EFFECTS OF THERMAL HYDROLYSIS TEMPERATURE ON DEGRADATION PRODUCT SPECIATION, METHANE POTENTIAL AND RHEOLOGY

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAIʻI AT MĀNOA IN PARTIAL FULLFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CIVIL ENGINEERING

AUGEST 2020

By

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Keywords: thermal hydrolysis pretreatment (THP), sewage sludge, compound speciation, biochemical methane potential (BMP), dewaterability, energy simulation

ACKNOWLEDGEMENT

I would like to express my appreciation to the following people and institutions that have supported me throughout my Ph.D.

I would like to extend my deepest gratitude to my supervisor, Dr. Roger Babcock, the completion of my dissertation would not be possible without his guidance, patience and support. I also wish to thank the committee members: Dr. Michael J. Cooney, Dr. Tao Yan, Dr. Samir K. Khanal and Dr. Sayed M. Bateni for their insightful suggestions in my research.

I gratefully acknowledge the assistance of Kexin Rong, research associate of Water Resources Research Center, for her help of sample analysis; my lab mates and co-workers, Joachim Schneider, Sydney Le Cras, Connor Kagamida and Micah Tang, for helping with sewage sludge sample collection and digester maintenance. Thanks should also go to Dr. Prakit Saingam, Dr. Bo Li and Dr. Sabrina Diemert, my graduate student friends for their support during the five years of study, research and work.

Lastly, I am also greatful to the encouragement and strong support from my families, especially my husband, Zhening Zhang, who always inspires me and helps with taking care of our baby Lucas at many nights.

ABSTRACT

The effects of low to medium temperature (44-121°C) thermal hydrolysis (THP) treatment of primary (PS) and secondary (WAS) municipal wastewater sludge on formation of carbohydrates, proteins, Melanoidins and methane generation potential were evaluated. Results show that between 1.5 and 12% of volatile solids (VS) was hydrolyzed into filtered dissolved solids (FDS), with 55-100% represented as carbohydrates and proteins depending on sludge type and THP temperature. Proteins are produced at 160 to 350% of the values for carbohydrates in terms of g gVS^{-1}, and WAS values are 4 to 5 times as large as PS values. Much more low molecular weight (LMW) proteins are formed than high MW (HMW) proteins at all temperatures for both PS and WAS. The same is true for carbohydrates from PS, but the quantities of LWM and HWM produced are similar for WAS. Low-medium temperature THP increased biomethane potential (BMP) of WAS from 145 ml CH_4 gVS^{-1} in untreated WAS to up to 230 ml CH_4 gVS^{-1} (44 to 57% increase depending on temperature), and only nominally increased BMP of PS (by 0 to 7.5%). THP caused the formation of much more Melanoidins in WAS than PS and showed little dependence on temperature in the range evaluated herein. There was a nearly 20-fold increase in supernatant color for both PS and WAS that was well correlated with increases in THP temperature. Overall, the effects of low-medium temperature THP are significant for WAS and limited for PS.

Product speciation of soluble components in secondary sewage sludge during THP is investigated in this research. The dissolved components concentrations increased with increasing THP temperatures (between 80 and 220°C) and reaction time (between 0 and 60 min), including dissolved solids, COD, TOC, carbohydrates, VFA, TN, protein,

amino acids, and ammonium. At low temperature THP as 80℃, the carbohydrate and protein portion to sCOD is higher than the high temperature THP (110-200℃) due to THP releases nutrients from intercellular to free water but temperature not high enough to break down these structures. Proteins are highly denatured at 200℃ that ammonium concentration goes much higher than other conditions. The liquid brown color which is mainly from melanoidins generated during THP goes darker with temperature up and reaction duration. Melanoidins concentrations are also calculated from high molecular weight material, protein and carbohydrate, whereas the results fail to follow with the color results because of inaccurate conducted in measurements.

The effects of THP pre-treatment of PS and WAS on particle size distribution (PSD), apparent viscosity and dewaterability prior to and following anaerobic digestion (AD) were studied. Results showed that when THP there was a shift in particle size distribution during THP of WAS, with particles in the range of 10 to 40 μm decreasing and 2-3 μm particles increasing. The apparent viscosity of WAS at a shear rate of 5 s^{-1} and 15-min reaction time increased relative to a control (4071 cP) at lower temperatures (80-110℃) due to gelation (up to 5880 cP) and then decreased dramatically in proportion to temperature increases to 140, 170 and 200℃ (2261, 1131 and 678 cP, respectively). Anaerobic digestion of the THP-treated mixed PS+WAS sludge further decreased the viscosity. The dewaterability of digestate from lab-scale ADs fed THP-treated mixed sludge improved compared to a control. The total solids (TS) of centrifuged sludge cake increased from 19.8 to 30.4% for pre-treated at 170℃ THP treated sludge compared to non-THP-treated. This result suggests a lower energy usage in the downstream sludge drying process.

THP has been used prior to AD in sewage sludge treatment to increase digestion reaction rate, methane generation, and digested sludge dewaterability. All of these benefits point toward energy savings and the potential for net zero energy. Energy simulations were performed for a medium-sized municipal wastewater treatment plant (WWTP) that is in the process of adding THP, co-digestion of high energy wastes, thermal sludge drying, and combined heat and power (CHP). Laboratory experiments were conducted to determine site-specific efficiencies for THP, AD and BMP as inputs to the model. Historic and future projected facility energy use was also incorporated. The electricity energy input for sludge treatment decreased when applying THP to secondary sludge at 140°C (421 kW input when flow rate is 509 kg hr^{-1}) and 170°C (258 kW input) compared to no THP treatment (463 kW). THP has little effect on the energy balance for PS because the methane yield improvement is minimal compared to WAS. Energy input for PS without THP is 537 kW when the flow rate is 927 kg hr^{-1}, which decreased to 327 kW with THP at 170°C. Net zero energy can be achieved only by conducting co-digestion with a high-energy substrate such as 20% of VS loading added as fats oils and grease (FOG).

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LIST OF ABBREVIATIONS

WWTPs:	Wastewater treatment plants
AD:	Anaerobic digestion
THP:	Thermal hydrolysis pretreatment
PS:	Primary sludge
WAS:	Waste activated sludge
VS:	Volatile solid
VFA:	Volatile fatty acid
BMP:	Biochemical methane potential
CHP:	Combined heat and power
FOG:	Fat oil and grease
TS:	Total solids
TDS:	Total dissolved solids
LMW:	Low molecular weight
HWM:	High molecular weight
TOC:	Total organic carbon
TN:	Total nitrogen
SRT:	Solid retention time
COD:	Chemical oxygen demand
AA:	Amino acid
PSD:	Particle size distribution
CST:	Capillary suction time

CHAPTER 1. INTRODUCTION

In wastewater treatment plants (WWTPs), anaerobic digestion (AD) is usually used to stabilize residual sludges and also generate methane-rich biogas at the same time. To increase biogas yield, reaction speed and solids destruction during AD, various pretreatment techniques are available. The common pretreatment methods are Thermal Hydrolysis Process (THP), mechanical pretreatment (microwave pretreatment, freeze-thaw pretreatment, ultrasonic pretreatment), chemical pretreatment (alkali, ozonation), and biological pre-treatment (enzymatic solubilization). Among all these methods, THP is one of the most popular and has been commercialized with 67 full-scale facilities worldwide, mostly located in Europe.

According to the treatment temperature, THP can be divided into high-temperature THP (130-200ºC), medium-temperature THP (100-130ºC) and low-temperature THP (40-100ºC). Low-temperature THP has been investigated for a long time, but currently there is an increasing interest on high-temperature THP recently because it provides greater enhancements during AD. High-temperature THP is conducted at high pressure to prevent boiling and the structure of particulate matter in primary sludge (PS) is partially liquefied and the biological cells in waste biological sludges (WAS) are destroyed with cell contents being liberated. This action on the WAS is normally achieved biochemically via enzymes in the AD and is the rate-limiting step in the process. After THP treatment, there are increased dissolved and hydrolyzed nutrients which are ready for biodegradation (acidification-acetification-methanogenesis). The effects of THP treatment are different for PS and WAS and for different temperatures and reaction times.

During THP, a series of reactions occur among different components of the sludge. Hydrolyzation results in smaller molecular weight materials formation which have faster degradability leading to more rapid methane generation. With increasing temperature, more organic matter (volatile solids, VS) dissolves, the solid mass of particles decreases and the particles become liquified. However, inhibitors and recalcitrant compounds are also synthesized especially at the highest temperatures, including ammonium, Melanoidins and Amadori compounds. Soluble protein and soluble carbohydrate all increase strongly with increased reaction temperature, but decrease when sludge is overheated because of the Maillard reaction that forms the Melanoidins and Amadori from the low molecular weight carbohydrates and proteins/amino acids. These compounds cause a brown color in the liquid phase. Ammonium is also produced from decomposition of protein/amino acids. Volatile fatty acids (VFA) concentrations are linked to lipids degradation. All the physical and chemical changes that occur during THP changes the biodegradability of WAS and PS. It is known that the biochemical methane potential (BMP) of WAS increases significantly after THP, whereas the BMP of PS is not improved. This is because THP breaks down the cell structure in WAS, but the components in PS are mostly readily-degradable already so it is not improved improved by THP.

When looking at the sludge physical properties, sludge dewaterability (i.e during centrifugation) is improved because viscosity and sludge particle size are reduced during THP treatment. One important benefit of dewaterability improvement is a drier sludge cake which reduces the heat energy input if there is a downstream sludge drying process. THP requires energy for heating but leads to enhanced energy recovery via combined

heat and power (CHP) the sludge treatment (THP-AD-CHP) energy flow system can be simulated. By including co-digestion of high energy substrates, such as food waste, fats, oil and grease (FOG), the net energy of the WWTP can reach the zero point.

In this dissertation, the sludge property changes with THP were studied based on reaction temperature, treatment duration, and its effects in the following AD process. There are four specific research objectives included in the dissertation, with an introduction in Chapter 1 and a summary of the major findings in Chapter 6 to finish. The Chapter 2,3,4,5 consist of journal manuscripts either submitted or in final preparation. Chapter 2 investigates the products formed during low/medium-temperature (44-121℃) THP of PS and WAS, including dissolved solids, carbohydrates, proteins and melanoidins. The chemical components changes of different types of sludge during THP were investigated. Chapter 3 investigates THP of WAS at medium and high temperatures (80-200ºC) treated at different reaction times from 15 to 60 min. Chapter 4 studies the physical properties of THP-treated sludges and their digestates, including sludge particle size, viscosity and dewaterability following AD. Chapter 5 is a study on the energy aspects of THP incorporated in several different ways at a WWTP.

CHAPTER 2.

RESEARCH ARTICLE

Formation of Carbohydrates, Proteins and Melanoidins During Low-Temperature Thermal Hydrolysis of Primary and Secondary Sewage Sludge

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Abstract

The effects of low to medium temperature (44-121^{o}C) thermal hydrolysis (THP) treatment of primary (PS) and secondary (WAS) municipal wastewater sludge on formation of carbohydrates, proteins, Melanoidins and methane generation potential were evaluated. Results show that between 1.5 and 12% of volatile solids (VS) was hydrolyzed into filtered dissolved solids (FDS), with 55-100% represented as carbohydrates and proteins depending on sludge type and THP temperature. Proteins are produced at 160 to 350% of the values for carbohydrates in terms of g gVS^{-1}, and WAS values are 4 to 5 times as large as PS values. Much more low molecular weight (LMW) proteins are formed than high MW (HMW) proteins at all temperatures for both PS and WAS. The same is true for carbohydrates from PS, but the quantities of LWM and HWM produced are similar for WAS. Low-medium temperature THP increased BMP of WAS from 145 ml CH_4 gVS^{-1} in untreated WAS to up to 230 ml CH4 gVS^{-1} (44 to 57% increase depending on temperature), and only nominally increased BMP of PS (by 0 to 7.5%). THP caused the formation of much more Melanoidins in WAS than PS and showed little dependence on temperature in the range evaluated herein. There was a nearly 20-fold increase in supernatant color for both PS and WAS that was well correlated with increases in THP temperature. Overall, the effects of low-medium temperature THP are significant for WAS and limited for PS.

Keywords: primary sludge, waste activated sludge, thermal hydrolysis process (THP), carbohydrates, proteins, melanoidins, biomethane potential (BMP)

Introduction

Two types of sludge generated in typical municipal wastewater treatment plants (WWTPs) are primary sludge (PS) and waste activated sludge (WAS). These sludges contain large amounts of degradable organics, metals, and pathogenic microorganisms and thus must be properly treated and disposed or made safe for reuse to limit potential environmental and public health problems [1]. Sludge treatment is a major concern in

wastewater treatment facilities due to high costs of facilities, operation and maintenance [2]. Anaerobic digestion (AD) is the most frequently used sludge treatment method because it both stabilizes sludge and can also recovery energy through conversion of complex organic substrates into methane-rich biogas [3,4,5]. There are four biological process steps in AD: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is known as the rate limiting step in which the complex biopolymers are broken down into monomers and oligomers [6,7,8]. Pretreatment processes can be employed prior to AD to accelerate hydrolysis, and thereby increase biochemical methane potential (BMP) and accelerate reaction rate (reduce digestion time) [9,10,11,12,13]. This can be accomplished thermally, chemically, or mechanically. Some pretreatment methods can also improve sludge dewaterability and viscosity (reducing energy needs is downstream drying is employed) and also kill pathogens which is helpful for applications were biosolids production/reuse in employed [14,15,16,17,18,19]. Thermal hydrolysis process (THP) pretreatment is an AD pretreatment process that has been commercialized [13].

In THP pretreatment, the sludge substrate is treated at an elevated temperature and pressure (usually 130-220℃ and 0.7-0.8 MPa) for 10 to 30 min [4]. The complex particulate substrates (volatile solids, VS) are solubilized/hydrolyzed/de-natured into products which can be consumed more rapidly and thoroughly in AD and result in improvement of methane production and reaction kinetics [4]. It has been reported that THP improves biodegradability of sewage sludge, improves VS reduction, allows a higher organic loading rate and a smaller reactor, reduces sludge viscosity, improves dewaterability of digested sludge, reduces odor, and reduces pathogen regrowth [11,20,21]. Commercialized THP processes include: CAMBI (most widely established with 67 full-scale systems in operation worldwide, Asker, Norway), BIO THELYS™ from Veolia (Paris, France), Lystek THP® Reactor (Cambridge, United Kingdom), TurboTec® from Sustec (Wageningen, Netherlands), LysoTherm® from ELIQUO (Barneveld, Netherlands) Aqualysis from Aqualogy (Groningen, Netherlands) and tH4+ from teCH4+ (Madrid, Spain). CAMBI's THP includes three sequential units, including a pre-heat tank, a steam-heated reactor (140-165^{o}C), and a flash tank to erupt biomass cells. The main operating issues are pumping under pressure and corrosion in heat exchangers [17,21,22]. In the BIO THELYS™ Batch Thermal Hydrolysis process, dewatered sludge is heated through direct steam injection to 150-180℃ and then is cooled down to feed the AD [21,23,24].

