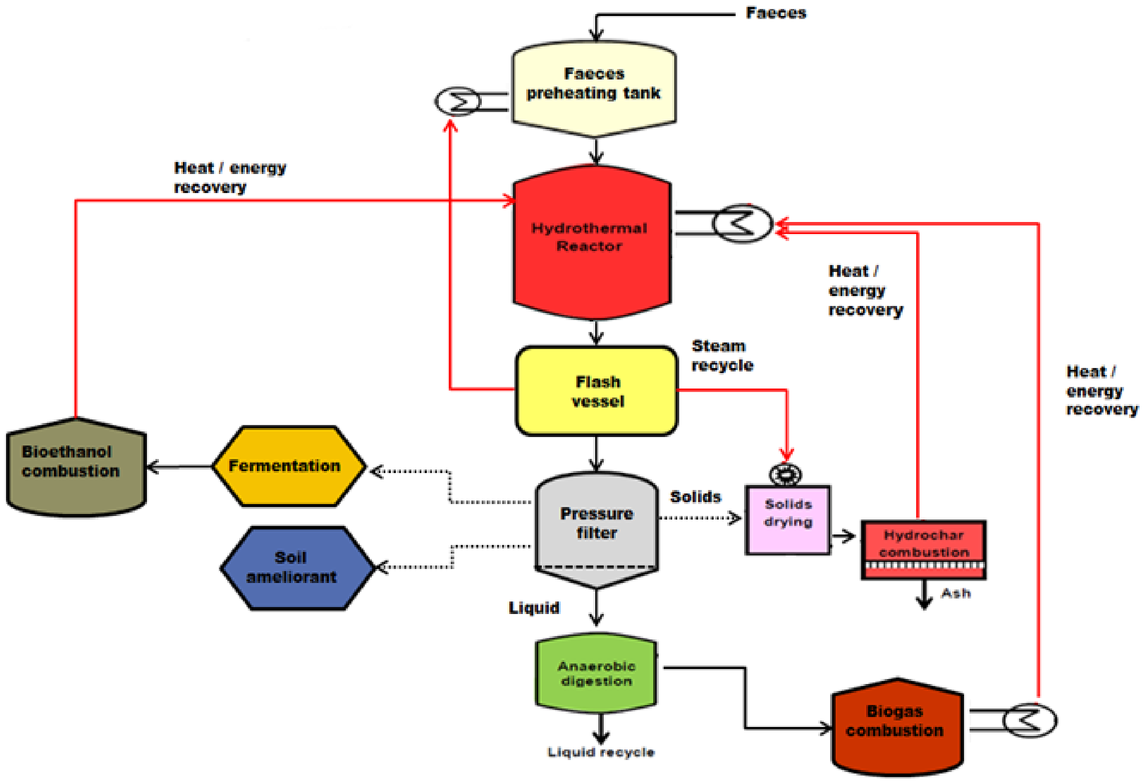


Figure 1: Flow diagram of the HTC-AD combined faeces treatment method.

2-MATERIALS AND METHODS

2.1- HTC process

A custom designed rig was used for the HTC process, which was operating using a 5 L reactor. A faecal simulant formulated by the recipe of Wignarajah *et al* (2006) was used which comprised of 37.5% cellulose, 37.5% yeast, 20% peanut oil, 4% KCl, 1% $Ca(H_2PO_4)$ in a suspension of 90% moisture (i.e. 10% solids). The material is pumped into the reactor and heated to the required temperature: 140-200°C (via an oil heater unit) under corresponding pressure and maintained for the required contact time: 30-240 min. Following the hydrothermal treatment the slurry was transferred into a flash tank where it the pressure was dropped and the material allowed to cool to room temperature. The carbonised material was then filtered using a 60 micron stainless steel filter under a slight residual pressure. This filtrate was used for the anaerobic digestion experiments. The operation of the rig was controlled by a LabView software program. Analytical characteristics of

HTC filtrates are given in Table 1. In order to investigate the increase of the biodegradability in lower temperatures, 140°C was chosen as the lowest safe-limit temperature to ensure sterilized hydrochar and filtrate (> 130°C recommended autoclave temperature).

