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Comparative assessment of pre- and inter-stage hydrothermal treatment of municipal sludge for increased methane production

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Abstract

Hydrothermal treatment (HT) is a promising technology to enhance anaerobic digestion (AD) of municipal sludge. However, the capacity of pre- and inter-stage HT (i.e., HT-AD and AD-HT-AD, respectively) to enhance the digestibility of municipal sludge has not been sufficiently explored. This study compared the efficacy of pre- and inter-stage HT performed from 90 to 185°C to enhance methane production from a mixture of primary sludge and waste activated sludge using mesophilic (35°C) biochemical methane potential tests. In both configurations, sludge solubilization increased with HT temperature. HT-AD, and to a greater extent AD-HT-AD, increased the release of ammonium nitrogen. Even though HT at 185°C dramatically increased sludge solubilization, the overall specific methane yield with HT at 185°C was lower than or comparable to that at lower HT temperatures in the HT-AD and AD-HT-AD configurations, respectively. Up to 155°C HT, the overall specific methane yield with the HT-AD configuration was higher by 4.9%–8.3% compared to the AD-HT-AD configuration. However, when the HT energy was considered, compared to the control (i.e., AD of sludge without HT), the net energy gain (ΔE) decreased as the HT temperature increased, becoming negative at an HT of 185°C. The AD-HT-AD configuration resulted in a higher overall volatile solids destruction (by 8.1 to 20.1%). In conclusion, for municipal sludge with a relatively high ultimate digestibility, as was the case in this study, HT-AD is preferable as it has a smaller footprint and is easier to operate than the AD-HT-AD configuration. However, given the significantly higher volatile solids destruction in the AD-HT-AD configuration, compared to the HT-AD configuration, AD-HT-AD may be more beneficial considering post-AD sludge handling processes. © 2021 Water Environment Federation

Practitioner points

- Hydrothermal treatment (HT) increased the rate and extent of methane production from municipal sludge mixture.
- 155°C was the optimal temperature for either pre- or inter-stage HT to increase biogas production.
- Pre- and inter-stage HT resulted in comparable ultimate methane production.
- Pre-stage HT is preferable to inter-stage HT (smaller footprint, easier to operate).
- AD-HT-AD resulted in significantly higher volatile solids destruction compared to the HT-AD configuration.

Key words

anaerobic digestion; biogas production; BMP test; energy balance; hydrothermal treatment; methane production; municipal sludge; sludge solubilization

Introduction

Water resource recovery facilities (WRRFs) in the United States produce over 12 million dry metric tons of municipal sludge annually (Seiple et al., 2017). Sludge

Table 1. Characteristics of sludge mixture and pre-stage HT sludge

PARAMETER	SLUDGE MIXTURE (CONTROL)	PRE-STAGE HT SLUDGE AFTER HT AT			
		90°C	125°C	155°C	185°C
pH	6.34	6.04	5.84	5.67	5.41
TS (g/L)	59.36 ± 0.56[a]	59.42 ± 0.37	58.36 ± 0.23	58.76 ± 0.34	53.32 ± 0.54
VS (g/L)	45.33 ± 1.06	46.29 ± 0.09	45.55 ± 0.68	45.22 ± 0.39	39.87 ± 0.70
Total COD (mg/L)	72,757 ± 718	73,513 ± 76	73,360 ± 344	75,655 ± 153	74,667 ± 766
Soluble COD (mg/L)	8,767 ± 55	24,942 ± 128	28,298 ± 52	32,736 ± 73	36,312 ± 106
Solubilization (%)[b]	NA[c]	25.3	30.5	37.5	43.0
Ammonium (mg N/L)	501 ± 11	431 ± 1	420 ± 2	585 ± 3	885 ± 8
UV_{254}	7.56 ± 0.09	61.94 ± 0.19	84.33 ± 0.10	90.14 ± 0.15	143.00 ± 0.37

[a]Mean ± standard deviation (n = 3).

[b]COD basis.

[c]NA, not applicable.

must be appropriately treated before its final disposal or utilization (e.g., land application) to minimize its negative impact on the environment and public health, as well as to recover resources (e.g., methane as renewable energy and nutrients, such as N and P). Anaerobic digestion (AD) is the most common means to stabilize sludge, reduce its odor, inactivate pathogens, and convert waste organic matter to methane, a renewable biofuel (Aragón-Briceño et al., 2021; Grady et al., 2011; Kumar & Samadder, 2020; McCarty et al., 2011). Hydrolysis, acidogenesis, acetogenesis, and methanogenesis are the four key sub-processes in AD (Grady et al., 2011; Pavlostathis, 2011). Hydrolysis is usually the rate-controlling step for AD of particulate organic wastes (Chen et al., 2020; Malhotra & Garg, 2019), especially waste activated sludge (WAS), which contains complex structures such as cellular polymers (Şahinkaya & Sevimli, 2013; Xu et al., 2018). Slow hydrolysis strongly hinders AD performance. Sludge pre-treatment technologies, such as mechanical, thermal, chemical, biological, and their combinations accelerate AD through disruption of cell wall/envelope, transformation of extracellular polymeric substances (EPS), and conversion of complex, particulate organic matter to simpler, readily biodegradable substrates (Atelge et al., 2020; Nazari et al., 2017; Xu et al., 2020; Zhen et al., 2017). Among these technologies, hydrothermal treatment (HT) is very effective in enhancing sludge biodegradability and biogas production, improving sludge dewaterability, inactivating pathogens, and intensifying treatment for full-scale application (Biswal et al., 2020; Choi et al., 2018; Kor-Bicakci & Eskicioglu, 2019; Lu et al., 2008; Pilli et al., 2015; Wu et al., 2021).

Numerous studies have explored the effect of HT as a pre-stage process (i.e., HT-AD) in enhancing organic matter degradation and biogas production (Biswal et al., 2020; Kakar et al., 2020; Liu et al., 2021; Pilli et al., 2015; Taboada-Santos et al., 2019; Wu et al., 2021). Municipal sludge contains both complex, particulate and simpler, readily biodegradable organic matter. Conventional AD degrades the readily biodegradable sludge substrates efficiently and a small portion of the complex organic matter. Thus, the anaerobic digestate contains mostly hardly biodegradable organic matter and is an ideal feedstock for HT (i.e., inter-stage HT) to increase the extent of sludge conversion to methane (Aragón-Briceño et al., 2017; Liu et al., 2021). However, only a limited number of studies evaluated the efficacy of inter-stage HT (i.e., AD-HT-AD) in increasing methane production from municipal sludge (Nuchdang et al., 2018; Ortega-Martinez et al., 2016; Yang et al. 2019; Yuan et al., 2019).