The changes to sludge properties facilitated by THP which improve digestion performance should be less pronounced for PS than for WAS. PS contains mainly relatively readily biodegradable organic materials; however, WAS mainly consists of biomass where a large portion of the organic matter is inside of microbial cells protected by a strong cell wall. Thus, THP of WAS has been found to improve digestion effectively by destroying the cell wall [4] and the same effect can be achieved by chemicals (e.g. high pH base-hydrolysis), freeze-thaw, and mechanical disruption (e.g. ultrasonic). The breakdown of the cell wall would normally occur biochemically in the AD via enzymes. The macromolecular components, such as proteins, lipids and polysaccharides, are broken down, and some recalcitrant organics (Melanoidins and Amadori products from sugars + proteins) are produced, especially at high temperatures [25,26].

Most THP research and practice is focused on high temperature THP from 130 to 220C, with much less on component speciation at lower temperatures. Kuglarz et al. [27] investigated WAS thermal treatment at temperatures from 30 to 100^{o}C and found the COD solubilization improved gradually with temperature, reaching about 15% at 80-100^{o}C. The soluble protein concentration reached the highest level at 60-70^{o}C then slightly decreased at 80-100^{o}C due to Maillard reactions (production of Melanoidins). They found that methane yield values were not significantly impacted at temperatures greater than 40^{o}C (up to 100^{o}C). The Maillard reactions are known to produce Melanoidins high temperatures [28], but there is a scarcity of data at low/medium temperature THP. High solubilization rates of carbohydrates and proteins were found in thermally treated (55^{o}C) mixed sewage sludge with long reaction times (3 to 13 hr) [29]. Salsabil et al. [30] found that thermal treatment of WAS induced organic matter solubilization by 5 to 16%. Liao et al. [31] found THP of mixed PS+WAS at 60-80^{o}C improved biogas production up to 24.4%. Climent et al. [32] found a 50% increase in biogas production of 70^{o}C thermally treated WAS. A study on thermal-chemical treatment of WAS from a dairy WWTP found that the optimized condition was 60^{o}C at pH 12 which improved COD solubilization by 23%, suspended solids reduction by 22% and biogas production by 51% compared the performance of the control anaerobic digester treating un-altered WAS [33].

In this study, PS and WAS were treated under low/medium temperature THP from 44 to 121^{o}C and hydrolysis product changes as a function of treatment temperature as well as biomethane potential changes were investigated.

Materials and Methods

PS and WAS were obtained from a trickling-filter-solids-contact (TF/SC) secondary WWTP that receives an average flow of 98 million liters per day (MLD)(26 million gallons per day, MGD) of municipal wastewater with no industrial component. Samples were stored at 4°C and used within 48 hours of collection. Thermal treatment was conducted by placing 100 ml capacity Teflon lined stainless-steel hydrothermal synthesis reactors (BAOSHISHAN, Hangzhou, China), containing 90ml of sludge sample (containing 6 to 16 g volatile solids [VS]) into a pre-heated oven. The reactor vessels can tolerate pressures up to 3 MPa. These reactors have a large thermal mass and thus require time to heat up the sludge contents. Temperature indicator tape placed inside the reactors was utilized to determine internal temperatures and required heating times. Seven different reaction temperatures were utilized (44, 60, 72, 77, 88, 104 and 121^{o}C) by heating to the stated temperature for 60 min. The hot reactors were transferred into an ice water bath to rapidly cool to room temperature prior to analyses of the contents. For this study, 44, 60, 72, 77, and 88°C are considered "low" temperature THP and 104 and 121°C are considered "medium" temperature THP.

Sludge samples were centrifuged at 3260 G for 5 min. Supernatant was then filtered via a 0.45 μm membrane filter (Millipore, Millex® – HN Filter Unit, Ireland). The 0.45 μm filtrate was further filtered using an Amicon stirred cell (Millipore, Amicon®, Germany) containing an Ultracel 10kDa ultrafiltration disc (Millipore, Ultracel® 10kDa Ultrafiltration Discs, U.S.A.). Approximately 30 ml of 0.45 μm filtrate was processed in the stirred cell at a headspace pressure of 0.38 MPa (55 psi) for 20 min in order to yield 15 ml filtrate.

Filtered dissolved solids (FDS) of 0.45 μm and 10 kDa filtrates were measured after freeze drying. 7 ml liquid samples in sealed glass vials were frozen in a -40^{o}C refrigerator for 12 hours, then the vials were unsealed and placed in the freeze dryer (SP scientific, Model # 6KBTES-55, Qarminster, PA, USA) . Freeze drying took 24-48 hrs for ice sublimation and the fully dry powder remaining was weighed as FDS. The remaining 0.45 μm and 10 kDa filtrates (8 ml) were analyzed for various components. Carbohydrates were measured using the phenol-sulfuric acid method [34]. Proteins were measured using the Lowry-Folin assay [35]. The 10 kDa filtrate is considered the low molecular weight (LMW) material. The high molecular weight (HMW) material was calculated by subtracting the 10 kDa filtrate concentrations from the 0.45 μm filtrate concentrations. The Melanoidins concentration was calculated by subtracting the HMW protein and HMW carbohydrate fractions from the total HMW material. [28,36].

Total solids (TS), VS, alkalinity, total dissolved solids (TDS), and Color (Co-Pt units) were measured by Standard Methods 2540B, 2540E, 2320B, 2540C, and 2120C, respectively [37]. Biochemical methane potential (BMP) was measured using an automated AMPTS II device (Bioprocess Control AB, Lund, Sweden) that employs 500-ml volume reactors, temperature control, stir paddles, and continuous methane gas flow rate measurements for 15 reactors. Inoculum for BMP assays was digested sludge from the AD at the same TF/SC treatment plant. The working volume is 400ml and inoculum to sludge VS ratio (I/S ratio) of 2.5 was used. The headspace was flushed using pure nitrogen for 3 mins to remove oxygen before being sealed, and the stirrer was activated for 10 min at 200 rpm every hour. The sealed reactors were maintained at 38^{o}C in the water bath until biogas production stopped for a period of 24 hours. All BMP measurements were conducted in duplicate including the seed blank. The biogas was analyzed by GC using a thermal conductivity detector (TCD, Thermo Scientific, Waltham, MD) and an Rt-Q-Bond column (30 m x 0.25 mm x 8μm, Restek, Bellefonte, PA). The inlet and oven temperatures were maintained at 30^{o}C and helium was used as the carrier gas at a flow rate of 1.2 ml min^{-1}. 80μl of the gas sample was injected manually with a gas-tight syringe, at a split ratio of 40. TCD polarity was set to positive, and TCD and filament temperatures were set to 200 and 250^{o}C, respectively.

Results and Discussion

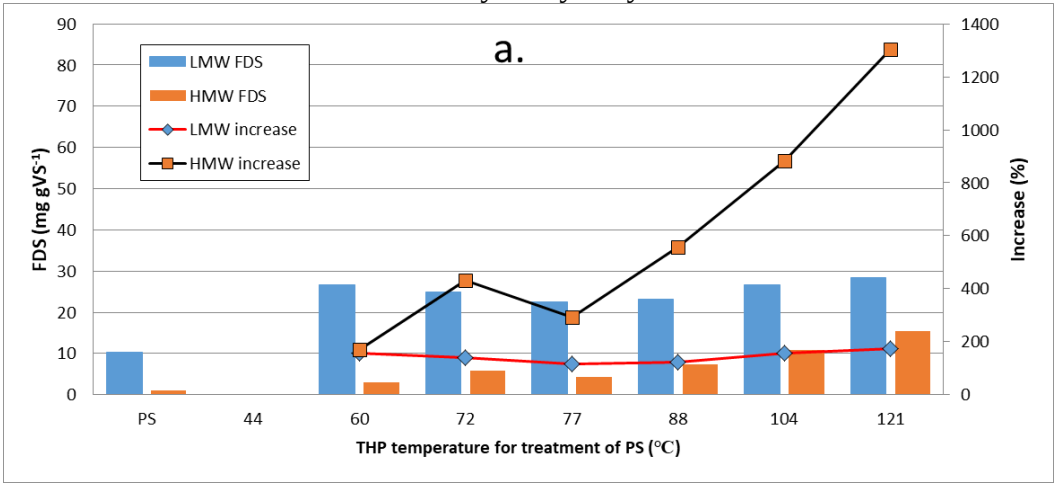
Table 1 shows the basic characteristics of the PS and WAS used in this study. The amounts of HMW and LMW FDS in untreated and THP-treated PS and WAS are shown in Figure 1. The increased amounts of FDS in THP-treated samples represent the total quantity of sludge solids solubilized (mg) into the liquid phase per gram of VS (mg FDS gVS^{-1}). The LWM FDS is the 10 kDa filtrate FDS. The HWM FDS is the 0.45 μm filtrate FDS minus the 10 kDa filtrate FDS. THP increased HWM FDS from 1.1 mg gVS^{-1} in untreated PS to 3.0 to 15.5 mg gVS^{-1} (2-14 mg g^{-1} increase; 170 to 1300%) in good proportion to increase in hydrolysis temperature (Figure 1a). The effects of THP on LMW FDS in PS is quite different. For PS, THP increased LMW FDS from 10 mg gVS^{-1} to 23 to 28 mg gVS^{-1} (13-17 mg g^{-1} increase; 120 to 175%), with no discernable influence of temperature. More VS is solubilized to LMW FDS at all temperatures, especially the lower temperatures. The quantity of LMW material solubilized at 60℃ is only slightly less than the mount solubilized at 121℃. The LMW products can therefore be considered the “readily soluble” or the “low-temperature soluble” portion of the PS solids. Also, the

data would seem to indicate that it is not a stepwise process of solubilization from sludge solids to HMW solids to LMW solids.

Table 1: Basic characteristics of PS and WAS collected at a municipal TF/SC WWTP

	pH	Alkalinity (mg L^{-1} as $CaCO_3$)	VFA (mg L^{-1})	TDS (mg L^{-1})	TS (%)	VS (%)
PS	5.6	1,000	3,543	1,733	19.686	16.351
WAS	6.3	200	263	967	7.653	6.186

The effect of THP on WAS solubilization is much greater than for PS at all of the temperatures tested here (Figure 1b). THP increased the HMW fraction of FDS from 26 mg gVS^{-1} in untreated WAS to 35 – 85 mg gVS^{-1} (9-49 mg g^{-1} increase; 35 to 225%) in a manner that is not consistently proportional to temperature increases. The amount solubilized at 44°C is greater than at 60°C and about the same as at 104°C; while much larger and constant amounts were solubilized at 72, 77, and 88°C, and a large further increase was observed at 121°C. In a repeat experiment, the same phenomena (lower solubilization at 60 and 104°C) was observed and it is unclear why this occurs. The LMW fraction of FDS from WAS increased more than the HMW fraction, going from 19 mg gVS^{-1} to between 48 and 80 mg gVS^{-1} (28-61 mg g^{-1} increase; 150 to 315%). The effect of increasing THP temperature on WAS is similar to PS where the amounts of FDS created are fairly constant between 44 and 77°C and then begin a steady increase in proportion to temperature at 88, 104, and 121°C. Another notable difference is that THP solubilization of WAS produces close to equal amounts of HMW and LMW FDS, while for PS there is much more LMW than HMW material produced. Overall, low/medium-temperature THP solubilizes about 3 times as much VS to FDS when treating WAS (4.5 to 12%) as compared to PS (1.8 to 3.2%) (see Table 2). Still, these quantities are not very large, and 88 to 98% of the VS remains intact/un-solubilized. The differences observed for PS and WAS are related to the different types of VS involved. The WAS VS consists of mainly microbial cells, and solubilization consists of breaking the cell wall and release of liquid cell contents. The VS component of PS is particulate organic matter such as feces (residual/digested food), food scraps, fats, grease, various colloids, etc. These materials are not as easily liquefied by simple heating and may require chemical assistance such as acid or base or enzyme hydrolysis.



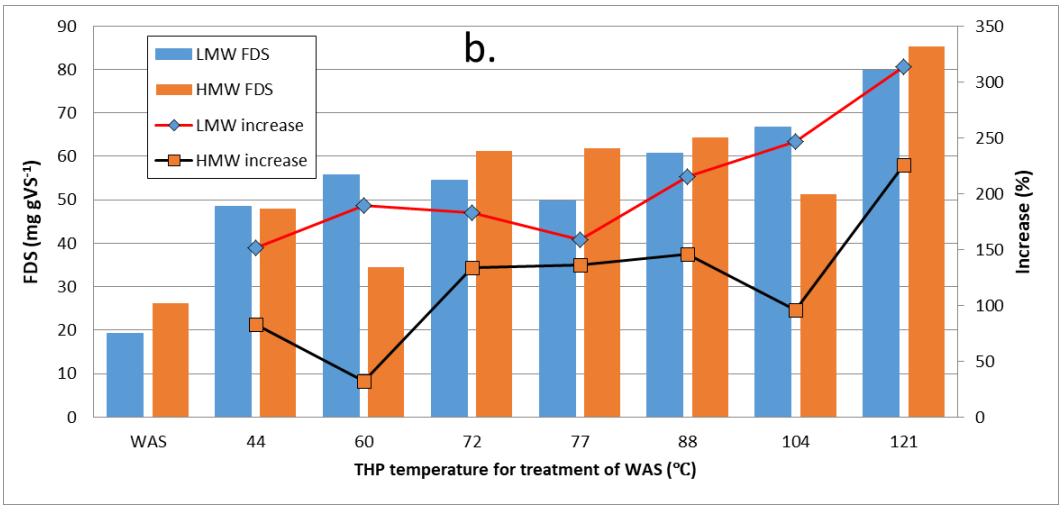


Figure 1: High and low molecular weight quantities of filtered dissolved solids following low/medium-temperature THP of PS (a) and WAS (b).

Table 2: Quantities of materials solubilized from VS in PS and WAS during low/medium-temperature THP.