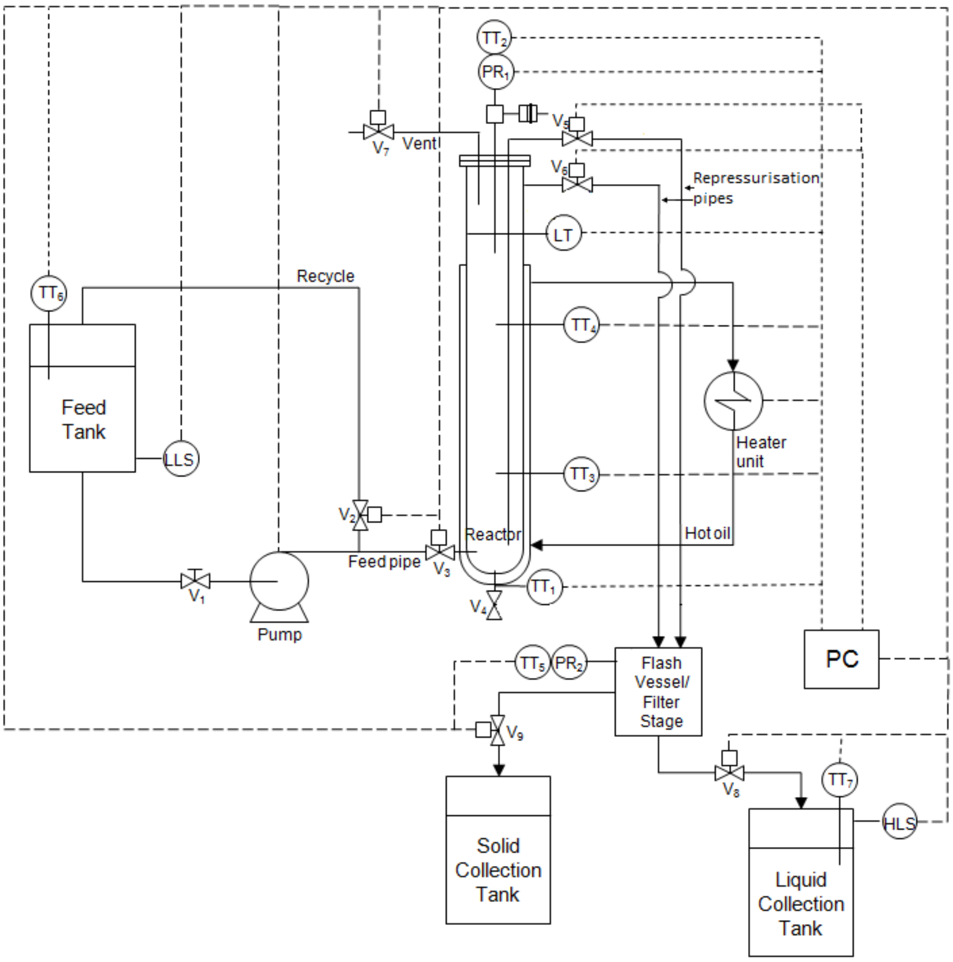


Figure 2: Schematic of the HTC plant.

Table 1: Overview of the analytical characteristics of the HTC filtrate processed at 140-200°C for 30-240 min.

	COD soluble (g/L)	COD total (g/L)	TOC (g/L)	TS (g/L)	TS %	VS (g/L)	VS%	pH	VFA (g/L)
200℃, 30min	30.19	54.52	10.38	44.07	4.06	34.83	80.21	4.41	4.55
180℃, 30min	27.19	47.53	8.70	18.65	1.88	15.11	20.98	5.06	2.14
180℃, 90min	25.90	41.52	7.98	22.53	2.64	17.93	80.36	4.58	3.61
180℃, 120min	12.18	15.81	3.89	12.05	1.94	9.88	82.01	4.59	2.94
170℃, 60min	20.07	36.45	5.90	25.04	2.47	18.75	74.88	4.92	2.78
140℃, 30min	19.95	33.67	6.78	26.60	2.66	20.89	78.28	6.91	3.23
140℃,60min	24.57	26.6	9.11	27.03	2.70	19.66	72.80	7.79	3.38
140℃,120,min	30.99	97.63	8.92	24.85	2.49	18.78	75.60	5.06	2.96
140℃,240min	38.39	85.02	10.18	26.77	2.68	20.73	77.44	3.83	2.39