Previous studies are inconsistent or even contradictory regarding the efficacy of pre-stage and inter-stage HT in enhancing methane production from biowastes. Several studies showed that, compared with pre-stage HT, inter-stage HT leads to a higher extent of methane production (Nielsen et al., 2011; Ortega-Martinez et al., 2016; Takashima, 2008). However, a recent study found that pre-stage HT was more energy efficient even though pre- and inter-stage HT resulted in comparable improvement of the extent of methane production from concentrated primary sludge (PS) (Yuan et al., 2019). This study raised a critical, yet not-well-answered question: which configuration (i.e., HT-AD or AD-HT-AD) is more efficient in converting municipal sludge to methane? The HT-AD configuration is simpler and has a smaller footprint. In the HT-AD configuration, HT would convert a portion of the hardly biodegradable organic matter to soluble, thus more bioavailable substrates, which along with the original readily biodegradable organic matter would be converted to methane by the subsequent AD. The AD-HT-AD configuration is more complex to operate and has a larger footprint. The premise of the AD-HT-AD configuration is that the first AD would mainly convert most bioavailable and readily biodegradable organic matter to methane, leaving the hardly biodegradable organic matter mostly unaltered. A portion of the hardly biodegradable organic matter would then be solubilized by the inter-stage HT, potentially converting it to methane by the second AD.

The objective of this study was to assess and compare the efficacy of HT-AD and AD-HT-AD in increasing the biodegradability and thus methane production from municipal sludge. The study addressed the above-stated question relative to the comparative efficacy of pre- and inter-stage HT in converting municipal sludge to methane by providing more information on the benefits of the combined HT and AD processes.

Materials and methods

Materials

Thickened sludge mixture, a blend of PS and WAS, referred to as sludge mixture hereinafter, was obtained from the F. Wayne Hill Water Resources Center (FWHWR Center; Buford, GA, USA). At the FWHWR Center, PS and WAS are mixed and passed through a Waste Activated Sludge Stripping to Remove Internal Phosphorus (WASSTRIP®) process (retention time 6-12 h) to release phosphorus from phosphate-accumulating bacteria, and then, polymer is added to the sludge mixture to enhance its dewaterability. Then, the sludge mixture passes through a rotary drum thickener. The filtrate is used to recover phosphorus via struvite crystallization, while the thickened sludge mixture is fed to mesophilic (35°C) anaerobic digesters with a solids retention time (SRT) of ca. 20 d. The characteristics of the sludge mixture are shown in Table 1. In addition, secondary wastewater effluent (before membrane filtration and disinfection) and anaerobic digestate were collected at the FWHWR Center. The sludge mixture and the secondary wastewater effluent were stored in the laboratory at 4°C in the dark. The anaerobic digestate was pre-incubated in the laboratory at 35°C for over 60 d until biogas production was negligible and then used as anaerobic inoculum for the biochemical methane potential (BMP) tests described below.

Preparation of pre-digested sludge

For the AD-HT-AD configuration, in order to obtain pre-digested sludge, the first batch AD was carried out in a 9-L glass reactor with a liquid volume of 6 L, which contained (initial values): sludge mixture (see Table 1), 10 g volatile solids (VS)/L; anaerobic inoculum, 1 g VS/L; secondary wastewater effluent, 4.15 L; and $NaHCO_3$, 1.4 g/L. It should be noted that instead of pre-reduced medium, secondary wastewater effluent was used because the digestates at the end of the incubation were used to assess the speciation of several elements (nutrients and metals) in a companion, parallel study without any interference from the medium (Wang, Zhang, Liu, et al., 2020; Wang, Zhang, Patel, et al., 2020; Wang, Zhang, Jung, et al., 2021). For the same reason, a low VS-based inoculum-to-substrate ratio (ISR) of 1:10 was chosen to avoid over diluting the sludge mixture. The reactor's liquid content was continuously mixed magnetically. A seed blank reactor was also set up in a 580-ml aspirator glass bottle without sludge mixture, continuously agitated on an orbital shaker (220 rpm). The two reactors were incubated at 35°C for 15 d. Table S1 (Supplementary Data) shows the difference in sludge mixture characteristics before and with 15-d pre-digestion. The pre-digestion reactor produced 14,615 ml of methane at 15 d of incubation (seed blank corrected data), corresponding to a specific methane production (SMP) of 0.339 g $COD_{Methane}$/g tCOD. The VS destruction for 15-d incubation was 30.3% (Table S1), in good agreement with the above-mentioned SMP of 33.9%. Aliquots of the 15-d digested sludge (referred to as pre-digested sludge hereinafter) were removed from the 9-L reactor and hydrothermally treated at 90, 125, 155, and 185°C as described below. The pre-digested and pre-digested/hydrothermally treated samples were used as substrate in BMP test II.

Hydrothermal treatment (HT)

For each HT batch, six replicate aliquots of ca. 130 ml of sludge mixture or pre-digested sludge were added to 200-ml polypropylene-lined stainless steel hydrothermal reactors (COL-INT Tech.; Irmo, SC, USA). The HT reactors were sealed and heated in a forced air oven (VWR; Radnor, PA, USA), which was maintained at a pre-set target temperature (90, 125, 155, and 185°C). After heating for 4 h, the HT reactors were removed from the oven, allowed to cool down to room temperature. Preliminary tests showed that target HT temperatures would be reached after 3 h of heating (Text S1, Supplementary Data). Therefore, the total heating time of 4 h included 3 h of ramping and 1 h of holding at the target temperature. The hydrothermally treated sludge slurries (hereinafter referred to as pre-stage HT sludge for the sludge mixture after the pre-stage HT and inter-stage HT sludge for the pre-digested sludge after the inter-stage HT) were stored in glass bottles at 4°C in the dark until used in the BMP tests described below.

BMP tests

Two BMP tests, one for the HT-AD configuration (BMP test I with sludge mixture) and a second for the AD-HT-AD configuration (second AD; BMP test II with pre-digested sludge mixture) were carried out in 580-ml aspirator glass bottles with a liquid volume of 400 ml (180 ml headspace). Briefly, sludge mixture and pre-stage HT sludge (BMP test I) or pre-digested sludge and inter-stage HT sludge (BMP test II) was added to the bottles (2 g VS/L) along with anaerobic inoculum (2 g VS/L) and $NaHCO_3$ (1.4 g/L). Secondary wastewater effluent was then added to reach a total liquid volume of 400 ml. As mentioned above, instead of pre-reduced medium, secondary wastewater effluent was used to avoid any interference from the medium as the digestates at the end of the incubation for the BMP tests I and II were used in a companion, parallel study which assessed the speciation of several elements (nutrients and metals) (Wang et al., 2021; Wang, Zhang, Liu, et al., 2020; Wang, Zhang, Patel, et al., 2020). Preliminary experiments showed that substituting secondary wastewater effluent for medium in BMP tests did not significantly affect the rate and extent of methane production (data not shown). The VS-based ISR for the BMP tests (1:1) was in the typical range from 1:1 to 1:4 (Holliger et al., 2016; Koch et al., 2020). Seed blank series were set up without sludge mixture or pre-digested sludge. The reactors were incubated at 35°C in the dark for more than 70 d (79 d for BMP test I and 74 d for BMP test II), their contents continuously mixed with an orbital shaker (220 rpm).

Analytical methods

pH, COD, total solids (TS), volatile solids (VS), and ammonium (steam distillation/titrimetric method) were measured according to standard methods (APHA, 2012). For soluble

COD (sCOD), ammonium, and ultraviolet absorbance at 254 nm (UV_{254}) measurements, the sample liquid portion was passed through a 0.22-μm membrane filter. UV_{254} of filtered and diluted liquid samples was measured with a quartz cuvette (path length 1 cm) and a Cary 60 UV-Vis Spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). Biogas volume was measured periodically by displacing tap water in a graduated column. Gas composition (CH_4 and CO_2) was measured by gas chromatography/thermal conductivity detection, as previously reported (Tugtas & Pavlostathis, 2007). All biogas volume data are at 35°C and 1 atm.