	THP Temp (°C)	Total FDS hydrolyzed (mg/gVS)	VS hydrolyzed (%)	Total Carbohydrates hydrolyzed (mg/gVS)	Total Proteins hydrolyzed (mg/gVS)	Total Carbs + Prot hydrolyzed (mg/gVS)	Carbs + Prot percent of FDS (%)	Melanoidins (mg/gVS)	Portion of Carbs + Prot to Melanoidins (%)
PS	60	18.2	1.8	3.1	6.9	10.0	55	1.2	12
	72	19.2	1.9	2.8	7.8	10.6	55	3.6	34
	77	15.4	1.5	3.4	8.3	11.7	76	2.1	18
	88	18.8	1.9	4.2	8.5	12.6	67	3.2	26
	104	26.1	2.6	6.4	10.4	16.8	64	7.1	43
	121	32.4	3.2	7.2	12.8	20.0	62	9.0	45
WAS	44	50.8	5.1	2.7	31.6	34.3	68	28.4	83
	60	44.7	4.5	10.1	35.6	45.7	102	18.7	41
	72	70.2	7.0	10.4	36.6	46.9	67	23.8	51
	77	66.1	6.6	13.3	39.5	52.8	80	35.6	67
	88	79.6	8.0	24.0	65.8	89.8	113	32.7	36
	104	72.5	7.2	25.9	71.4	97.3	134	21.8	22
	121	119.5	12.0	33.2	83.2	116.4	97	29.2	25

Figure 2 shows the amounts of carbohydrates solubilized during the low/medium-temperature THP of PS (2a) and WAS (2b). THP increased HWM carbohydrates from 0.07 mg gVS^{-1} in untreated PS to 0.5 to 3.3 mg gVS^{-1} (0.4-3.2 mg g^{-1} increase; 580 to 4500%) in good proportion to increase in temperature (Figure 2a). THP increased LMW carbohydrates from 0.3 mg gVS^{-1} to 2.6 to 5.6 mg gVS^{-1} (2.3-5.3 mg/g increase; 750 to 1400%), with no temperature influence between 60 and 88C (low temperature), followed by significant increases at 104 and 121°C (medium temperature). Mirroring the FDS, more VS is solubilized to LMW carbohydrates at all temperatures, especially the lower temperatures. The effect of THP on WAS solubilization is much greater than for PS at all the temperatures tested here (Figure 2b). THP increased the HMW fraction of carbohydrates from 1.5 mg gVS^{-1} in untreated WAS to 5 – 17 mg gVS^{-1} (0.03-2.2 mg g^{-1} increase; 215 to 1000%) in proportion to temperature increases in the range of 44 to 88°C, but then leveled off at 104 and 121°C. Unlike the HWM fraction, the LMW fraction of carbohydrates increased very proportionally with temperature increases for the whole range, going from 1.5 mg gVS^{-1} to between 4.6 and 25 mg/L (3-23 mg g^{-1}

increase; 200 to 1600%). For WAS, at most of the temperatures between 44 and 88°C, the amounts of LMW and HMW carbohydrates hydrolyzed are similar in magnitude with the HMW values being larger. At the medium temperatures (104 and 121°C), there is more LWM than HMW carbohydrates. This trend is different than PS carbohydrates and all the FDS data which indicates that there exists both HMW and LMW carbohydrate materials to be released from within bacteria cells while mostly only smaller compounds can be hydrolyzed from PS particulate solids. Low/medium-temperature THP solubilizes about 3 to 4 times as much VS to total carbohydrates when treating WAS (10 to 33 mg gVS^{-1}) as compared to PS (3 to 7 mg gVS^{-1}) (see Table 2).

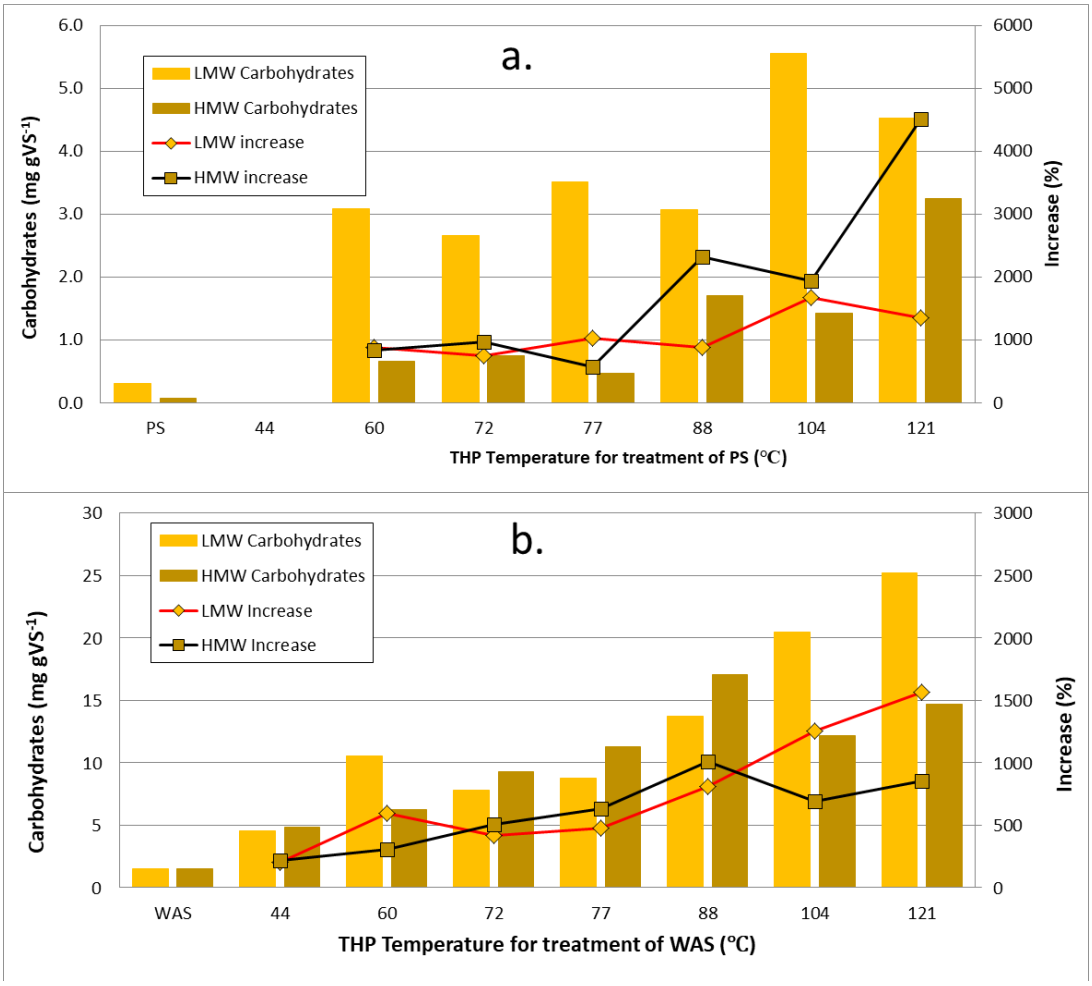


Figure 2: High and low molecular weight quantities of carbohydrates following low/medium-temperature THP of PS (a) and WAS (b).

Figure 3 shows the amounts of proteins solubilized during the low/medium-temperature THP of PS (3a) and WAS (3b). THP increased HWM proteins from 0.07 mg gVS^{-1} in untreated PS to 0.5 to 2.3 mg gVS^{-1} (0.4-3.2 mg g^{-1} increase; 70 to 3100%) in good proportion to increase in temperature (Figure 3a). The LMW proteins amounts are more than twice as large as the carbohydrates and display a similar trend with nearly constant quantities generated between 60 and 88°C and then increases at 104 and 121°C (medium temperatures). Just like for carbohydrates, the effect of THP on WAS

solubilization production of proteins is much greater than for PS at all the temperatures tested here (Figure 3b). THP increased the HMW fraction of carbohydrates from 1.0 mg gVS^{-1} in untreated WAS to 4 – 23 mg gVS^{-1} (3-22 mg g^{-1} increase; 330 to 2200%) in proportion to temperature increases in the range of 44 to 88°C, but then decreased at 104 and 121°C. Like the HWM fraction in PS, the LMW fraction of proteins was fairly constant between 44 and 77°C and then increased very proportionally with temperature from 88 to 121°C, going from 6 mg gVS^{-1} to between 34 and 82 mg/L (28-76 mg g^{-1} increase; 490 to 1300%).

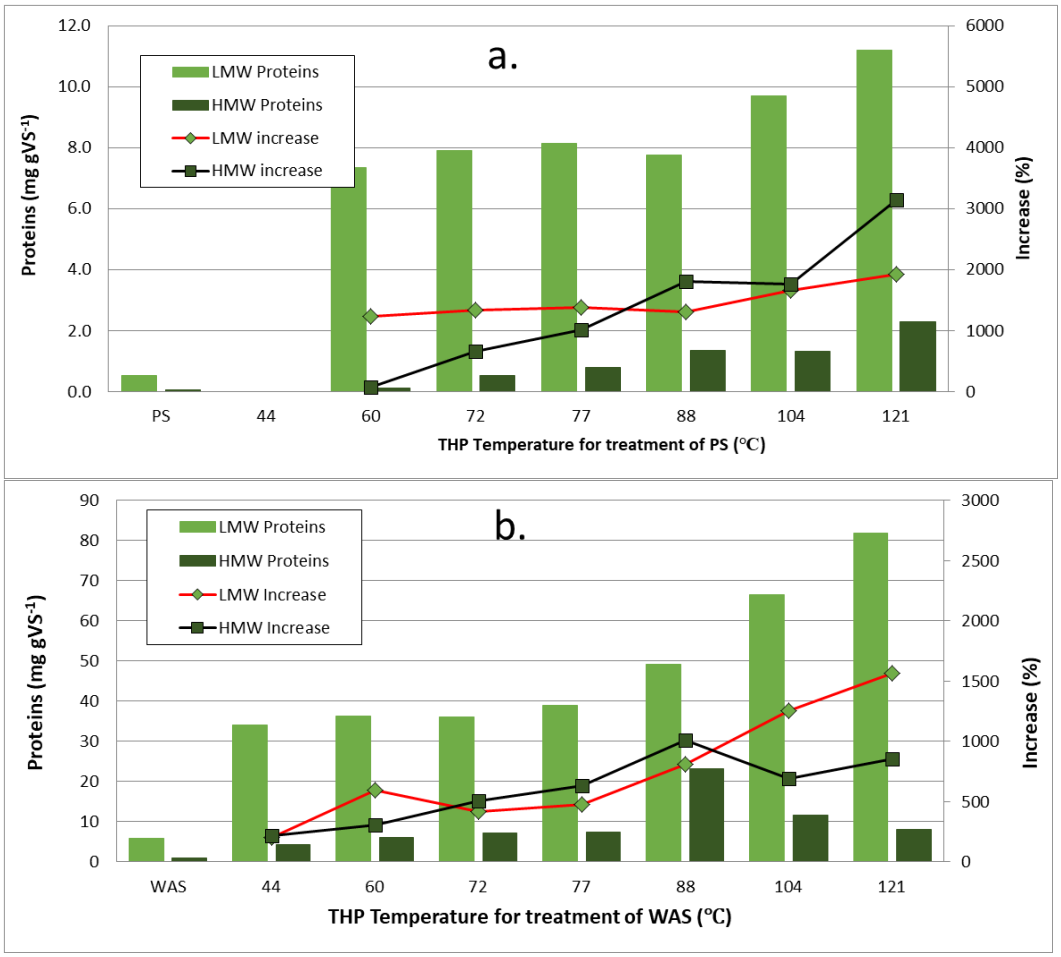


Figure 3: High and low molecular weight quantities of proteins following low/medium-temperature THP of PS (a) and WAS (b).

Table 2 shows that more total proteins than total carbohydrates are hydrolyzed from VS in both PS (about 2-fold) and WAS (about 3-fold). This difference is due to LMW proteins. The quantities of HMW proteins produced are about the same as HMW carbohydrates, which is true for both PS and WAS. It is apparent that THP liberates the LMW carbohydrates and especially LMW proteins from inside the cells in the WAS. The LMW proteins are only 7-11 mg gVS^{-1} in THP-treated PS, but they are 34-81 mg gVS^{-1} in THP-treated WAS. Table 2 shows that the total carbohydrates plus proteins generated account for between 55 and 75% of the FDS for PS, and between 67 and 100% of FDS for WAS.

Figure 4 shows the amount of Melanoidins formed during the THP process. Melanoidins are formed in the Maillard reaction between LMW carbohydrates and LMW proteins and the quantity is calculated rather than measured directly. For PS, the Melanoidins increased from 1.2 mg gVS^{-1} to 2-9 mg gVS^{-1} because there were only small amounts of LMW proteins and carbohydrates present. For WAS, the Melanoidins increased from 3 mg gVS^{-1} to 19-35 mg gVS^{-1} due to the large amounts of LMW carbohydrates and proteins available to react (Table 2). Figure 4 also shows that Melanoidins formation during THP of PS is fairly proportional to increases in temperature, however, for WAS, there does not seem to be a relationship with THP temperature as the formation rate is high even at the low temperatures. Melanoidins are brown-colored compounds that are considered recalcitrant to biodegradation and thus would not contribute to methane production during AD. Table 2 shows the ratio of Melanoidins formed to the total quantity of carbohydrates and proteins formed that are not bound up as Melanoidins. The ratio is between 12 and 67% with a mean of 39% which means that a substantial portion of the hydrolyzed carbohydrates and proteins are "lost" to Melanoidins.

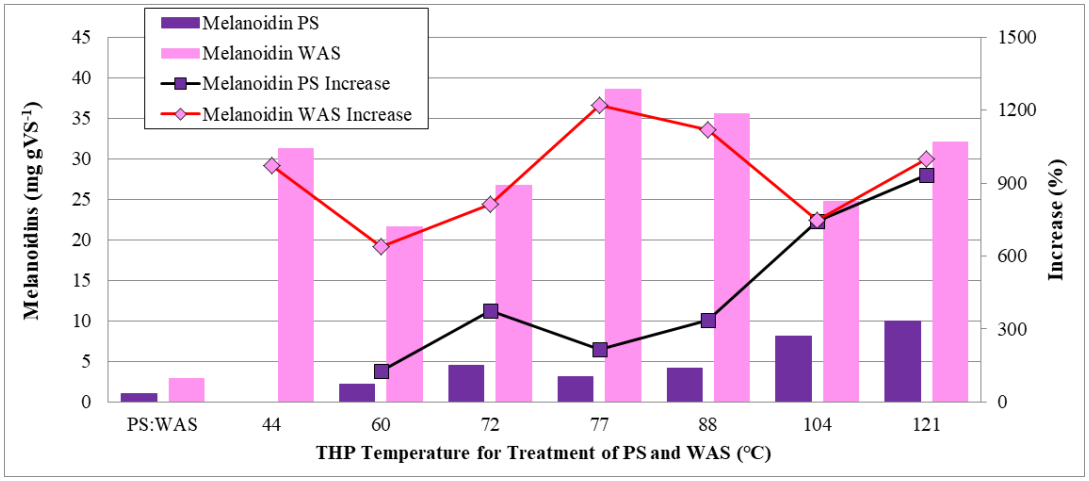


Figure 4: Melanoidins in low/medium-temperature THP-treated PS and WAS.