2.2- Anaerobic digestion

Two identical, anaerobic, fixed-film, digesters, each of 9 litres (working volume) were operated continuously at the standard 37□C. An initial experiment with direct feeding of the raw waste led to digester instability which resulted in a low conversion of COD to gas and finally acidic inhibition. Dilution by recycling was successfully used as a method to cope with the strong HTC filtrate. It was shown that a dilution ratio of (10:1) provided optimum buffering and recycling of nutrients. This was achieved by recycling the effluent from each digester back into the feed tank (as shown in the Figure 3) recycle ratios of between 2 and 10:1 are widely used in higher rate digesters to buffer strong feeds and recycle trace nutrients.

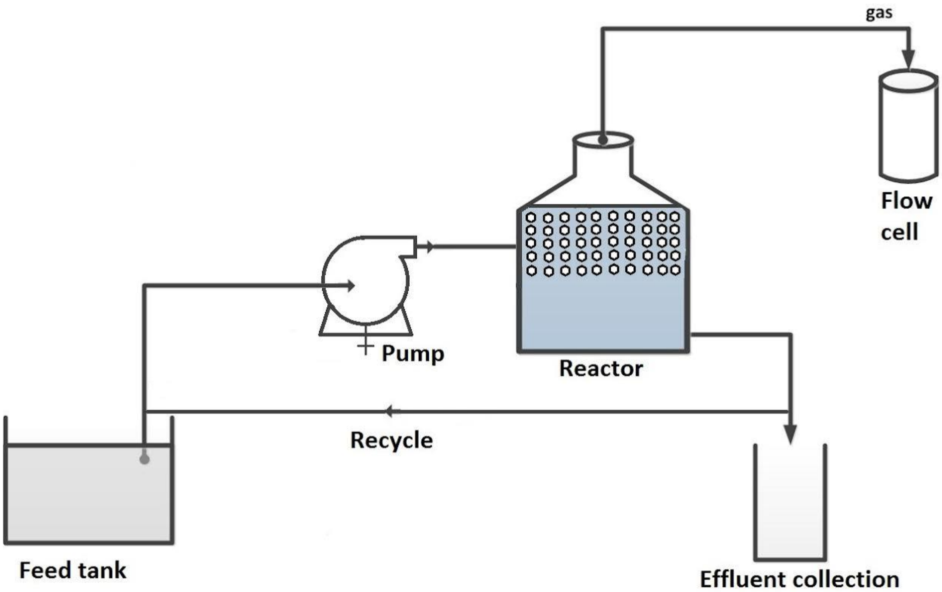


Figure 3: Schematic of the anaerobic digestion process operated in a warm room (37°C).