Total and fecal coliform levels of the pre- and inter-stage digestates were measured using the US Environmental Protection Agency (US EPA) lauryl tryptose broth tubes [Most Probable Number (MPN) Method 8001A] and the US EPA A-1 medium broth tubes (MPN Method 8368), respectively. Briefly, the digestate was 10-fold serially diluted with phosphate-buffered saline (8 g/L NaCl, 0.2 g/L KCl, 1.44 g/L Na_2HPO_4, 0.24 g/L KH_2PO_4; pH 7.4). Then, three consecutive serially diluted digestate samples were selected for incubation. For each dilution, five broth tubes were used, and 10 ml of the diluted digestate was added to each tube. Presence of total and fecal coliforms in the diluted digestate was confirmed by examining gas formation captured in the Durham vial of each broth tube after incubation for 3 d at 35°C and 44.5°C, respectively.

Data and statistical analysis

The solubilization of the sludge mixture and the pre-digested sludge after HT, based on COD measurements, was calculated as follows:

$$\text{COD}_s\,(\%) = \frac{\text{sCOD}_{\text{HT}} - \text{sCOD}_0}{\text{tCOD}_0 - \text{sCOD}_0} \times 100\% \quad (1)$$

where COD_S is the sludge solubilization (%); tCOD_0 and sCOD_0 are the tCOD and sCOD concentrations of the sludge without HT (i.e., sludge mixture or pre-digested sludge) (g/L), respectively; and sCOD_{HT} is the sCOD concentration of the pre- or inter-stage HT sludge (g/L).

The specific, overall cumulative methane yield, that is, methane produced in the entire HT-AD configuration (BMP test I; all seed blank corrected data), was calculated as follows:

$$Y_1 = M_1 \left(\frac{\text{tCOD}_{1\text{HT}}}{\text{tCOD}_{\text{Raw}}} \right) \quad (2)$$

where Y_1 is the COD equivalent of the overall cumulative amount of methane produced per initial tCOD unit of the sludge mixture in the case of pre-stage HT (g COD_M/g tCOD based on 395 ml methane produced at 35°C and 1 atm per g COD destructed) (subscript 1 refers to the HT-AD configuration); M_1 is the COD equivalent of the cumulative methane yield per tCOD unit of the pre-stage HT sludge (g COD_M/g tCOD); and $\text{tCOD}_{1\text{HT}}$ and tCOD_{Raw} are the tCOD concentrations (g tCOD/L) of the pre-stage HT sludge and the sludge mixture, respectively. The ratio of $\text{tCOD}_{1\text{HT}}$ to tCOD_{Raw} reflects the change in sludge tCOD concentration due to the pre-stage HT. For the control (i.e., the sludge mixture without HT), Y_1 is the COD equivalent of the cumulative methane yield per initial tCOD unit of the sludge mixture (g COD_M/g tCOD).

The specific, overall cumulative methane yield, that is, methane produced in the entire AD-HT-AD configuration (i.e., methane production from the first AD batch and from BMP test II; all seed blank corrected data), was calculated as follows:

$$Y_2 = M_{2A} + M_{2B} \left(\frac{\text{tCOD}_{2\text{HT}}}{\text{tCOD}_{2\text{A}}} \right) \left(1 - C \cdot M_{2\text{A}} \right) \quad (3)$$

where Y_2 is the COD equivalent of the overall cumulative amount of methane produced per initial tCOD unit of the sludge mixture when inter-stage HT is applied (g COD_M/g tCOD) (subscripts 2 refer to the AD-HT-AD configuration); $M_{2\text{A}}$ is the COD equivalent of the cumulative amount of methane produced in the first AD (g COD_M/g tCOD); $M_{2\text{B}}$ is the COD equivalent of the cumulative amount of methane produced in the second AD per tCOD unit of the inter-stage HT sludge (i.e., BMP test II) (g COD_M/g tCOD); $\text{tCOD}_{2\text{HT}}$ and $\text{tCOD}_{2\text{A}}$ are the tCOD concentrations (g tCOD/L) of the inter-stage HT sludge and of the pre-digested sludge, respectively; and C is a unit conversion factor (g tCOD/g COD_M). The ratio of $\text{tCOD}_{2\text{HT}}$ to $\text{tCOD}_{2\text{A}}$ reflects the change in sludge tCOD concentration due to the inter-stage HT. $(1 - C{\cdot}M_{2\text{A}})$ is the fraction of the residual tCOD of the pre-digested sludge mixture relative to the sludge mixture. For the control (no inter-stage HT), Y_2 is equal to $M_{2\text{A}}$ plus $(1 - C{\cdot}M_{2\text{A}})$ times the COD equivalent of the cumulative amount of methane generated by the pre-digested sludge during the second AD (i.e., BMP test II).

The overall VS destruction for the AD-HT-AD configuration was calculated as follows:

$$D_{total} = D_1 + D_2 \left(1 - D_1 \right) \quad (4)$$

where D_{total}, D_1, and D_2 are the VS destruction (fractions) for the entire configuration, first AD (i.e., pre-digestion), and second AD (i.e., BMP test II), respectively.

The rate and extent of AD were determined based on the experimentally obtained methane production data during the BMP tests assuming pseudo first-order kinetics for the overall digestion process, as follows:

$$P_t = P_u \left(1 - e^{-[k(t-\lambda)]} \right) \quad (5)$$

where P_t is the seed blank corrected, specific methane production (SMP) at time t (g COD_M/g tCOD), P_u is the ultimate SMP (g COD_M/g tCOD), k is the pseudo first-order rate constant (d^{-1}), t is the incubation time (d), and λ is the lag phase time (d). COD_M is the COD equivalent of methane (395 ml CH_4/g COD at 35°C and 1 atm). The values of P_u, k, and λ were estimated by non-linear regression by fitting Equation (5) to the seed blank corrected SMP data over the incubation time using the Levenberg–Marquardt fitting algorithm in SigmaPlot (version 14; Systat Software Inc., San Jose, CA, USA). The pseudo first-order kinetic model is widely used to simulate batch AD tests, especially when the overall degradation rate is relatively slow and the rates of the two sub-processes, that is, acidogenesis and methanogenesis, are matched, which is typical for municipal sludge (Pavlostathis & Giraldo-Gomez, 1991; Tandukar & Pavlostathis, 2015).

Paired *t* tests were conducted to evaluate if the experimentally measured specific methane production values for the two configurations (HT-AD vs. AD-HT-AD) were statistically significantly different; $p \le 0.05$ was considered to be statistically significant.

Energy balance

Energy balance between energy production (i.e., methane) and energy consumption (i.e., heating) for the two configurations, that is, HT-AD and AD-HT-AD, was analyzed according to a previously described methodology (Lu et al., 2008; Passos & Ferrer, 2014, 2015). Processing of 100 m^3 of raw sludge mixture was considered for both configurations. Assumptions, equations, as well as the description and value of each parameter used for the energy balance calculations are summarized in Text S2, with results shown in Table S2.