Melanoidins have a brown color. There are other possible reactions such as carmelization that can also produce brown color during heating of sewage sludge, so it is not expected that color would necessarily correlate well with Melanoidin concentration. The color quantities in THP-treated PS and WAS are shown in Figure 5. The increase in color is consistently proportional to increases in THP temperature for both PS and WAS at the temperatures evaluated herein.

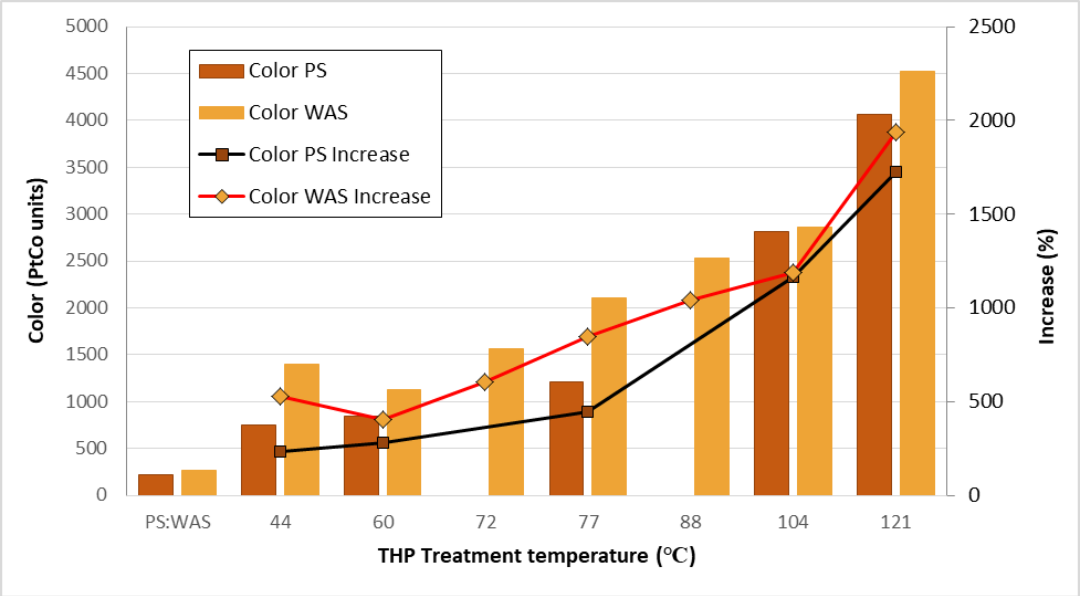


Figure 5: Color quantities in low/medium-temperature THP-treated PS and WAS.

Figure 6 shows the BMP of un-treated and low/medium-temperature THP-treated PS and WAS. THP treatment did not have a significant effect on BMP of PS, causing either a slight increase (1 to 7.5%) or even a slight decrease at each of the low and medium temperatures tested herein. However, the BMP values of all THP-treated and un-treated PS samples (338-401 ml CH_4 gVS^{-1}) are larger than all of the WAS BMP values (147-231 ml CH_4 gVS^{-1}). THP treatment increased the WAS BMP by 44 to 57% and the effects were mostly proportional to THP temperature. At the lowest THP temperatures (44 and 60°C) the improvement is 48%, which increased to 55-57% at 77-93°C, then decreased at 104°C and increased again by 57% at 121°C. This data suggests that THP of PS is not helpful for increasing methane production and that THP of WAS causes a significant increase in methane production and the lowest temperatures provide benefits similar to the medium temperatures. The methane content of the biogas produced in the BMP reactors over the course of the tests are shown in Figure 7. The data indicates that the biogas contained approximately 60% methane at day 2 which increased to over 70% by day 8 and close to 75% at day 15.

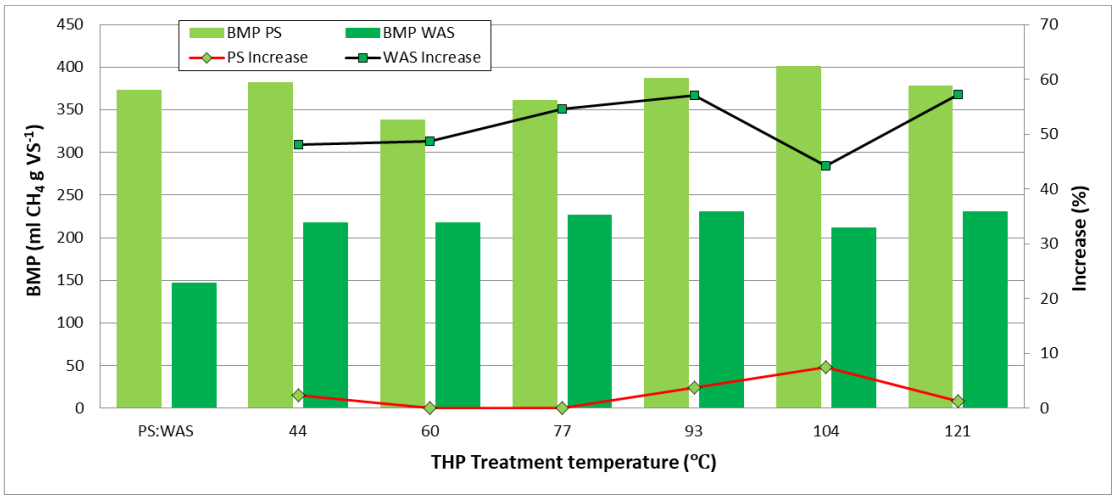


Figure 6: Biomethane potential of low/medium-temperature THP-treated PS and WAS

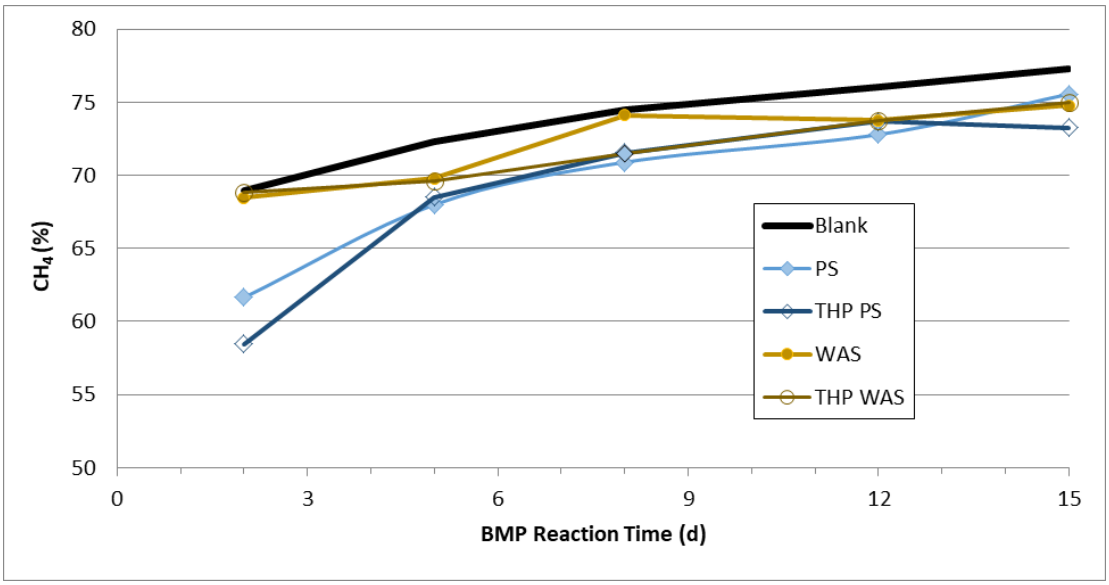


Figure 7: Methane content of biogas during BMP tests of low/medium-temperature THP-treated PS and WAS

Results from other studies of low/medium-temperature THP treatment of PS and WAS are mixed. Kuglarz et al. [27] evaluated low-temperature THP on thickened WAS at 30-100°C. The highest protein concentration was observed at temperatures of 70 to 100°C (which were relatively constant around 2,770 mg L^{-1}) which is about a 22-fold increase versus un-treated. In the present study, the proteins concentration for thickened WAS at 72°C was 3,764 mg L^{-1} which is about 20-fold increase compared to un-treated WAS (191 mg L^{-1}) which is similar to Kuglarz's findings [27]. However, in the present study, we found that proteins continued to increase at temperatures greater than 70°C with the the highest protein concentration observed at the highest temperature (121°C) at 6,074 mg L^{-1} which is about 32-fold increase compared to un-treated. Kuglarz postulated

that the slight decrease in proteins at THP higher than 70°C was due to Maillard reactions [27]. However, in the present study, we found that proteins continued to increase in proportion to temperature increases from 70 to 121°C while about the same amount of Melanoidins were produced at all tested temperatures from 44 to 121°C for THP-treated WAS. Neumann et al. [29] tested THP of mixed sewage sludge (PS:WAS ratio of 65:35 based on TS) at 55°C for 3-13 hours and they found that soluble protein increased by 230-342% and soluble carbohydrates increased by 427-436%. Herein, we found that that soluble protein and carbohydrates increased by 1952% and 2117% for WAS, and increased by 1102% and 880% for PS, respectively, at 60°C THP treatment. The differences could be due to different sludge characteristics and/or different types of reactors. Our reactors were sealed and under pressure and theirs were open [29]. Salsabil et al. [30] evaluated THP of WAS at four temperatures: 40, 60, 90, and 121°C. They found large percentages of VS solubilization as follows: 6.5% (40°C), 11.7% (60°C), 21.2% (90°C), and 4.8% (121°C) which they calculated directly as change of VS weight. Their 121°C data are inconsistent with the other temperatures. Our data show much smaller VS solubilization of VS via production of FDS which was 5.1% at 44°C, 4.5% at 60°C, 8.0% at 88°C, and 12% at 121°C. The differences can be attributed to different measurement methods. Salsbil et al. also measured production of carbohydrates and proteins, however, their results indicate only small amounts of solubilization from less than 1% to a maximum of 38% and 45% for carbohydrates and proteins, respectively, at 90°C [30]. These values are many-fold less than our findings and those of Kugalrz et al. and Neumann et al. described above [27,29].

The average methane yield measured by Kuglarz et al. for THP of WAS between 50 and 100°C was 222 ml CH4 gVS-1 with no correlation to temperature [27]. Compared to the untreated BMP (147 ml CH4 gVS-1) this represents an increase of 51%. The results of the present study are almost identical (147 initial and 211-230 for 44-121°C). Liao et al. reported that the specific biogas production of mixed sewage sludge increased by 7.3%, 15.6% and 24.4% after THP at 60°C, 70°C and 80°C, respectively [31]. Biswal et al. [38] also found smaller increases in BMP of 14 to 30% when THP-treated at 60 to 120°C. Climent et al [32] found the biogas production increased by 50% for 70°C THP of WAS and Rani et al. [33] found an increase of 51% when treating WAS at 60°C at pH 12, both of which are very similar to our findings.

Conclusions

The commercial THP technologies/equipment use high temperatures of around 170°C to solubilize, pasteurize and liquefy PS and WAS prior to AD and thus most studies of THP look at temperatures between 130 to 220°C. There are several studies that have evaluated lower temperature THP to possibly use less energy, including some that have also compared high-pH, ultrasonic, and ozone oxidation processes with low-temperature THP. Herein, we evaluate temperatures between 44 and 121°C to systematically determine the benefits of this lower-energy THP process and we normalized our results per gram of VS since the amount of FDS, carbohydrates, and proteins produced has to be related to the mass of VS treated. Our results generally agree with most of the few other low-temperature THP studies. Low temperatures, between 44 and 121°C are capable of solubilizing between 2 and 3% of the VS in PS and 4.5 to 12%

of VS in WAS into FDS. Carbohydrates and proteins account for the majority of the FDS (55 to 100%), and there are more proteins than carbohydrates at all temperatures (generally 1.6 to 3.5 times as much). The solubilization also produces recalcitrant Melanoidin compounds from a portion of the carbohydrates and proteins (average of 28%) which increase the brown color of the fluids 19-fold. The solubilization also facilitates enhanced methane production of WAS (approximately 50%) but not for PS. The overall effects of low-temperature THP on PS are much less than for WAS. This leads to two possible considerations: first, that THP of PS is not necessary for the goals of enhanced methane production or VS destruction, and second, that THP of WAS is effective and only requires a relatively low temperature to break the cells and have the effect of enhancing downstream digestion speed and methane production. However, high temperature THP has other benefits including greater pathogen inactivation, reduced viscosity, and improved dewaterability [18].

Acknowledgement

This research received funding from R.M. Towill Corporation.