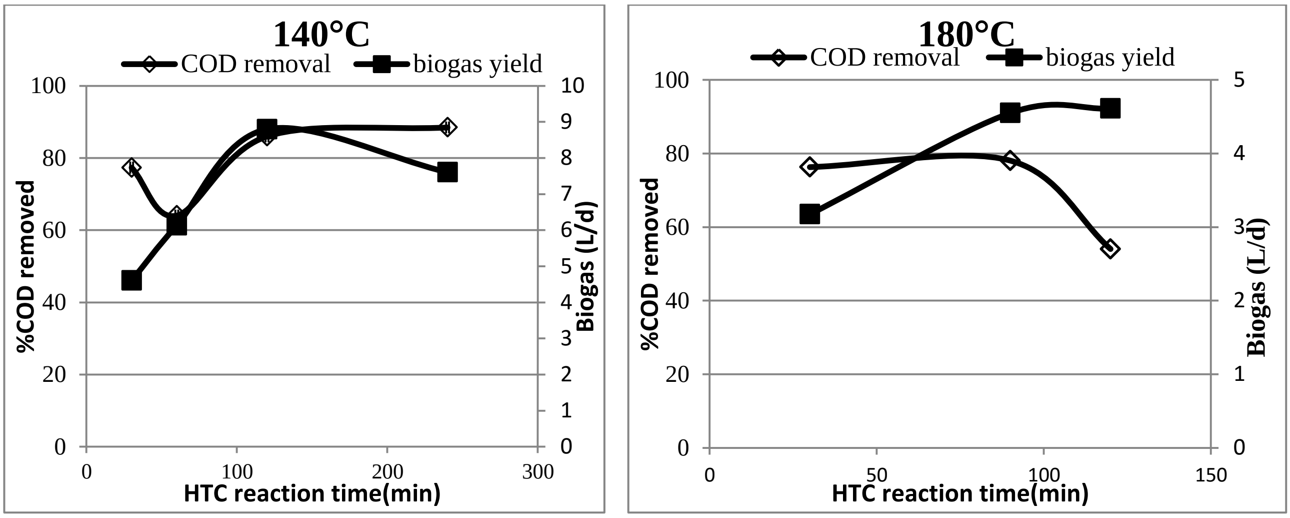
2.3- Analytical methods

The influent and effluent of the anaerobic reactors was analysed for chemical oxygen demand (COD), total organic carbon (TOC), total solids (TS), volatile solids (VS), pH, Ripley's ratio, biochemical oxygen demand (BOD) and volatile fatty acids (VFA), all according to standard ISO methods (APHA 2005). The volume and composition of the biogas produced were monitored using a FLO CELL^{TM} flow meter and a GMF 400series infra-red, respectively.

3-RESULTS AND DISCUSSION

3.1-Effect of HTC reaction conditions on AD performance

Figure 4 illustrates the COD removal and biogas production, for filtrates processed at 140 ^{o}C and 180^{o}C for 30-240 min, as averages from 40 days of continuous AD operation. Ripley's ratio was measured daily and during the whole duration of the experiments it was monitored below 0.5, which indicates a stable AD operation. Increasing the HTC reaction time increases the solubilisation of COD, increases the load and gives better conversions of COD to biogas up to 120 min at 140°C and 90min at 180°C. Total organic carbon on the other hand was less affected by HTC conditions (Figure 5) suggesting the sub 60 micron solids in the filtrate are significant. It can be suggested that some COD removal may be from coagulation with the biofilms but this need more extensive data. Further increase in reaction time reduces AD performance.



Figures 4: Percentage of COD removed and the biogas produced for digestion of: 140°C and 180°C HTC filtrate.

More experiments were conducted using HTC filtrates at a range of temperature 140-200°C and reaction time30-240 minutes (Table 2, Figure 5). From figure 5 it was concluded that the extent of carbonisation as it affects COD removal and biodegradability was both temperature and reaction time dependant. Charing or blackening of the HTC solids was not observed at 140°C at any retention times tested but occurred at 180°C and above, after 30 minutes, as confirmed by previous study (E.Danso-Boateng et al, 2015). The results suggest biogas production is more sensitive, where there is a trend of lower temperatures leading to greater biogas yield.

Methane percentage in the biogas yield was stable throughout the experiment ranging from 63.5-77.7%. Typical percentage of methane after AD of organic solids and liquid waste is around 60%. Stoichiometrically, 1kg of COD releases about 15,625 moles of methane gas. Thus, 1kg of COD is producing 0.35 m^3 or 0.25 kg of methane at STP regarding an ideal substrate as acetate, (S.K.Khanal,2008).Yields from the 140°C HTC filtrate digestion was at STP 0.097- 0.168 LCH_4 /g COD removed and 0.093-0.209 LCH_4 /g COD removed at 180°C. The lowest AD efficiency was recorded from treatment at 200°C when the biogas yield was 0.026 LCH_4 /g COD removed. Wirth et al reported, using real sewage sludge treated at 200°C for 6 hours, methane yields in rate of 0.144-0.178 LCH_4 /g COD for different OLRs (1-5 g/L). As the feedstock in this study is simulant performance differences are expected, but it can be suggested that treatment in lower HTC temperatures is affecting positively the production of biogas during the AD of the liquor.

Table 2: Overview of AD performance for HTC filtrates processed at different temperatures and reaction times. Standard deviations are given in parenthesis.