Results and discussion

Changes in sludge characteristics due to HT

Table 1 shows the characteristics of the sludge mixture and pre-stage HT sludge. In line with previous studies (Fang et al., 2020; Higgins et al., 2017), the pH decreased after the pre-stage HT. The UV_{254} of the sludge soluble portion increased ca. linearly with pre-stage HT temperature, reaching a 19-fold increase with HT at 185°C compared to the control (i.e., sludge mixture with no HT). The decrease in pH and increase in UV_{254} indicate that HT broke down complex and/or particulate organic matter and released lower molecular weight compounds, such as organic acids, humic substances, and/or aromatic compounds with carbon-oxygen, or carbon-carbon double bonds (Wang & Li, 2015; Wilson & Novak, 2009).

Table 2 shows the characteristics of the pre-digested sludge and inter-stage HT sludge. Inter-stage HT also decreased the pH and increased the UV_{254} of the pre-digested sludge, reaching an 11-fold increase with HT at 185°C compared to the control (i.e., pre-digested sludge without HT); however, the effect of inter-stage HT on both pH and UV_{254} was less pronounced compared with the pre-stage HT. It is noteworthy that at the highest HT temperature tested (185°C), the UV_{254} of the inter-stage HT sludge was over 4-fold lower compared to that of the pre-stage HT sludge. Thus, the pre-digested sludge had a lower content of heat-labile organic matter compared to the undigested sludge mixture, a result of conversion of a significant portion of the sludge mixture biodegradable organic matter to methane during the 15-d AD.

The tCOD of the sludge after HT at 90–185°C fluctuated within a narrow range (less than 4% change; Tables 1 and 2). Similarly, in a previous study, the sludge tCOD concentration fluctuated with increasing HT temperature, but no clear trend was observed (Appels et al., 2010). In a recent study, the tCOD concentration of swine manure and WAS increased after HT at 125 and 225°C, possibly due to dehydration and decarboxylation reactions during HT, resulting in a lower oxygen (O) content of the treated biowaste (Fang et al., 2020). HT dramatically increased the sCOD concentration of the sludge mixture (Table 1) and the pre-digested sludge (Table 2), suggesting that HT solubilized particulate, complex organic matter. Indeed, the COD-based solubilization of both pre- and inter-stage HT sludge increased linearly and significantly with HT temperature. With HT at 185°C, the sCOD of the sludge mixture and pre-digested sludge increased by 27,545 and 6,531 mg/L, corresponding to 43.0% and 49.8% solubilization, respectively (Tables 1 and 2). Organic matter in municipal sludge, especially WAS, is predominantly particulate, complex, and difficult to degrade anaerobically (Şahinkaya & Sevimli, 2013; Xu et al., 2018). HT breaks down and solubilizes particulate organic matter, increasing its bioavailability, potentially enhancing sludge digestibility. In fact, the degree of sludge solubilization after HT was considered as the best descriptor for the enhancement of biogas production (Bougrier et al., 2008). On the other hand, other studies found that sludge digestibility increased with HT temperature up to a threshold value (Fang et al., 2020; Higgins et al., 2017; Kim et al., 2015; Pilli et al., 2015). HT above the threshold temperature value further increased sludge solubilization but decreased its digestibility due to the formation of refractory and/or inhibitory organic substances (Bougrier et al., 2008; Higgins et al., 2017; Wilson & Novak, 2009). Although

Table 2. Characteristics of the pre-digested sludge and inter-stage HT sludge

PARAMETER	PRE-DIGESTED SLUDGE (CONTROL)	INTER-STAGE HT SLUDGE AFTER HT AT			
		90°C	125°C	155°C	185°C
pH	7.60	7.53	7.26	7.24	6.91
TS (g/L)	13.78 ± 0.04[a]	13.79 ± 0.12	13.70 ± 0.12	13.21 ± 0.03	12.22 ± 0.05
VS (g/L)	9.02 ± 0.08	9.04 ± 0.06	8.96 ± 0.06	8.52 ± 0.06	7.57 ± 0.04
Total COD (mg/L)	14,655 ± 81	14,299 ± 48	14,425 ± 112	14,131 ± 96	14,086 ± 209
Soluble COD (mg/L)	1,531 ± 6	3,642 ± 13	5,297 ± 15	7,020 ± 12	8,062 ± 5
Solubilization (%)[b]	NA[c]	16.1	28.7	41.8	49.8
UV_{254}	3.12 ± 0.02	7.22 ± 0.01	11.40 ± 0.02	19.91 ± 0.01	34.14 ± 0.18

[a]Mean ± standard deviation ($n = 3$).

[b]COD basis.

[c]NA, not applicable.

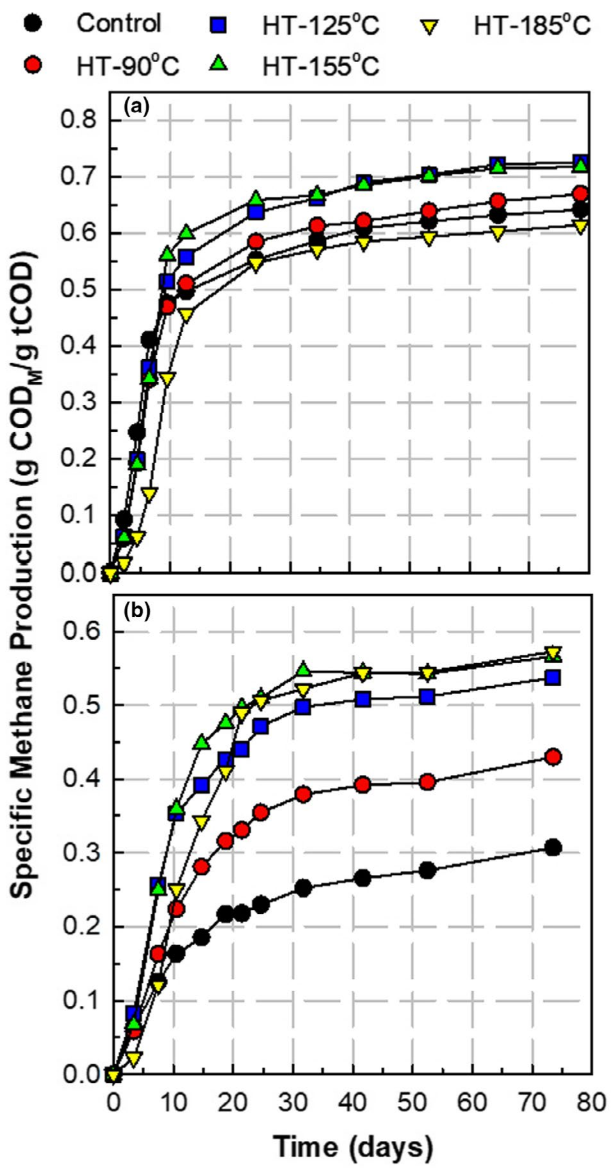

Figure 1. Specific methane production (i.e., seed blank corrected, methane COD produced normalized to the initial total COD). (a) BMP test I (sludge mixture and pre-stage HT sludge); (b) BMP test II (pre-digested sludge mixture and inter-stage HT sludge).

reported HT threshold temperature values vary with sludge and reactor type, as well as organic loading rate, for most studies the HT threshold value was between 170 and 190°C (Higgins et al., 2017).