References

1. Bolobajev J, Kattel E, Viisimaa M, Goi A, Trapido M, Tenno T, Dulova N (2014) Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment. Chem Eng J 255: 8–13.
2. Huang P, Li L, Kotay SM, Goel R (2014) Carbon mass balance and microbial ecology in a laboratory scale reactor achieving simultaneous sludge reduction and nutrient removal. Water Res 53: 153–167.
3. Edelmann W, Baier U, Engeli H (2005) Environmental aspects of the anaerobic digestion of the organic fraction of municipal solid wastes and solid agricultural wastes. Water Sci Technol 53(1-2): 203-208.
4. Carrère H, Dumas C, Battimelli A, Batstone DJ, Delgenes JP, Steyer JP, Ferrer I (2010). Pretreatment methods to improve sludge anaerobic degradability: a review. J Haz Matls 183: 1-15.
5. Hartmann H, Moller HB, Ahring BK. Efficiency of the anaerobic treatment of the organic fraction of municipal solid waste: collection and pretreatment. Waste Manage Res 22:35–41.
6. Vavilin VA, Fernandez B, Palatsi J, Flotats X (2008) Hydrolysis kinetics in anaerobic degradation of particulate organic materials: an overview. Waste Manage 28: 939–951.
7. Appels L, Degreve J, Bruggen BV, Impe JV, Dewil R (2010) Influence of low temperature thermal pre-treatment on sludge solubilization, heavy metal release and anaerobic digestion. Bioresour Technol 101:5743–5748.
8. Khalid A, Arshad M, Anjum M, Mahmood T, Dawson L (2011) The anaerobic digestion of solid waste: a Review. Waste Manage 31:1737–1744.
9. Skiadas IV, Gavala HN, Lu J, Ahring BK (2005) Thermal pre-treatment of primary and secondary sludge at 70°C prior to anaerobic digestion. Water Sci Technol 52(1-2): 161–166.
10. Ariunbaatar J, Panico A, Esposito G, Pirozzi F, Lens PNL (2014) Pretreatment methods to enhance anaerobic digestion of organic solid waste. Applied Energy 123:

143-156.
11. Barber WPF (2016) Thermal hydrolysis for sewage treatment: A critical review. Water Res 104: 53-71.
12. Cano R, Pérez-Elvira SI, Fdz-Polanco F (2015). Energy feasibility study of sludge pretreatments: A review. Applied Energy 149: 176-185.
13. Zhen G, Lu X, Kato H, Zhao Y, Li YY (2017) Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. Renewable and Sustainable Energy Reviews 69: 559-577.
14. Zhang J, Li N, Dai X, Tao W, Jenkinson IR, Li Z (2018). Enhanced dewaterability of sludge during anaerobic digestion with thermal hydrolysis pretreatment: New insights through structure evolution. Water Res 131: 177-185.
15. Svensson K, Kjørlaug O, Higgins MJ, Linjordet R, Horn SJ (2018) Post-anaerobic digestion thermal hydrolysis of sewage sludge and food waste: Effect on methane yields, dewaterability and solids reduction. Water Res 132: 158-166.
16. Feng G, Tan W, Zhong N, Liu L (2014). Effects of thermal treatment on physical and expression dewatering characteristics of municipal sludge. Chemical Eng J 247: 223-230.
17. Kepp U, Machenbach I, Weisz N, Solheim OE (2000) Enhanced stabilization of sewage sludge through thermal hydrolysis-three years of experience with full scale plant. Water Sci Technol 42: 89-96.
18. Neyens E, Baeyens J (2003) A review of thermal sludge pre-treatment processes to improve dewaterability. J Haz Matls 98: 51-67.
19. Higgins MJ, Beightol S, Mandahar U, Suzuki R, Xiao S, Lu HW, Le T, Mah J, Pathak B, DeClippeleir H, Novak JT, Al-Omari A, Murthy SN (2017) Pretreatment of a primary and secondary sludge blend at different thermal hydrolysis temperatures: Impacts on anaerobic digestion, dewatering and filtrate characteristics. Water Res 122: 557-569.
20. Hii K, Baroutian S, Parthasarathy R, Gapes DJ, Eshtiaghi N (2014) A review of wet air oxidation and thermal hydrolysis technologies in sludge treatment. Bioresource Technol 155: 289-299.
21. Pilli S, Yan S, Tyagi RD, Surampalli RY (2015) Thermal pretreatment of sewage sludge to enhance anaerobic digestion: A review. Critical Reviews in Environ Sci Technol 45: 669-702.
22. Higgins M., Murthy SN, Schafer P, Cooper A, Kasirga E, Lee K, Machisko J, Fountain P, Kelleher K (2011) Dewatering characteristics of Cambi thermal hydrolysis biosolids: centrifuges vs. BFPs. Proceedings of WEFTEC 2011: 678-684.
23. Chauzy J, Cretenot D, Patria L, Fernandes P, Sauvegrain P, Levasseur JP (2003). BioTHELYS: A new sludge reduction process. Proc. International Water Association (IWA) Specialist Conference, BIOSOLIDS: 473-479.
24. Chauzy J, Cretenot D, Bausseron A, Deleris S (2008) Anaerobic digestion enhanced by thermal hydrolysis: First reference BIOTHELYS® at Saumur, France. IWA Water Practice and Technol 3(1).
25. Wilson CA, Novak JT (2009) Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. Water Res 43(18): 4489-4498.

26. Mottet A, Steyer JP, Déléris S, Vedrenne F, Chauzy J, Carrère H. (2009) Kinetics of thermophilic batch anaerobic digestion of thermal hydrolysed waste activated sludge. Biochem Eng J 46: 169-175.
27. Kuglarz M, Karakashev D, Angelidaki I (2013) Microwave and thermal pretreatment as methods for increasing the biogas potential of secondary sludge from municipal wastewater treatment plants. Biores Technol 134: 290-297.
28. Dwyer J, Starrenburg D, Tait S, Barr K, Batstone DJ, Lant P (2008) Decreasing activated sludge thermal hydrolysis temperature reduces product colour, without decreasing degradability. Water Res 42: 4699-4709.
29. Neumann P, González Z, Vidal G (2017) Sequential ultrasound and low-temperature thermal pretreatment: process optimization and influence on sewage sludge solubilization, enzyme activity and anaerobic digestion. Biores Technol 234: 178-187.
30. Salsabil MR, Laurent J, Casellas M, Dagot C (2010) Techno-economic evaluation of thermal treatment, ozonation and sonication for the reduction of wastewater biomass volume before aerobic or anaerobic digestion. J Haz Matl 174: 323-333.
31. Liao X, Li H, Zhang Y, Liu C, Chen Q (2016) Accelerated high-solids anaerobic digestion of sewage sludge using low-temperature thermal pretreatment. Intl Biodeter Biodegrad 106: 141-149.
32. Climent M, Ferrer I, del Mar Baeza M, Artola A, Vázquez F, Font X (2007) Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions. Chem Eng J 133: 335-342.
33. Rani RU, Kumar SA, Kaliappan S, Yeom IT, Banu JR (2012) Low temperature thermo-chemical pretreatment of dairy waste activated sludge for anaerobic digestion process. Biores Technol 103: 415-424.
34. Dubois M, Gilles KA, Hamilton JK, Rebers PT, Smith F (1956) Colorimetric method for determination of sugars and related substances. Analytical Chem 28(3), 350-356.
35. Lowry OH, Rosebrough NJ, Farr AL, Randall RJ (1951) Protein measurement with the Folin phenol reagent. J Biological Chem 193: 265-275.
36. Lopes GR, Ferreira AS, Pinto M, Passos CP, Coelho E, Rodrigues C, Figueira C, Rocha SM, Nunes FM, Coimbra, MA (2016) Carbohydrate content, dietary fibre and melanoidins: Composition of espresso from single-dose coffee capsules. Food Research International, 89: 989-996.
37. APHA. Standard Methods for the Examination of Water and Water Water. 21th ed. Washington DC, USA: American Public Health Association/American Water Works Association/Water Environment Federation, 2005
38. Biswal, B. K., Huang, H., Dai, J., Chen, G. H., & Wu, D. (2020). Impact of low-thermal pretreatment on physicochemical properties of saline waste activated sludge, hydrolysis of organics and methane yield in anaerobic digestion. Bioresource Technology, 297: 122423.

CHAPTER 3.

Article

Comparison of High and Low Temperature THP on Product Speciation of Sewage Sludge

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Received: date; Accepted: date; Published: date

Abstract: Product speciation of soluble components in secondary sewage sludge during THP is investigated in this research. The dissolved components concentrations increased with increasing THP temperatures (between 80 and 220℃) and reaction time (between 0 and 60 min), including dissolved solids, COD, TOC, carbohydrates, VFA, TN, protein, amino acids, and ammonium. At low temperature THP as 80℃, the carbohydrate and protein portion to sCOD is higher than the high temperature THP (110-200℃) due to THP releases nutrients from intercellular to free water but temperature not high enough to break down these structures. Proteins are highly denatured at 200℃ that ammonium concentration goes much higher than other conditions. The liquid brown color which is mainly from melanoidins generated during THP goes darker with temperature up and reaction duration. Melanoidins concentrations are also calculated from high molecular weight material, protein and carbohydrate, whereas the results fail to follow with the color results because of inaccurate conducted in measurements.

Keywords: thermal hydrolysis pretreatment, waste activated sludge, speciation

1. Introduction

Thermal hydrolysis process (THP) pretreatment of sewage sludge prior to anaerobic digestion (AD) provides benefits including reduced stabilization time, improved dewaterability of both THP sludge and digested sludge, reduced sludge viscosity, reduced odors and pathogens [9, 10, 11, 31, 17, 33].Some disadvantages of THP include high energy demand, potentially higher ammonia concentrations in the digester, and post cooling requirements before feeding to AD [3, 32]. There is a lot of interest THP because of the potential benefits, however, there are fewer than 80 systems in operation worldwide, with most located in Europe [12].

It has been found that the methane production from THP-treated waste activated sludge (WAS) during subsequent AD is much improved, because the organic compounds contained in cellular material in WAS can be released into the liquid phase during THP [31,11,22,23,25]. The enhancement of methane production is observed to be greater when the untreated sludge

biodegradability is lower [27]. High molecular weight (HMW) substances and particulate volatile solids (VS) in sludge can be hydrolyzed via THP (instead of the normal enzyme-catalyzed hydrolysis in AD) into low molecular weight (LMW) substrates ready for acidogenesis in the AD process. This facilitates a decrease of required solids retention time (SRT) and accelerated methane production [13, 14, 15]. The commercialized THP process by Cambi has shown that biogas yield increased by 25% in WAS-only THP and chemical oxygen demand (COD) load could be increased from 301 to 486 lb d-1 [26]. Because of physical/structural changes occurring during THP, the viscosity is decreased which improves dewaterability of the AD-treated sludge which reduces necessary energy input in cases where drying is utilized for final processing into reusable biosolids [16, 17]. Dewaterability improved by 28-29% during WAS-only Cambi THP [26]. THP is usually conducted at high temperature (160 – 200°C) and high pressure (0.7 – 0.8 MPa), conditions under which pathogens are very effectively killed so that THP+AD-treated sludges can easily reach Class A biosolids standards of the US EPA [8].

Several studies have been conducted to better understand the physical and chemical changes occurring during THP. Soluble COD (sCOD) increased linearly with treatment temperature from 90 to 200°C during THP of WAS [27]. The breakdown of proteins, polysaccharides and lipids was temperature dependent, and caramelization and Maillard reactions that form recalcitrant Melanoidin compounds were observed at temperatures higher than 200°C [3]. A study by Lu et al. [29] revealed that high temperature THP (172oC) of sludge mainly improved the release of low molecular weight (LMW) proteins and polysaccharides. Carbohydrate availability decreased at temperatures higher than 130oC because of Maillard reactions with other carbohydrates and/or solubilized proteins [27]. The physical and chemical effects of THP were much greater at higher feed sludge concentrations, higher temperatures, and longer duration of treatment, including sCOD release and apparent viscosity decrease [30].

Recalcitrant compounds with brown color known as Amadori products and Melanoidins are produced from other organic materials during THP [1, 9, 17, 18, 24]. The Melanoidins remain following AD and dewatering fluids (e.g. in centrate) will have a pronounced brown color that could cause problems in some cases for downstream UV disinfection [3]. Melanoidins are produced by polymerization of LMW intermediates of carbohydrates and amino/proteins at high temperature through a reaction known as the Maillard reaction that has been well studied in food/coffee preparation processes [20]. Melanoidins are quantified indirectly by subtracting the LMW carbohydrates and proteins from total HMW material [Lopes, et al., 2016]. In food-industry situations, Melanoidins can be estimated using color dilution techniques [21], however, this method cannot be used for THP-treated sludge samples as the liquid is initially colored, and caramelization which also generates brown color, also occurs during THP [3].

In this study, the speciation of solubilized products from WAS treated at low to high temperature (80 - 200°C) THP for 15 to 60 min duration was investigated. This fills a gap in the literature for a wide temperature range of THP and a practical range of reaction times.

2. Materials and Methods

Gravity-belt-thickened WAS was obtained from a trickling-filter-solids-contact (TF/SC) secondary WWTP that receives an average flow of 98 million liters per day (MLD)(26 million gallons per day, MGD) of municipal wastewater with no industrial component. Samples were stored at 4°C and used within 48 hours of collection. Thermal treatment was conducted by placing 100 ml capacity Teflon lined stainless-steel hydrothermal synthesis reactors (BAOSHISHAN, Hangzhou, China), containing 90 ml of sludge sample with 3 to 4 g volatile solids (VS) into a pre-heated oven. The reactor vessels can tolerate pressures up to 3 MPa. These reactors have a large thermal mass and thus require time to heat up the sludge contents. Temperature indicator tape placed inside the reactors was utilized to pre-determine internal temperatures and required heating times. The heating-up time depended on the THP temperature: 30 min for 80°C, 38 min for 110°C, 45 min for 140°C, 53 min for 170°C and 70 min for 200°C. Four reactors were heated simultaneously for each temperature. Once the heating-up time ended, one of the reactors was taken out and used as the 0 min THP sample. Then the oven temperature was set to 10°C above the THP test temperature, and the other reactors were taken out after 15, 30 or 60 min. The hot reactors were put into an ice-water bath immediately to rapidly cool to room temperature, then samples were stored at 4°C and analyzed within 48 hours. For this study, 80°C is considered "low" temperature THP, 110°C is considered "medium" temperature THP, and 140, 170, and 200°C are considered "high" temperature THP.

Sludge samples were centrifuged at 3260 G for 5 min. Supernatant was then filtered via a 1.5 μm glass fiber filter (Whatman 934AH), followed by 0.45 μm and 0.1 μm membrane filters (Millipore, Millex® – HN Filter Unit, Ireland). The 0.45 μm filtrate was further filtered using a stirred cell (Millipore, Amicon®, Germany) containing either an Ultracel 10kDa or 100kDa ultrafiltration disc (Millipore, Ultracel® Ultrafiltration Discs, U.S.A.). Approximately 30 ml of 0.45 μm filtrate was processed in the stirred cell at a headspace pressure of 0.38 MPa (55 psi) for 20 min in order to yield 15 ml filtrate. Dissolved solids in 0.45 μm, 100 kDa, and 10 kDa filtrates were measured after freeze drying. 7 ml liquid samples in sealed glass vials were frozen at -40°C for 12 hours, then the vials were unsealed and placed in the freeze dryer (SP scientific, Model # 6KBTES-55, Qarminster, PA, USA) . Freeze drying took 24-48 hrs for ice sublimation and the fully dry powder remaining was weighed as total dissolved solids (TDS). The remaining 0.45 μm, 100 kDa, and 10 kDa filtrates (8 ml) were analyzed within 24 hours for various constituents. Carbohydrates were measured using the phenol-sulfuric acid method [5]. Proteins were measured using the Lowry-Folin assay [6]. The 10 kDa filtrate is considered the low molecular weight (LMW) material. The high molecular weight (HMW) material was calculated by subtracting the 10 kDa filtrate concentrations from the 0.45 μm filtrate concentrations. The Melanoidins concentration was calculated by subtracting the HMW protein and HMW carbohydrate fractions from the total HMW material. [Lopes et al 2016]. For some analyses (TOC,

TN) the middle molecular weight materials (MMW) was also calculated as the 100 kDa filtrate minus the 10 kDa filtrate and in that case the HMW was the 0.45 μm filtrate minus 100 kDa filtrate.