HTC reaction T	140°C				170°C	180°C			200°C
HTC reaction time (min)	30	60	120	240	60	30	90	120	30
OLR (gCOD/L/d)	2.217	2.730	3.674	4.755	1.115	3.223	3.646	1.842	1.813

COD removal %	77.3 (±0.979)	64.0 (±6.383)	85.9 (±3.517)	88.4 (±4.115)	58.2 (±12.942)	76.3 (±2.315)	78.0 (±3.844)	40.2 (±5.567)	62.0 (±6.066)
Biogas yield (Lgas/ Lreactor/d)	0.511 (±0.168)	0.681 (±0.362)	0.977 (±0.176)	0.845 (±0.290)	0.369 (±0.262)	0.352 (±0.208)	0.505 (±0.300)	0.512 (±0.279)	0.080 (±0.089)
CH_4 (L/gCOD removed)	0.126 (±0.015)	0.168 (±0.015)	0.146 (±0.016)	0.097 (±0.012)	0.158 (±0.0.17)	0.106 (±0.008)	0.093 (±0.007)	0.209 (±0.015)	0.026 (±0.001)
COD effluent (g/L)	4.52	9.60	4.56	4.89	8.41	6.88	7.20	7.27	11.83

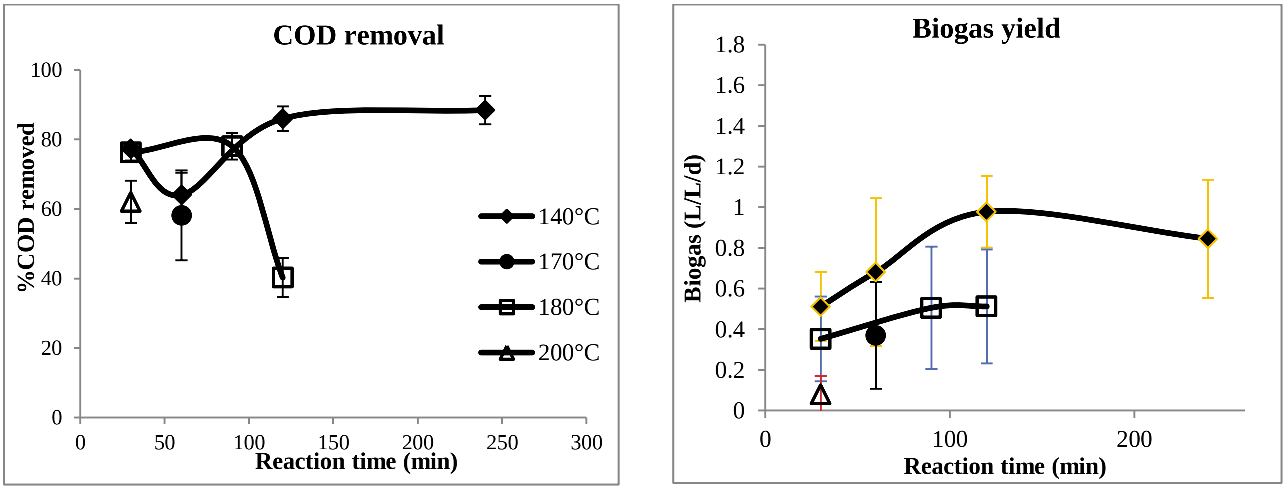


Figure 5: Results of COD removal and biogas yield during AD treatment of HTC effluent at 140°C- 200°C for 30- 240 minutes.

The reduction in biodegradability with increased temperature was supported by both BOD and respiration rate measurements shown in Figures 7 a-b. The graphs of these two indicators show the same tendency as biogas yields. With the increase of temperature the decrease of the respiration rate and the BOD occurs. Standard Biological Methane Potential (BMP) tests were also used but gave poor reproducibility compared to respiration rates and were abandoned.