Compared to the control sludge, the ammonium concentration of the pre-stage HT sludge hydrothermally treated at 90 and 125°C was lower by less than 16%, presumably due to ammonium loss during sludge handling. However, compared to the control, HT at 155 and 185°C resulted in increased ammonium release by 17% and 77%, respectively (Table 1), which is indicative of protein destruction. Ammonium release from municipal sludge with HT from 130 to 200°C, associated with protein destruction, was previously reported by Wilson and Novak (2009).

Effect of HT on sludge digestibility

Digestion of the sludge mixture to prepare pre-digested sludge used in BMP II ended in 15 d of incubation. Seed blank corrected, SMP data were used to fit the pseudo first-order kinetic model (Equation 5), resulting in a pseudo first-order rate constant (k) of 0.112 ± 0.007 d^{-1} (R^2 = 0.991).

BMP tests I and II were conducted at 35°C to assess and compare the effect of HT, performed at 90, 125, 155, and 185°C as pre- and inter-stage processes, on sludge biodegradability and methane production. In the HT-AD configuration, the sludge mixture (control) and pre-stage HT sludge were used to conduct BMP test I. In the AD-HT-AD configuration, the pre-digested sludge (control) and inter-stage HT sludge were used to conduct BMP test II.

BMP test I. Incubation for BMP test I lasted for 79 d. The pH in all series was between 7.5 and 8.0. The cumulative volume of biogas, CO_2, and CH_4 produced increased with HT temperature, except for the pre-stage HT sludge at 185°C (Figure S1). For the first 10 d of incubation, the pre-stage HT sludge at 185°C generated less biogas, CO_2, and CH_4 than the pre-stage HT sludge at lower HT temperatures and the control (i.e., sludge mixture with no HT). The lower initial biogas production from the pre-stage HT sludge at 185°C might be due to refractory, and/or inhibitory organic substances, such as aromatic compounds (i.e., organic compounds with a strong UV_{254}), generated during the high temperature HT as discussed above. However, after ca. 30 d of incubation, the pre-stage HT sludge at 185°C generated a comparable volume of biogas and CH_4 to those of the pre-stage HT sludge at lower HT temperatures and the control (Figure S1). After ca. 10 d incubation, the biogas and CH_4 production from the pre-stage HT sludge at 90°C was higher than that of the control but significantly lower than those from the pre-stage HT sludge treated at higher HT temperatures (125, 155, and 185°C). On the other hand, the biogas and CH_4 produced from the pre-stage HT sludge at 125 and 155°C were comparable. A recent study similarly showed that concentrated PS after pre-stage HT between 130 and 190°C produced comparable volumes of CH_4 in a BMP test (Yuan et al., 2019).

Figure 1a shows the seed blank corrected SMP (i.e., COD_M normalized to the initial tCOD) in BMP test I. After 79 d of incubation, the SMP was 0.620, 0.648, 0.702, 0.696, and 0.596 g COD_M/g tCOD for the sludge mixture (i.e., control) and pre-stage HT sludge at 90, 125, 155, and 185°C, respectively (Table 3). Therefore, compared to the control, the pre-stage HT at 90, 125, or 155°C increased CH_4 production by 4.5%, 13.2%, and 12.3%, respectively. On the other hand, the pre-stage HT sludge at 185°C resulted in a lower SMP than the control during the entire incubation period (3.9% lower than the control after 79 d of incubation). This finding generally agrees with previous studies where the optimal HT temperature ranged from 140 to 190°C (Bougrier et al., 2008; Carrere et al., 2016; Higgins et al., 2017; Sapkaite et al., 2017; Yuan et al., 2019). Similarly, Fang

Table 3. Results of BMP test I[a]

PARAMETER	SLUDGE MIXTURE (CONTROL)	PRE-STAGE HT SLUDGE AFTER HT AT 90°C	125°C	155°C	185°C
TS destruction (%)	34.8	41.2	NA[b]	36.7	35.4
VS destruction (%)	42.9	45.9	NA	46.3	45.4
tCOD destruction (%)	52.6	56.9	NA	57.8	55.3
Methane produced (ml CH_4/reactor)[c]	303	324	354	361	360
Specific methane production (g COD_M/g tCOD added)	0.620	0.648	0.702	0.696	0.596
Methane yield (mL CH_4/g VS added)	430	465	NA	531	526
COD balance (%)[d]	−9.4	−7.8	NA	−11.8	−4.3
Ammonium (mg N/L)	81	118	NA	123	137
Total coliform (MPN/100 ml)	240 ± 2	240 ± 3	NA	240 ± 3	NM[e]
Fecal coliform (MPN/100 ml)	23	23	NA	23	NM

[a]End of 79-d incubation, seed blank corrected data, except for total and fecal coliform; all gas data are at 35°C and 1 atm.

[b]NA, not available (reactor damaged at the end of 79-d incubation).

[c]Reactor liquid volume, 0.4 L.

[d]$\text{COD balance}\,(\%) = \frac{COD_{Initial} - COD_{Final} - COD_{Methane}}{COD_{Initial}} \times 100\%$.

[e]NM, not measured.

et al. (2020) reported a decrease in SMP after HT at 225°C of swine manure and WAS by 41% and 16%, respectively, compared to the 125°C treatment. The lower CH_4 production from the pre-stage HT sludge at 185°C HT in the present study might be due to inhibition of methanogenesis by inhibitory organic substances formed during high temperature HT (Bougrier et al., 2008; Pilli et al., 2015). In addition to inhibitory substances, high temperature HT could generate refractory organic compounds (Higgins et al., 2017), which would suppress COD-normalized CH_4 production. Further studies are needed to more comprehensively understand the underlying mechanisms for the observed lower CH_4 production from sludge treated at high HT temperatures.

Seed blank corrected, SMP data (BMP test I, Figure 1a) were used to fit the pseudo first-order kinetic model (Equation 5) and results are given in Table 4. The lag phase increased as the HT temperature increased (Table 4). The pseudo first-order rate constant (k) for the pre-stage HT sludge at 90°C (0.152 d^{-1}) was lower than that for the control (0.178 d^{-1}), though not statistically significantly different ($p = 0.189$), and then increased as the HT temperature increased up to 155°C. The rate constant for the pre-stage HT sludge at 155°C (0.223 d^{-1}) was 1.25-fold higher than for the control (i.e., sludge mixture with no HT). However, the rate constant for the pre-stage HT sludge at 185°C (0.191 d^{-1}) was lower than that for the pre-stage HT sludge at 155°C (0.223 d^{-1}), though not statistically significantly different ($p = 0.169$). The lower rate constant value at 185°C is possibly due to inhibitory and/or refractory organic substances formed at this HT temperature, which in turn inhibited methanogenesis as mentioned above. It is noteworthy that the pre-digestion rate constant (0.112 ± 0.007 d^{-1}) is not significantly lower than the control rate in the BMP test I (0.178 ± 0.023 d^{-1}; Table 4). Thus, the relatively lower ISR used for the pre-digestion of the sludge mixture did not have a significant effect on the pre-digestion kinetics.

The ultimate SMP (P_u, g COD_M/g tCOD) followed a similar trend with increasing HT temperature as the CH_4 production rate constant (BMP test I; Table 4). The P_u increased as the HT temperature increased from 90 to 155°C. Specifically, the P_u for the pre-stage HT sludge at 155°C was 1.15-fold higher than the control. However, the P_u for the pre-stage sludge at 185°C was statistically significantly lower than that at 155°C ($p \leq 0.001$). In general, except for pre-stage HT at 185°C, the pre-stage HT increased CH_4 production from the sludge mixture, which had a relatively high ultimate digestibility of 62% (Table 3).