Color and sCOD were measured via Standard Methods 2120B and 5220D, respectively [APWA, 2005]. Total carbon (TC) and total nitrogen (TN) were measured on a Shimadzu TOC-VCSH with TNM-1 (Kyoto, Japan), and ammonium was measured using a Dionex ICS-1100 ion chromatograph (Thermo Fisher Scientific, Waltham, MA). Viscosity was measured by a Brookfield DV-II+ Pro viscometer (AMETEK Brookfield, Middleboro, MA) using sludge samples at room temperature (22°C). Volatile fatty acids (VFA) were extracted by MTBE solvent [7]. A Thermo Scientific Trace 1300 GC (Waltham, MD) equipped with a flame ionization detector (FID) was used for VFA analysis. Analytes were separated on a StabilwaxDA 30 m x 0.25 mm x 0.25 μm column and a 5 m x 0.25 mm polar deactivated guard column (Restek, Bellefonte, PA). Helium was used as the carrier gas at a flow rate of 1.4 ml min^{-1}, and inlet temperature was 240°C. Oven temperature started at 60°C for 1.55 min, ramped to 220°C at 12.5°C min^{-1}, then to 250°C at 25°C min^{-1} and held for another 9.45 min. A 1.0 μl splitless injection was performed with a splitless time of 1 min. The FID temperature was 250°C, air flow was 350 ml min^{-1}, makeup gas (nitrogen) flow was 40 ml min^{-1} and hydrogen flow was 35 ml min^{-1}.

Thermo Scientific Ultimate 3000 UHPLC with fluorescence (FLD) and diode array detectors (DAD) was used to analyze amino acid (AA). The method was adapted from "Automated in-needle derivatization applying a User-Defined Program for the Thermo Scientific Dionex WPS-300 Split-Loop Autosampler" (Dionex Technical Note 107), but the column used was a Hypersil Gold C18 (100 mm x 2.1 mm x 3 μm) with its corresponding guard column. The mobile phase gradient is shown in Table 1, where Eluent A was 10 mM Na_2HPO_4 and 10 mM $Na_2B_4O_7 \cdot 10H_2O$, adjusted to pH 7.8 with concentrated HCl and Eluent B was a mixture of acetonitrile, methanol and water at 45/45/10 v/v/v. Flow rate was set to 0.46 ml min^{-1}. Both UV (338 nm) and fluorescence (excitation 337nm, emission 442 nm) were used for detection/quantitation.

Table 1. Mobile Phase Gradient for AA analysis

Time (min)	Eluent B (%)	Curve
0.0	2	5
0.2	10	5
2.5	12	6
10.8	30	6
13.7	52	5
14.5	100	5
17.5	100	5
18.5	2	5
25.0	2	5

3. Results

Figure 1 shows the quantities of HMW (1a) and LMW (1b) TDS produced during THP at 80, 110, 140, 170, and 200°C for durations of 15, 30, and 60 min. The rightmost set of columns labeled WAS are the untreated WAS TDS values for HMW and LMW fractions. Different THP temperatures were tested on different days with different WAS samples and there is a slight variation in untreated WAS TDS observed. The zero duration set of columns are the results for the reactors which were removed immediately after the heat-up time was finished. These columns represent the thermal effects of heating from 25°C up to the test temperature (from 30 to 70 min) which are significant. The data show a steady increase in solubilized VS with reaction time and with reaction temperature. (Figure 1). Table 1 indicates that the total amount of VS hydrolyzed at the low (80°C) and medium (110°C) temperatures are quite similar at approximately 20 to 30%, while it increases quite a bit at the higher temperatures of 140°C (20-38%), 170°C (22-54%), and 200°C (36-61%). The effect of reaction time is also readily apparent for each reaction temperature, with total hydrolyzed increasing approximately 50% when the reaction time is increased from 15 to 60 minutes. Figure 1 and Table 1 also show how the THP process produces more LMW materials than HMW, but how much more depends on the temperature. At the low temperature (80°C), 65 to 80% is LMW; at medium temperature (110°C), 57 to 66%; at high temperatures (140-200°C) there is 58 to 77% LMW. For all temperatures tested, the amount of HMW TDS tends to increase with reaction time and thus, the percentage of LMW TDS decreases. Compared to untreated WAS, the increases in TDS are very large indeed; 5 to 8 times for LMW and 11 to 36 times for HWM.

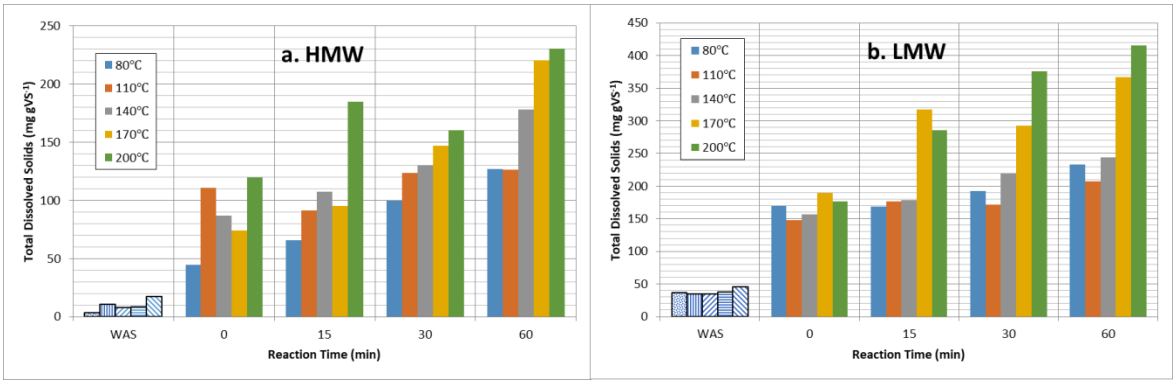

Figure 1. TDS of LMW filtrate (a) and HMW filtrate (b) following THP of WAS for 0 to 60 min at low (80°C), medium (110°C) and high (140, 170, 200°C) temperatures.

Table 1. Effect of THP temperature and reaction time on hydrolization of VS to HMW and LMW materials.

THP Temp (°C)	Reaction time (min)	Total TDS hydrolyzed (mg/gVS)	Total VS hydrolyzed (%)	VS hydrolyzed to HMW (%)	VS hydrolyzed to LMW (%)
80	0	174	17	21	79
	15	194	19	28	72
	30	252	25	34	66
	60	320	32	35	65
110	0	213	21	43	57
	15	222	22	34	66
	30	250	25	42	58
	60	288	29	38	62
140	0	200	20	36	64
	15	243	24	37	63
	30	306	31	37	63
	60	378	38	42	58
170	0	217	22	28	72
	15	367	37	23	77
	30	393	39	33	67
	60	541	54	37	63
200	0	363	36	38	62
	15	410	41	40	60
	30	530	53	39	61
	60	614	61	33	67

Similar to TDS, the sCOD and TOC concentrations also increased with THP temperature and reaction time (Figures 2 and 3). The sCOD and TOC comprise the majority of the organic fraction of TDS released or liquefied during THP [4,3].

The five treatment temperatures can be separated into three groups based on TOC increment amount at each treatment temperature: high temperature (200°C), mid temperature (170 and 140°C) and low temperature (110 and 80°C). Within each of these groups, the amounts of TOC solubilized are closer to the others at the same reaction time than the other temperature groups. This indicates that the reactions releasing TOC during THP occurred in steps of different temperatures. The increased TOC mainly consisted of LMW materials smaller than 10 kDa, especially for the 200°C THP sludge. The HMW TOC is also increased with THP treatment.

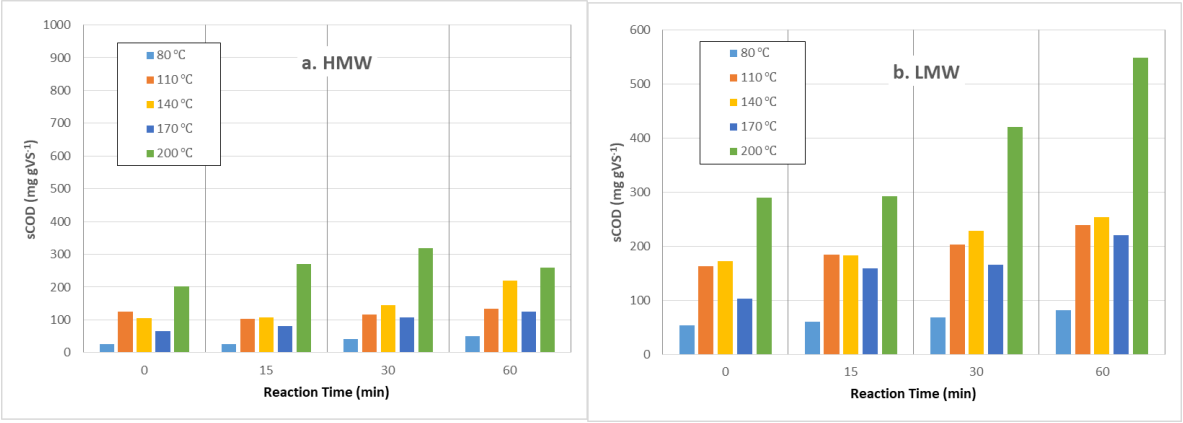

Figure 2. sCOD of HMW filtrate (a) and LMW filtrate (b) following THP of WAS for 0 to 60 min at low (80), medium (110) and high (140, 170, 200°C) temperatures

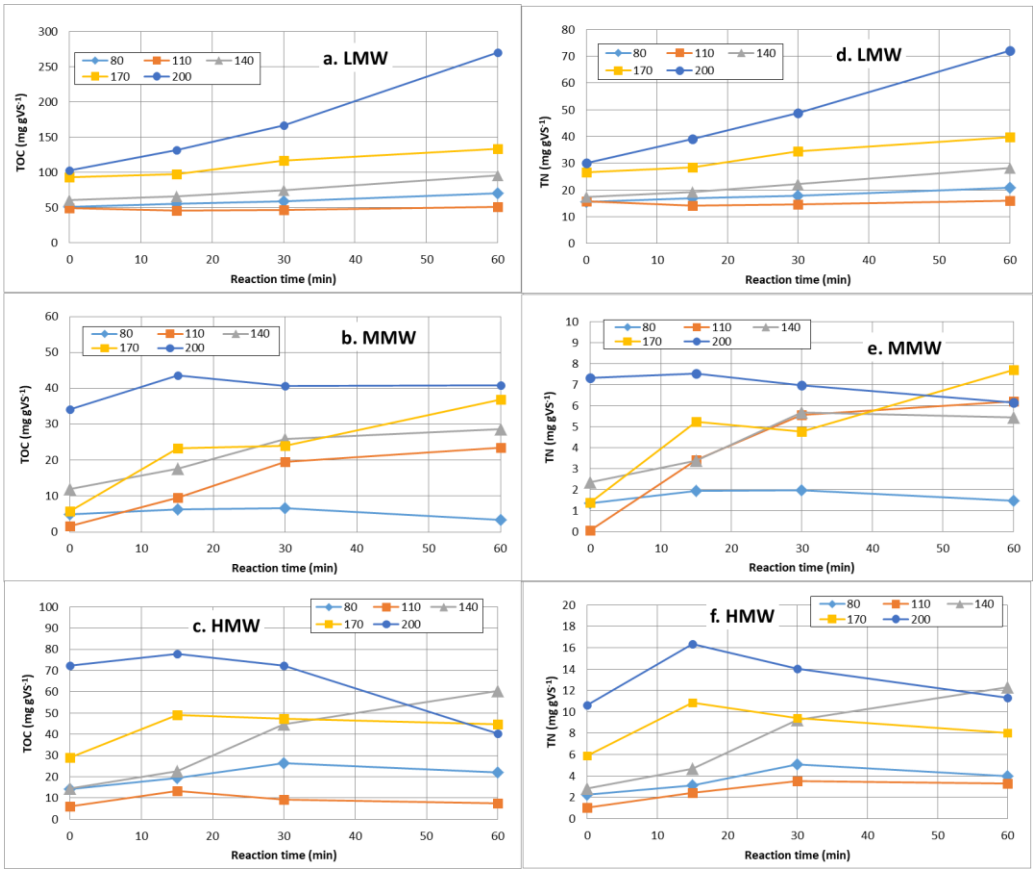

Figure 3. TOC and TN of LMW filtrate (a, d), MMW filtrate (b, e), and HMW filtrate (c, f) following THP of WAS for 0 to 60 min at low (80), medium (110) and high (140, 170, 200°C) temperatures

The carbohydrate vs. sCOD concentrations in Figure 4, show that low temperature THP-treated sludge has a higher proportion of carbohydrate in the sCOD. Biomass cell walls were destroyed so that intercellular material with large amounts of carbohydrates and proteins were liberated. However, with higher THP temperatures the carbohydrate and proteins decompose. Even though, this result is opposite than the result in research of Y.Xue [4] that they found high-temperature THP data led to a higher slope. This maybe because their THP procedure is different than this research that they did not count the heating-up time separately so the true temperature inside of sludge sample is not high as target THP temperature. And they also pointed out that with the highest temperature in their research (180 °C), soluble protein/COD ratio plot displayed a lower slope. Table 2 shows the slopes of the trendlines for the relationships in Figure 4.