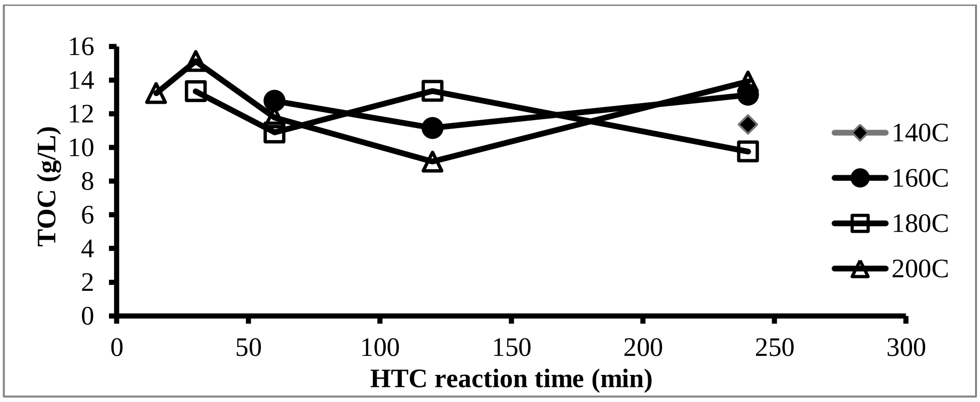


Figure 6: Total organic carbon (TOC) of liquid filtrates after 140-200°C and 30-240 min HTC treatment.

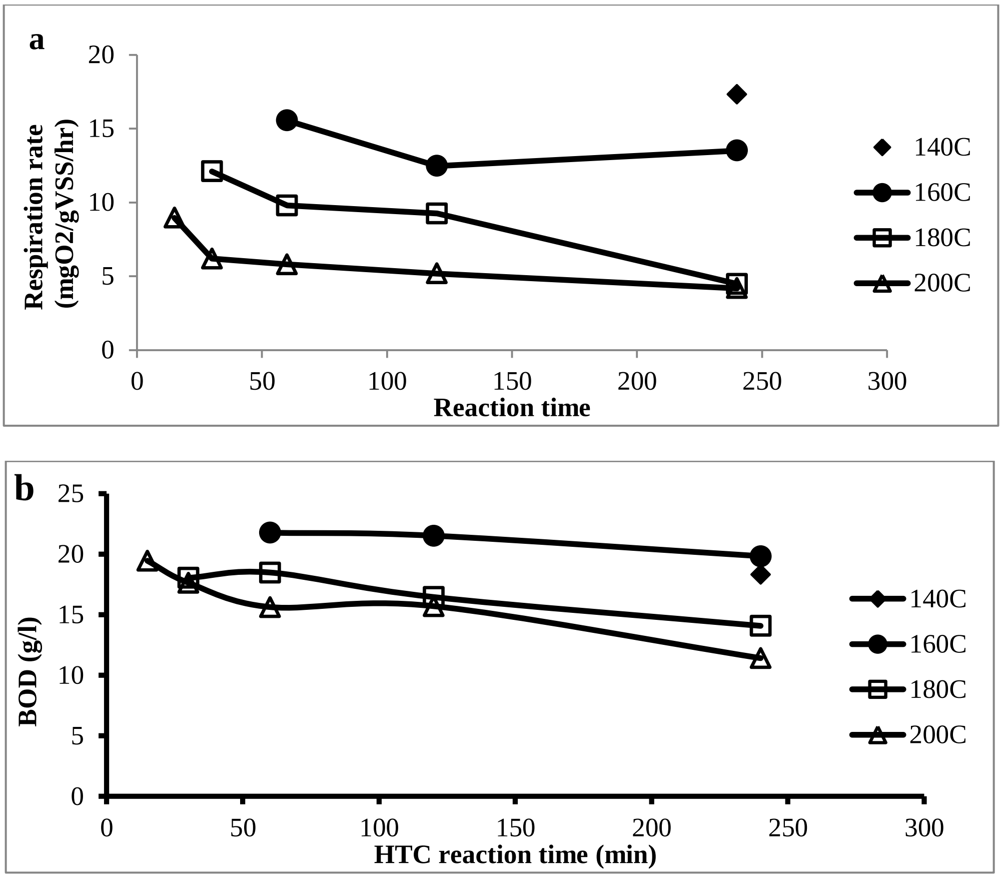


Figure 7: a) Respiration rate and b) BOD of liquid filtrates after 140-200°C and 30-240 min HTC treatment.