The high ultimate digestibility of the sludge mixture used in this study is attributed to its relatively lower WAS proportion compared to PS, which typically contains more readily biodegradable organic substrates (Solé-Bundó et al., 2019; Wu et al., 2010). Thus, the pre-stage HT is less effective in increasing CH_4 production from sludge with a relatively high content of readily biodegradable organic substrates. Most WRRFs combine PS and WAS, or thickened WAS, before AD. As mentioned above, the thickened sludge mixture was collected at the FWHWR Center, where PS and WAS are combined, pre-fermented to release orthophosphate, and then the thickened sludge mixture is fed to anaerobic digesters. Thus, to mirror the sludge management practice at the FWHWR Center, as well as in many other WRRFs, the pre-fermented and thickened sludge mixture was used in this study.

Table 3 shows the changes in select key parameters, such as TS, VS, and tCOD, due to the 79-d incubation in BMP test I. The VS and tCOD destruction of the pre-stage HT sludge was only 5.8%–7.9% and 5.1%–9.9% higher than that of the control (i.e., sludge mixture with no HT). In contrast, compared to the

Table 4. Pseudo first-order rate constant and ultimate specific methane production values for the degradable COD to CH_4 conversion of the sludge mixture and pre-stage HT sludge (BMP test I), and pre-digested sludge and inter-stage HT sludge (BMP test II)

HT TEMPERATURE (°C)	LAG PHASE (Λ, D)	RATE CONSTANT (K, D^{-1})	ULTIMATE SPECIFIC CH_4 PRODUCTION (P_U, G COD_M/G TCOD)	R^2
BMP test I				
None (Control)	1.3 ± 0.4[a]	0.178 ± 0.023[a]	0.579 ± 0.014[a]	0.978
90	1.7 ± 0.3	0.152 ± 0.013	0.607 ± 0.011	0.991
125	2.5 ± 0.5	0.173 ± 0.024	0.643 ± 0.013	0.982
155	3.2 ± 0.3	0.223 ± 0.027	0.664 ± 0.011	0.985
185	5.1 ± 0.3	0.191 ± 0.018	0.565 ± 0.007	0.993
BMP test II				
None (Control)	0	0.076 ± 0.003	0.261 ± 0.004	0.997
90	1.7 ± 0.1	0.088 ± 0.002	0.383 ± 0.002	0.999
125	1.7 ± 0.3	0.117 ± 0.010	0.485 ± 0.009	0.992
155	2.4 ± 0.2	0.125 ± 0.006	0.527 ± 0.005	0.998
185	5.3 ± 0.4	0.109 ± 0.011	0.535 ± 0.012	0.990

[a]Mean estimate ± standard error.

control, pre-stage HT from 130 to 190°C increased VS destruction by 23.0%–25.1% for concentrated PS in a 30-d BMP test at 35°C (Yuan et al., 2019). Another study showed that VS destruction over a 50-d BMP test at 35°C for WAS after pre-stage HT at 150, 180, or 210°C was comparable to that of the control (Kim et al., 2015). After 79-d incubation in the BMP test I, the combined effect of HT and AD resulted in higher ammonium concentrations in the series with pre-stage HT sludge compared to the control (Table 3). The ammonium concentration increased with HT temperature (46%–69% higher in the pre-stage HT digestates compared to the pre-stage control digestate).

The total and fecal coliform levels of the pre-stage digestate after BMP test I were as low as 240 and 23 MNP/100 ml, respectively, indicating that the pre-stage HT and/or the 35°C incubation for 79 d effectively destructed coliforms (Table 3). Similarly, pre-treatment at temperatures as low as 60 or 70°C dramatically increased the pathogen (*Escherichia coli*, *Enterococcus faecalis*, and bacteriophage MS-2) inactivation efficiency of municipal sludge AD (37°C, 15 d SRT) (Ziemba & Peccia, 2011). Therefore, AD with pre-stage HT is promising in inactivating pathogens in municipal sludge, thus improving the digestate and biosolids quality.

BMP test II. Incubation for BMP test II lasted for 74 d. The pH in all series was between 8.2 and 8.5. The cumulative volume of biogas, CO_2, and CH_4 produced in all series during the BMP test II are shown in Figure S2. The inter-stage HT sludge generated more biogas, CO_2, and CH_4 than the control (i.e., pre-digested sludge with no HT). In addition, the cumulative volume of biogas, CO_2, and CH_4 significantly increased with HT temperature from 90 to 155°C. For the first 20 d of incubation, the inter-stage HT sludge at 185°C generated less

Table 5. Results of BMP test II[a]

PARAMETER	PRE-DIGESTED SLUDGE (CONTROL)	INTER-STAGE HT SLUDGE AFTER HT AT			
		90°C	125°C	155°C	185°C
TS destruction (%)	20.7	23.4	31.8	26.5	30.1
VS destruction (%)	31.2	30.5	45.0	44.3	48.0
tCOD destruction (%)	25.3	36.0	42.5	49.3	44.9
Methane produced (ml CH_4/reactor)[b]	148	215	271	300	329
Specific methane production (g COD_M/g tCOD added)	0.291	0.411	0.517	0.546	0.553
Methane yield (ml CH_4/g VS added)	181	296	358	404	406
COD balance (%)[c]	−3.8	−5.1	−9.2	−5.3	−10.3
Ammonium (mg N/L)	133 ± 2	178 ± 3	201 ± 3	219 ± 2	244 ± 4
Total coliform (MPN/100 ml)	240	240	240	240	72
Fecal coliform (MPN/100 ml)	23	23	30	23	33

[a]End of 74-d incubation, seed blank corrected data, except for total and fecal coliform; all gas data are at 35°C and 1 atm.

[b]Reactor liquid volume, 0.4 L.

[c]$\text{COD balance}(\%) = \frac{COD_{Initial} - COD_{Final} - COD_{Methane}}{COD_{Initial}} \times 100\%$.

biogas, CO_2, and CH_4 than at 155°C (Figure S2). However, after 20 d, the cumulative biogas production by the inter-stage HT sludge at 185°C was higher than that produced by the other test series. The initial lower biogas production might be due to inhibitory and/or refractory organic substances formed at the high HT temperature (185°C) as discussed above.

Figure 1b shows the seed blank corrected, SMP (i.e., COD_M normalized to the initial tCOD) for BMP test II. After 74 d of incubation, the SMP was 0.291, 0.411, 0.517, 0.546, and 0.553 g COD_M/g tCOD for the control and the inter-stage HT sludge at 90, 125, 155, and 185°C, respectively (Table 5). It is noteworthy that the inter-stage HT sludge at 185 and 155°C had similar SMP. Compared to BMP test I results, inter-stage HT more significantly increased the CH_4 production in BMP test II relative to the controls (Figure 1a vs. 1b).