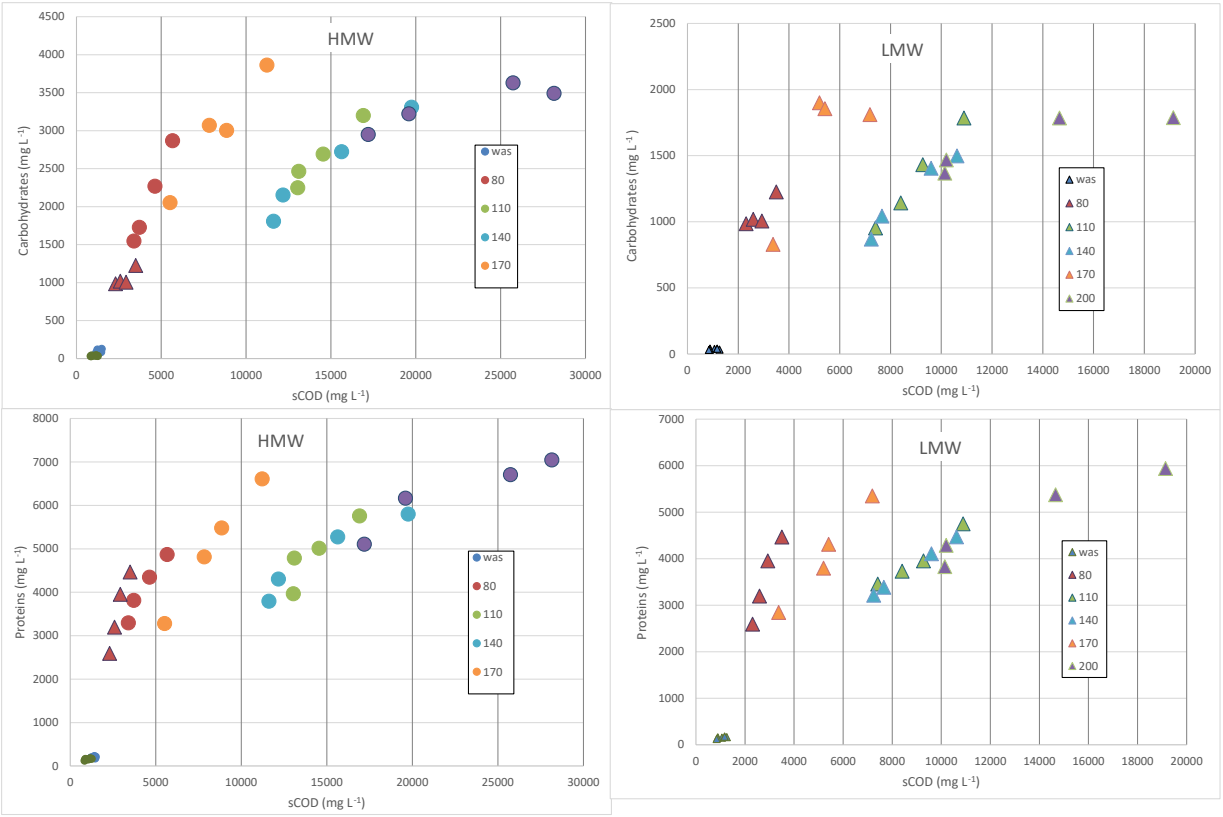

Figure 4. sCOD vs. Carbohydrate concentrations, and sCOD vs. Protein concentrations in THP-treated WAS

Table 2. Trend Line Slopes Between COD and Carbohydrate, COD and Protein in THP Sludges

THP temperature (°C)		80	110	140	170	200
Carbohydrate	**Trend line slope**	0.58	0.22	0.17	0.30	0.05
	R^2	0.99	0.96	0.97	0.95	0.83
Protein	**Trend line slope**	0.50	0.36	0.23	0.59	0.16
	R^2	0.95	0.80	0.93	0.99	0.89

Two main components of TOC in THP-treated sludge samples are carbohydrates and VFAs, where the carbohydrates are mainly from destroyed fibers and VFAs are from broken-down long chain fatty acids. For example, in the 170°C THP-treated for 30 mins sludge, 46% of TOC are carbohydrates and 8% are VFAs. Carbohydrates increased with THP temperature and reaction time. The fate of total VFA concentration after THP is the same as TOC which can be separated into three groups by temperatures.

The decomposition of long-chain fatty acids to VFAs is relatively thorough to the 2 to 4-carbon acids. Among the various C2-8 VFAs, more than half of the total are acetate (C2), about 30% are propionic (C3), about 10% are isobutyric and butyric (C4), and the rest which total less than 10% are C5-8. The increase in total VFAs is mainly from acetate and VFAs of C3-8

concentrations are almost unchanged by THP. The rapid increasing of acetate is only apparent at 200℃ THP because of amino acid decay when the treatment temperature is above 170℃ [4]. In their research, they also found that VFAs of low temperature THP sludge is even higher than others when the reaction time is very long (72 hrs). In the present study, the data show that at 80℃, total VFAs concentration is the lowest and this is because our reaction time is too short (15 to 60 min) for generating large amounts of VFAs. Interestingly, the majority of the VFAs do not increase with reaction times except for C2 at 200℃ THP sludge.

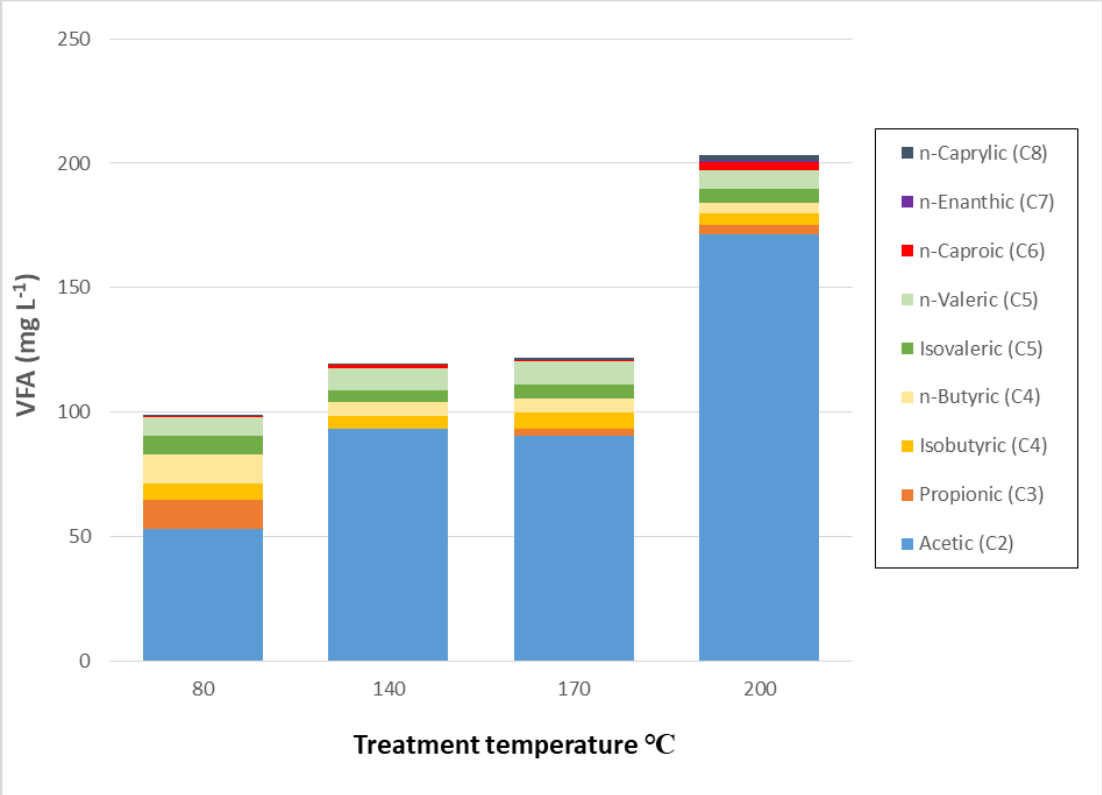

Figure 5. VFA concentrations of un-treated and THP-treated WAS at 80 to 200°C, for 15 to 60 min.

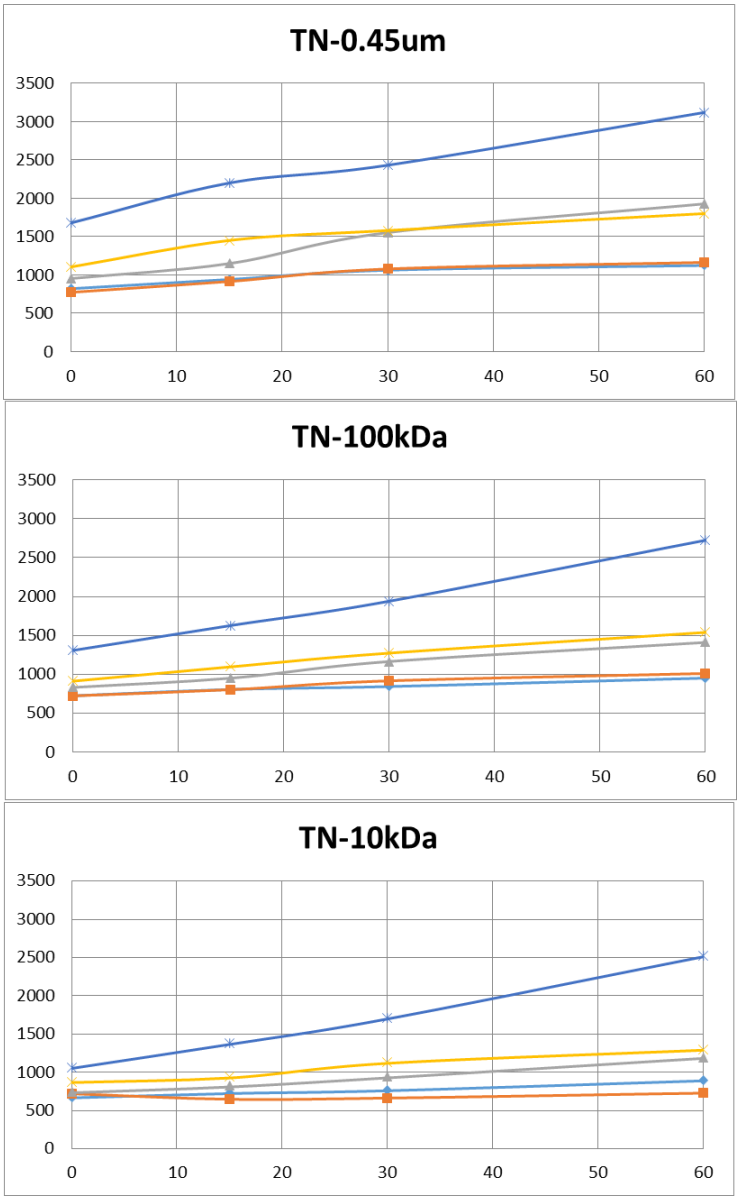

Figure 6. TN Concentrations of Untreated and THP-treated WAS at 80 to 200°C, for 15 to 60 min.

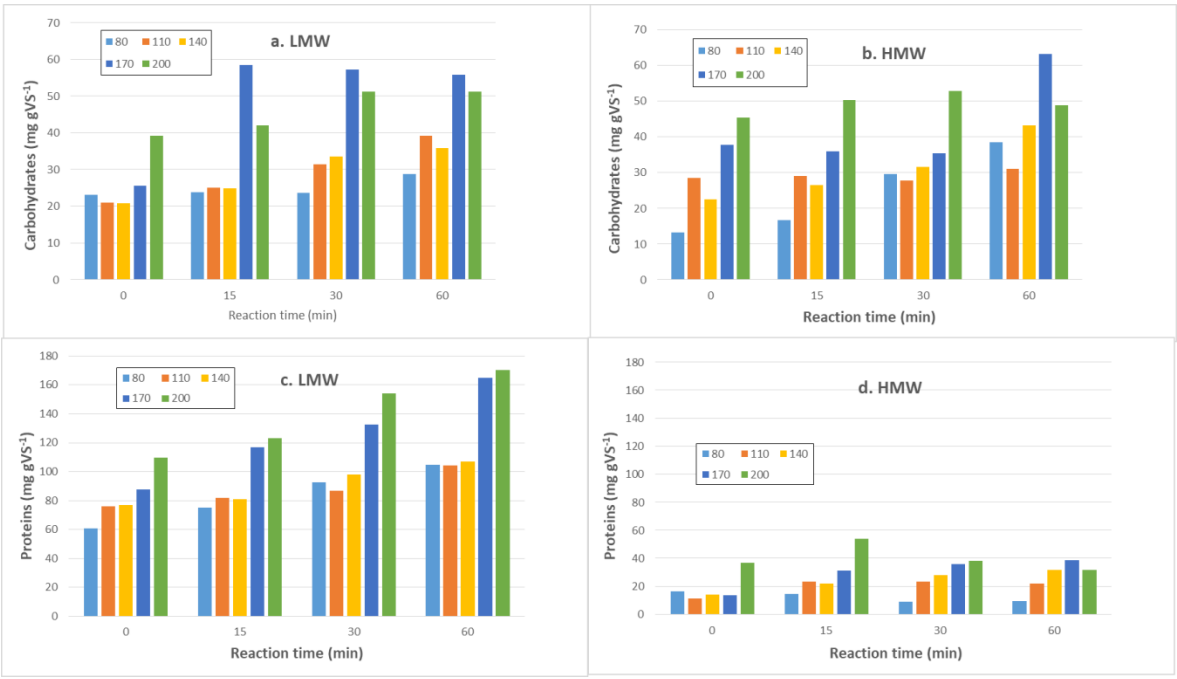

Figure 7. Protein Concentrations of Untreated and THP-treated WAS at 80 to 200°C, for 15 to 60 min.

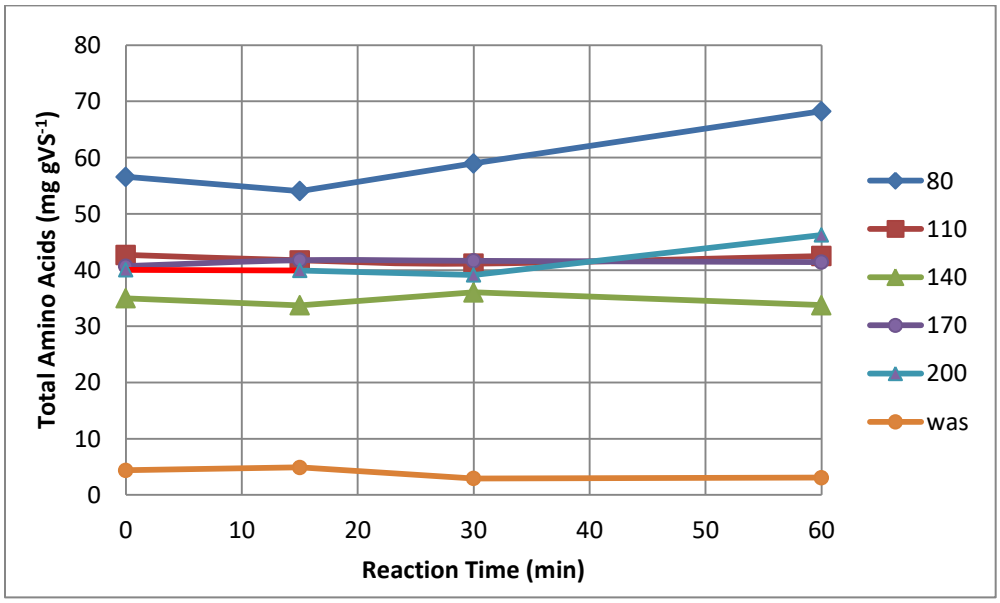

Figure 8. Total AA Concentrations in untreated and THP-treated WAS at 80 to 200°C, for 15 to 60 min.

The three temperature groups of THP are also shown in TN concentration changes (Figure 6), including protein, AA and ammonium (Figures 7-9). As another main component of TDS other than carbohydrate, protein weights higher especially in LMW. The LMW protein (size less

than 10kDa) is 80% of the total dissolved protein (size less than 0.45 μm), indicating thermal denaturing of large proteins and only a small amount of HMW proteins remains. With further decomposition, amino acids were released from protein. However, the concomitant rising of total amino acid concentration with reaction time is not continuous because some types of amino acids will break down into ammonium. Seventeen amino acids were measured.