The methanogenesis is considered to be the rate limiting step of AD from previous report using similar kind of feedstock (Writh et al, 2015) reporting a kinetic constant of 0.044. The Chapman model (Pohl, 2012) was used to determine the kinetic constants for the methane production (Equation 1, Table 4).

$$Y_{CH4}=Y_{CH4\,max}*(1\text{-}exp^{1-km*t})^{\,c} \qquad (1)$$

As the treating HTC temperature rises the methanogenesis is getting slower except of the filtrate of 180°C for 30 min which showed a much higher constant comparing with the one of 170°C and for the longer HTC treatment at the same temperature. A perfect substrate as the acetate produces methane with constant in range of 0.2-0.7 (Fukuzaki, 1990). Moestedt et al, reported methanogenesis constants of 0.02-0.09 during AD of food, slaughterhouse waste and glycerin considered as high biodegradable substrate.

Table 4: Methanogenesis contants for each HTC filtrate

	Reaction time (min)	**Methane production constant (k_m)**
140°C	30	$6.96*10^{-4}$
	60	$1.01*10^{-2}$
	120	$9.46*10^{-3}$
	240	$6.70*10^{-2}$

170°C	60	$1.59*10^{-4}$
180°C	30	$3.27*10^{-2}$
	90	$2.35*10^{-7}$
	120	$1.37*10^{-7}$
200°C	30	$8.92*10^{-8}$

The COD concentrations in the effluent of the digesters range between 4.52-11.83 g COD/L for the different filtrates. The percentage of COD removed is satisfactory and stable throughout the operation as reported by the standard deviations (Table 2). However, the organic load coming out in the effluent is still high so further treatment is needed if disposal to the environment is considered. The option of recycling as flashing water is an alternative but still it may cause problems of accumulation and health risks.

The COD removal was also calculated by the methane production using the theoretical relation mentioned above (0.35g COD for 1L of methane). A great difference between these calculation was noted (Figure 8) as only 16.58-42.81% of COD was converted to methane although the COD degradations based on the soluble effluent were a lot higher. This can be referred to the microbial growth, the accumulation in the AF digesters of solids. However, due to the fluctuation of the biogas measurements reported and to the high solid removal achieved, the assumption was made that some of the gas was unaccounted for.

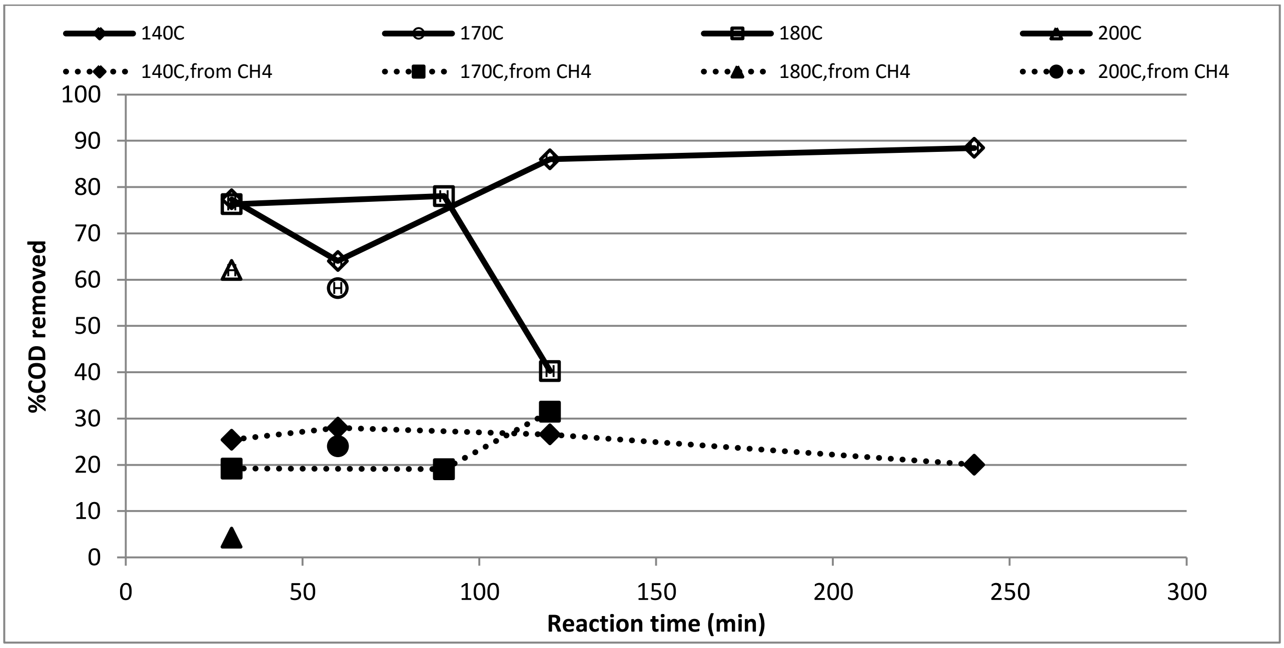


Figure 8: COD removal rates calculated based on dissolved COD in the effluent and on the methane production measurements.