In the present study, the 79-d BMP test I converted ca. 62% of the tCOD of the sludge mixture (control) to methane (Figure 1a), indicating that the sludge mixture had a relatively high content of readily biodegradable organic substrates. On the other hand, the 15-d pre-digestion for the AD-HT-AD configuration converted ca. 34% of the tCOD of the sludge mixture to CH_4 resulting in pre-digested sludge, which mainly contained hardly biodegradable organic substrates. As a result, in the 74-d BMP test II, only ca. 29% of the tCOD of the pre-digested sludge (control) was converted to methane (Figure 1b), compared to ca. 55% for the inter-stage HT sludge at 185°C. Therefore, compared to the control, inter-stage HT significantly increased CH_4 production during BMP test II. A previous study assessed the effect of HT on five WAS samples with varying ultimate digestibility and found that the higher the digestibility of the raw WAS, the lower the beneficial effect of HT was in terms of CH_4 production (Bougrier et al., 2008).

It is noteworthy that the decrease in SMP observed with the pre-stage HT sludge at 185°C compared to that at 90, 125, and 155°C in BMP test I (Table 3) was not observed with the inter-stage HT sludge at the same HT temperatures (BMP Test II; Table 5). This difference between the HT-AD and AD-HT-AD configurations may possibly be due to two main reasons. First, as discussed above, inhibitory and/or refractory organic substances may be formed during high temperature sludge HT, which hinder CH_4 production during subsequent AD (Bougrier et al., 2008; Higgins et al., 2017; Wilson & Novak, 2009). As the sludge mixture had a higher content of labile organic matter compared to the pre-digested sludge, formation of inhibitory organic substances at a higher concentration more likely occurred in the case of the sludge mixture as opposed to the pre-digested sludge. Indeed, as mentioned above, the filtrate UV_{254} value of the pre-stage HT sludge at 185°C was more than 4-fold higher than that of the inter-stage HT sludge at the same temperature. Second, the pre-digested sludge mostly contains hardly biodegradable organic matter. Therefore, HT at 185°C in the AD-HT-AD configuration significantly improved CH_4 production from the pre-digested sludge (Table 5), which might overcompensate for the negative effect of inhibitory and/or refractory organic substances formed at 185°C. Similar results have been reported by previous studies (Bougrier et al., 2008; Yuan et al., 2019).

Seed blank corrected, SMP data (BMP test II; Figure 1b) were used to fit the pseudo first-order kinetic model (Equation 5), and results are given in Table 4. Similar to BMP test I, the lag phase in BMP test II increased as the HT temperature increased. The pseudo first-order rate constant (k) increased as HT temperature increased from 90 to 155°C. However, the rate constant for the inter-stage HT sludge at 185°C (0.109 d^{-1}) was lower than that at 155°C (0.125 d^{-1}), though not statistically significantly different (p = 0.098), possibly because of the formation of inhibitory and/or refractory organic substances at the high temperature (185°C) as mentioned above. The observed slower methane production by the inter-stage HT sludge at 185°C during the initial incubation period (0–20 d) significantly affected the SMP rate, but not the ultimate SMP (i.e., the extent), as discussed below (Table 4). The ultimate SMP (P_u, g COD_M/g tCOD) followed the same trend with increasing HT temperature as the SMP rate constant (Table 4). It is noteworthy that, contrary to the results of BMP test I conducted with the sludge mixture and pre-stage HT sludge, in BMP test II, the P_u value for the inter-stage HT sludge at 185°C (0.535 g COD_M/g COD) was similar to that at 155°C (0.527 g COD_M/g tCOD; p = 0.397). The pre-digested sludge had a low ultimate digestibility of ca. 29% (Table 5), indicating that a low level of readily biodegradable organic matter remained after the first stage AD in the AD-HT-AD configuration. The much higher ultimate SMP of the inter-stage HT sludge compared with the control (i.e., pre-digested sludge without HT) confirms that inter-stage HT significantly increased CH_4 production.

The ultimate SMP (P_u) of the control in the BMP test II (0.261 ± 0.004 g COD_M/g tCOD; Table 4) was lower than that of the control in the BMP test I (0.579 ± 0.014 g COD_M/g tCOD; Table 4). This difference is expected as pre-digestion for 15 d removed degradable COD equivalent to 0.339 g COD_M/g tCOD. When the combined effect of the pre-digestion and second AD (i.e., BMP test II) is taken into account, the estimated overall methane yield is 0.600 g COD_M/g tCOD. Similarly, the rate constant for the control (i.e., pre-digested sludge) in BMP test II (0.076 ± 0.003 d^{-1}; Table 4) was lower than that of the control in the BMP test I (0.178 ± 0.023 d^{-1}; Table 4) and the pre-digestion (0.112 ± 0.007 d^{-1}).

Table 5 shows the changes in select key parameters, such as TS, VS, and tCOD, due to the 74-d incubation in BMP test II. The VS destruction of the inter-stage HT sludge increased with HT temperature above 90°C. Similarly, the tCOD destruction increased with HT temperature up to 155°C, then decreased at 185°C, and was significantly higher (by ca. 42%–95%) than that of the control. Previous studies also reported that inter-stage HT significantly increased solids destruction of concentrated PS (Yuan et al., 2019) and a mixture of PS and WAS (Takashima, 2008). Similar to BMP test I, after 74-d incubation in the BMP test II, the combined effect of HT and AD resulted in higher ammonium concentrations in the series with inter-stage HT sludge compared to the control (Table 5). The ammonium concentration increased with HT temperature (34%–84% higher in the inter-stage HT digestates compared to the inter-stage control digestate). The total and fecal coliform levels in the inter-stage digestate ranged from 72 to 240 and

23 to 33 MNP/100 ml, respectively, indicating that inter-stage HT and/or 35°C incubation for 74 d effectively inactivated coliforms (Table 5).

Pre-stage vs. inter-stage HT

Methane production. This study compared the efficacy of pre- and inter-stage HT relative to the overall CH_4 yield from a municipal sludge mixture by the entire, combined HT and AD processes (see Equations 2 and 3), with results shown in Table 6. The overall specific methane yield increased as the HT temperature increased from 90 to 155°C for both configurations; compared with the control (sludge mixture for the HT-AD configuration or pre-digested sludge for the AD-HT-AD configuration), the increase ranged from 5.5% to 16.8% for the HT-AD configuration and from 13.7% to 29.4% for the AD-HT-AD configuration. Up to 155°C HT, the overall specific methane yield with the HT-AD configuration was higher by 4.9%–8.3% compared to the AD-HT-AD configuration. Excluding the data for HT at 185°C, a paired *t* test indicates that the HT-AD configuration produced significantly more CH_4 than the AD-HT-AD configuration (one-tailed *p*-value 0.013, $n = 4$). However, overall, the Y_1 and Y_2 values are close with an absolute difference of less than 0.089 g COD_M/g tCOD and a relative difference of equal or less than 16.8% (Table 6). It is noteworthy that although the pre-stage HT sludge at 185°C resulted in a lower SMP ($Y_1 = 0.611$, Table 6) compared to that at lower HT temperatures and the control in the HT-AD configuration, inter-stage HT at 185°C in the AD-HT-AD configuration resulted in ca. 13% higher SMP ($Y_2 = 0.690$, Table 6) compared to the Y1 value of 0.611. Two plausible reasons for the difference in the performance of the HT-AD and AD-HT-AD configurations for HT at 185°C were offered in BMP test II section above. The results of the current study agree with those of a recent study in which pre- and inter-stage HT resulted in a similar increase of CH_4 production from concentrated PS (optimum HT temperature 130°C; BMP tests at 35°C) (Yuan et al., 2019). Continuous-flow AD (35°C, 20 d SRT) with a mixture of PS and WAS and inter-stage HT at 120°C resulted in a higher CH_4 production (0.56 g COD_M/g VS_{fed} for the entire AD-HT-AD configuration) than pre-stage HT at 120°C (0.48 g COD_M/g VS_{fed}) or without HT (0.48 g COD_M/g VS_{fed}) (Takashima, 2008). The reported differences in the degree of enhancement in terms of CH_4 production by pre- and inter-stage HT are attributed to the type of sludge used (PS, WAS, or their mixture) and its ultimate digestibility, HT temperature and duration, organic load rate, and reactor type (i.e., batch, semi-continuous or continuous flow).

VS destruction. Considering the 33.7% VS destruction by the first AD, using Equation (4), the overall VS destruction in the AD-HT-AD configuration was 54.4, 53.9, 63.5, 63.0, and 65.5% for the pre-digested control and inter-stage HT at 90, 125, 155, and 185°C, respectively. The overall VS destruction in the AD-HT-AD configuration compared to the HT-AD configuration increased by 8.0% (HT at 90°C) to 20.1% (HT at 185°C). Thus, inter-stage HT followed by the second AD contributed to the observed increased overall VS destruction.

Energy balance. Energy balance of the two configurations, that is, HT-AD and AD-HTP-AD, was calculated following a previously described methodology (Lu et al., 2008; Passos & Ferrer, 2014, 2015), summarized in Text S2. Energy balance results for processing 100 m^3 of raw sludge mixture are shown in Table S2. For both configurations, the net energy production (ΔE, GJ) decreased as the HT temperature increased, becoming negative at HT of 185°C (Figure 2). Within each configuration, the control, that is, raw sludge mixture or pre-digested sludge without HT resulted in the highest ΔE values. For HT up to 155°C, the ΔE values for the AD-HT-AD configuration were lower than for the HT-AD configuration by 14.5% (without HT) to 38.8% (HT at 155°C). Thus, although HT up to 155°C for the HT-AD configuration and up to 185°C for the AD-HT-AD configuration increased the specific methane yield compared to the control (i.e., no HT) (Table 6), the incremental methane production was not enough to compensate for the associated HT heating energy (Table S2). Similar results were obtained by a parallel study conducted using laboratory-scale, semi-continuous digesters fed with hydrothermally treated sludge mixture from the same WRRF (FWHWR Center; Liu et al., 2021), in which the highest ΔE was obtained with the control (i.e., sludge mixture AD without HTP); ΔE values became negative at HT ≥ 125°C without HT heat recovery. HT heat recovery greater than 85% was required to attain the same net energy as the control or higher.

Table 6. Overall specific methane yield from the sludge mixture using HT as pre-stage (HT-AD) or inter-stage process (AD-HT-AD)

HT TEMPERATURE (°C)	HT-AD Y_1 (G COD_M/G TCOD)[A]	AD-HT-AD Y_2 (G COD_M/G TCOD)[B]
None (control)	0.620	0.531
90	0.654	0.604
125	0.708	0.675
155	0.724	0.687
185	0.611	0.690

[a] Y_1, specific, overall methane produced in the entire HT-AD configuration (i.e., methane produced from the sludge mixture and pre-stage HT sludge in BMP test I; seed blank corrected data).

[b] Y_2, specific, overall methane produced in the entire AD-HT-AD configuration (i.e., sum of methane produced from the sludge mixture with 15-d pre-digestion and from the pre-digested sludge without HT as well as inter-stage HT sludge in BMP test II; seed blank corrected data).

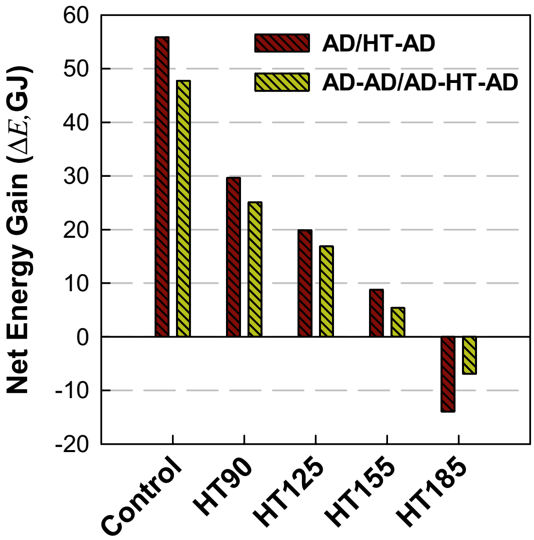

Figure 2. Net energy gain (ΔE, GJ) for 100 m^3 sludge mixture digestion without HT (i.e., control, AD and AD-AD configurations) and with HT at 90–185°C (HT-AD and AD-HT-AD configurations) (see Text S2).

Conclusions

This study assessed and compared the efficacy of HT-AD and AD-HT-AD configurations in increasing CH_4 production from a municipal sludge mixture, as well as VS destruction. For both configurations, HT (90–185°C) significantly increased sludge solubilization. HT and AD combined increased the ammonium N release by as much as 1.7- and 3.0-fold in the AD-HT and AD-HT-AD configuration, respectively. Inter-stage HT above 90°C followed by the second AD contributed to higher overall VS destruction than the HT-AD configuration. For either configuration, both the rate and extent of CH_4 production increased with HT from 90 to 155°C. However, compared with HT at 155°C, HT at 185°C resulted in either lower or similar CH_4 production with the HT-AD and AD-HT-AD configurations, respectively. Compared to the control (i.e., sludge without HT), pre-stage HT from 90 to 155°C increased CH_4 production by 5.5% to 16.8%, whereas inter-stage HT significantly increased the CH_4 production from the pre-digested sludge (i.e., by the first AD and BMP test II) by 13.7% to 29.4%. The overall specific methane yield with the HT-AD configuration was higher by 4.9% to 8.3% compared to the AD-HT-AD configuration for HT up to 155°C. When heating energy was considered, compared to the control (i.e., sludge AD without HT), the net energy gain (ΔE) decreased as the HT temperature increased, becoming negative at an HT temperature of 185°C. Thus, an HT temperature range between 125 and 155°C is optimal to maximize CH_4 production by either configuration for the sludge mixture used in this study.

However, increase in energy production through increased methane production by HT (either pre- or inter-stage) followed by AD cannot offset the energy/heat requirement. Thus, in the case of the present study conducted with municipal sludge with a relatively high ultimate digestibility, the HT-AD configuration is preferable as it has a smaller footprint and is easier to operate than the AD-HT-AD configuration. However, as the AD-HT-AD configuration resulted in higher VS destruction, AD-HT-AD may be more beneficial considering post-AD sludge handling processes, such as dewatering, incineration, etc.

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Author contributions

Chiqian Zhang: Data curation (lead); formal analysis (lead); methodology (equal); writing-original draft (lead). **Xiaoguang Liu**: Data curation (supporting). **Qian Wang**: Methodology (supporting). **Yuanzhi Tang**: Funding acquisition (lead); project administration (equal); resources (equal). **Spyros G. Pavlostathis**: Conceptualization (lead); methodology (supporting); supervision (equal); writing-review & editing (equal).

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