3.2-Effect of the hydraulic retention time to the efficiency of the anaerobic digestion

Two AD hydraulic retention times were tested 1.8 d and 0.9 d. The main difference was observed for the biogas production (Table 5). By decreasing the hydraulic retention time, so increase the flow rate, the performance meliorates dramatically. The yield was more than double for the lower retention time (0.9 d) in all the experiments. Specifically, when the lower HRT was applied the biogas produced was 1.8 to 6.8 times greater. This is supported by the literature on biomass retaining reactors which have a typical retention time of 5-10 hours and loading rates up to 40 kg COD/m3/day for the highly treatable wastes (Zheng et al., 2012). Further work is needed to identify the maximum load but this data presentation corroborates the earlier conclusion that the longer the HTC reaction time or the higher the temperature the greater the proportion of refractory organics.

Table 5: Biogas production after AD of different HTC conditions filtrates under two HRT times.

	Reaction time (min)	Biogas yield (L/L reactor/day)		COD removal %	
		HRT=1.8d	HRT=0.9d	HRT =1.8d	HRT=0.9d
140°C	30	0.284	0.514	73.9	77.3
	60	0.100	0.681	55.3	64.0
	120	0.244	0.978	90.3	85.9
	240	0.224	0.845	92.2	88.4
180°C	30	0.101	0.353	75.1	76.3

Additional AD HRT experiments were carried out on filtrate from the HTC run at 180°C for 90 min, since obvious char was produced at this temperature but not at 140°C. The data is shown in Figure 9.Gas yields at 0.45 days are similar to those achieved at 140°C and suggest that char production without prejudicing the treatability of the filtrate could be possible.

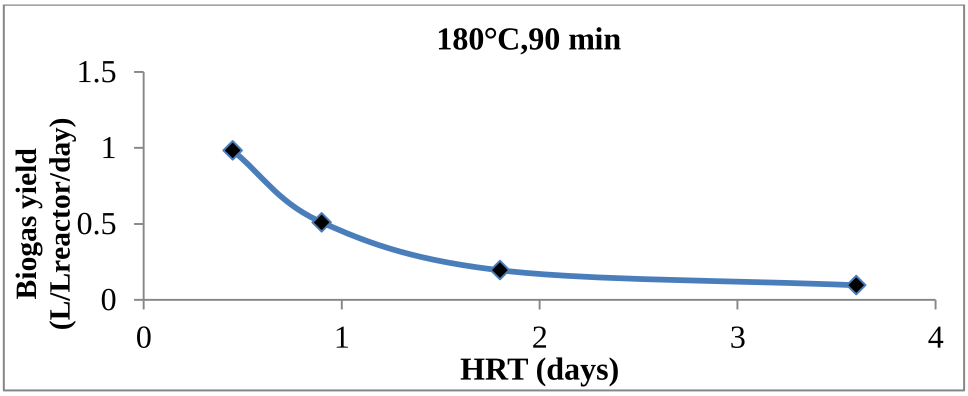


Figure 9: Biogas yield during AD treatment of HTC effluent at 180°C for 90 minutes with AD hydraulic retention times of 0.45-3.6 days.

4-CONCLUSIONS

A combined HTC-AD process could contribute to smaller, decentralised, energy efficient, safer waste treatment that could also be adjusted to local needs.

Lower HTC temperatures and retentions favour treatability while higher temperatures promote char and dewatering. HTC at 1800C at HRT < 90minutes could be a compromise.

The retained biomass digesters were able to operate at loads and levels of treatment typical of those used for food effluents when these treatability changes were taken account of.

ACKNOWLEDGMENTS
The authors gratefully acknowledge the support of the Gates Foundation who funded this work through the Reinvent the toilet programme.

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