The ammonium concentrations at different THP temperatures are displayed in Figure 9 The trend is same as TOC and TN that increments are proportion temperature and reaction times, and the increments are similar inside each temp group. Only 110 and 140 ℃ data are miss-ordered, and the reason is they are treated from sludges collected from different days which contain variability initially. Ammonium is one of the by-products of protein, amino acid and other organic compounds decomposition reactions during THP. Higher ammonium concentration indicates more organics are decomposed. It needs to be mentioned that high concentration of ammonium is a common problem in THP as it is a toxic by production in the following sludge treatment process, anaerobic digestion.

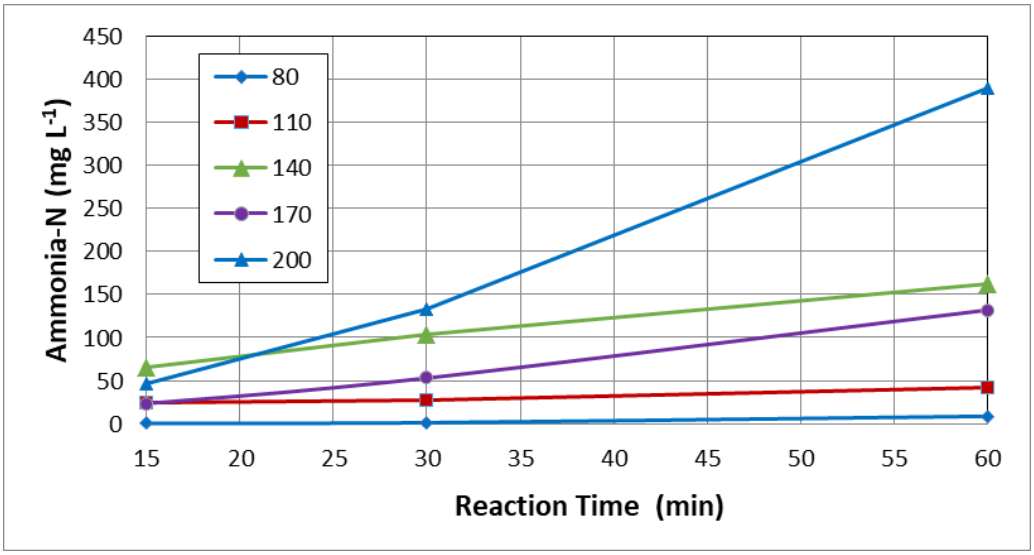

Figure 9. Ammonium Concentrations of Untreated and THP-treated WAS at 80 to 200°C, for 15 to 60 min**.**

The three temperature groups of THP are also shown in TN concentration changes (Figure 6), including protein, AA and ammonium (Figures 7-9). As another main component of TDS other than carbohydrate, protein weights higher especially in LMW. The LMW protein (size less than 10 kDa) is 80% of the total dissolved protein (size less than 0.45 μm), indicating thermal denaturing of large proteins and only a small amount of HMW proteins remains. With further decomposition, amino acids were released from protein. However, the concomitant rising of total amino acid concentration with reaction time is not continuous because some types of amino acids will break down into ammonium. Seventeen amino acids were measured.

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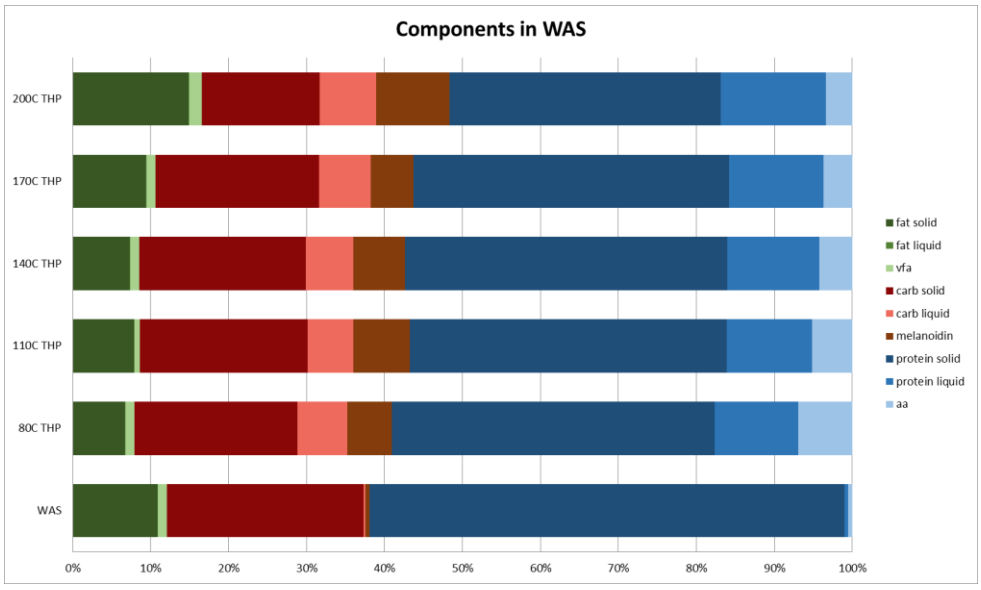
Components in THP-treated sludge are shown in Figure 10. The carbohydrates and proteins in sludge were dissolved into liquid after THP treatment and the solubility portion was slightly increased with reaction temperature. At the same time, melanoidins were produced through the Maillard reaction [17]. Protein denaturing also occurred during THP and amino acids were produced. However, with reaction temperature increases, amino acids were decomposed [28]. The fat oil and grease (FOG) is hydrophobic that mainly exists in solid phase and the concentration is relatively stable with THP.

The components increment follow nicely of the trend of THP temperatures and reaction times shown in Fig. Besides of the reactions mentioned above, it is shown that all these reactions do not reach equilibrium in 60 min, indicating THP is a slow reaction that been confirmed by Y. Xue et al. study.

a.



b.

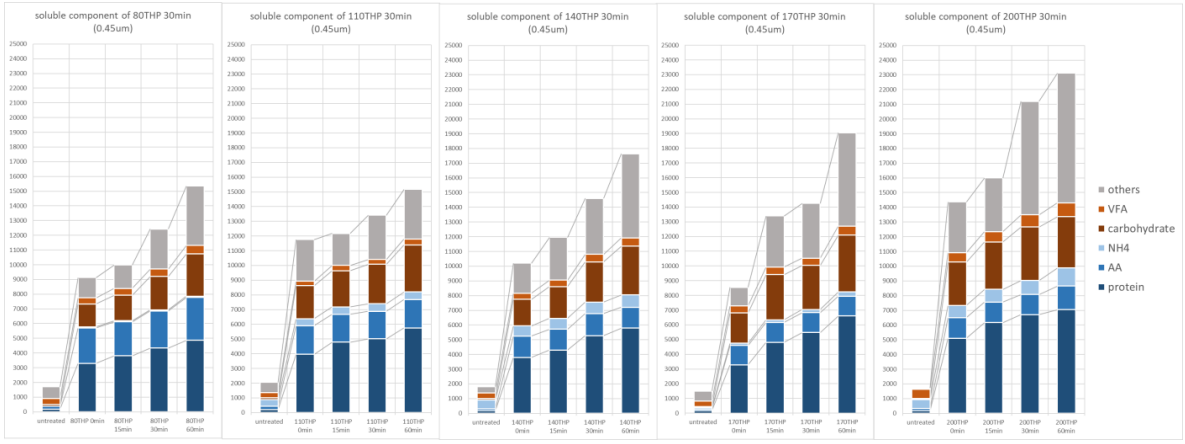


Figure 10. Components in Solid and Liquid of 30min THP WAS (a) and all Soluble Components in 30min THP treated samples (b)

The BMP of THP treated sludge increased by 32%-51% compared with untreated (Figure 11). The BMP increasing is because of biodegradability improvement and nutrients released from cell wall destruction. This result is confirmed by other publications [27].

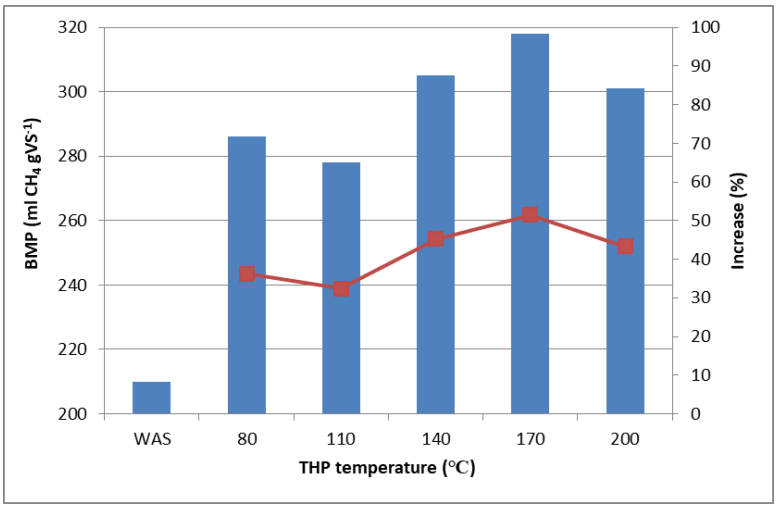


Figure11. BMP of 30 min THP treated WAS

The color changes and Melanoidin concentrations in sludge with different pretreatment temperature and reaction time are displayed in Figure 12. It is clearly that sludge color increases with thermal pretreatment temperature and the reaction time. Even though the color of untreated sludge is variable (32-253 Pt-Co unit) because of different sample collection days, all thermal treated sample colors are much higher (626 Pt-Co at 80℃ for 0 min, and 4906 Pt-Co at 200℃ for 60min) compared with the average value of untreated sludge (205 Pt-Co). The color is increased with pretreatment temperature and reaction time.

Under high temperature, colored recalcitrant compounds are generated from carbohydrates and amino compounds which are known as Maillard reaction [1]. The colored compounds are known as Melanoidins, and the data are shown in Fig.1.b. Same as the color, Melanoidin concentrations are also increase with pretreatment temperature and the reaction times. However, the maximum concentration is achieved at 30-60 min of reaction at 200°C but the darkest color within this research is only at the same temperature with 60 min of reaction time and very likely keep increasing with longer reaction time or higher temperature. The reason of color and Melanoidin increase out of synchronization is because Caramelization also occurs during the thermal treatment which would contribute to color in effusion [2]. It is also noticed that some of the Melanoidin concentration curve are miss-ordered within some temperatures, resulting of indirectly measurement where errors in each measurement step are accumulated.

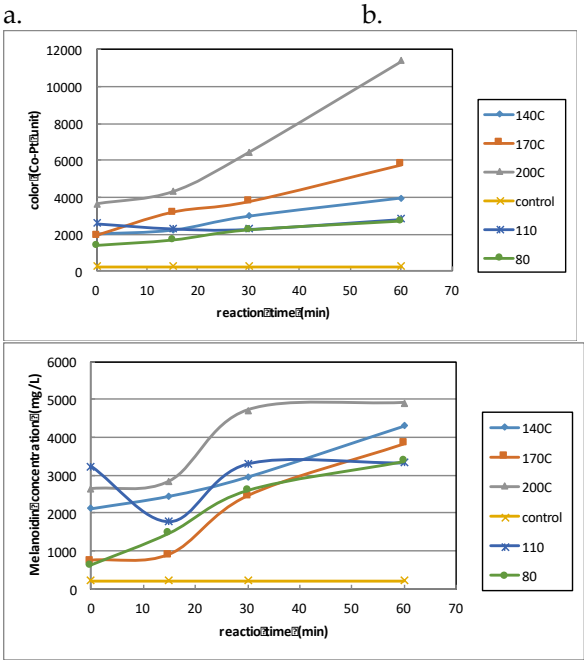


Figure 12. Color (a) and Melanoidin Concentrations (b) of Sludge Treated with Different THP Temperature and Reaction Time

4. Discussion

Previous studies found that organic matter is solubilized with THP, and the solubilization extent increases with higher temperature, longer treatment time, and sludge concentrations [3,4,17,15]. Farno reported the sCOD of 80°C THP treated sludge increased 2.5 times, and in our study the sCOD increased by 1.7-3.6 times at the same temperature for 0-60 min of treatment. The highest sCOD increase was achieved at 200°C THP for 60mins, and the increment is about 18 times of the untreated WAS. Feng (2014) observed the sCOD went up to 18.4-fold times of untreated WAS after a 170°C THP for 60min. Wilson (2009) found the sCOD of 220°C THP treated WAS increased by about 17 times. Our resuts agree with all of these previous reports. Same as the

sCOD, TOC, soluble protein and carbohydrates are increased in the same way when treated with THP [3,4].

The compounds investigated by molecular weight is for the Melanoidin measurement, so proteins and carbohydrates were measured by LMW (<10kDa) and HMW (10kDa-0.45um). And the data indicated that about 80% of the soluble proteins are consisted of LMW, and about 49% of the soluble carbohydrates are LMW. Lu (2018) found that the LMW proteins are more abundant than HMW proteins because of protein size is reduced when pre-treated at temperature higher than 150℃. However, their LMW portion was less than 350Da, which is a much smaller size than the LMW defined in this study, thus all the LMW proteins at different temperature THP took a bigger portion in our case, and the portion kept the same range with different temperature.

From the plots of sCOD vs soluble carbohydrate and sCOD vs soluble protein, the organic matter dissolution rate was studied. The data of low and medium THP temperatures at different reaction times fit with a good linear relationship (R^2 of these trend lines are 0.93-0.99). This indicated that liquefaction of the organic matter maintained a stable rate under the same temperature. However, the linearity decreased at 200C and this is may be because of Maillard reaction and decomposition/hydrolyzation. This conclusion is in agreement with Xue's report (2015) that they consist the phenomena happened at 180℃ or higher temperatures. Besides, the slopes were decreased with reaction temperature increase and that carbohydrate slopes wrer 0.58 to 0.05 and for protein slopes 0.50 to 0.16. The release of carbohydrates and proteins were dominant in the total organic matters/sCOD at low temperatures, and with temperature increase, other substrates (VFAs and unknowns) were dissolved to the liquid phase.

VFA concentrations remained stable at 60-80℃ THP within the first 24h, increased at 120-160 ℃ and exhibited a relatively high increase at 180C because of the AA decomposition [4]. We found a significant increase of VFA at temperature 200C compared to other temperatures that is in agreement with the previous publications, however, the VFAs started to increasing at low temperature treatment (80 ℃). It may be because of the intercellular materials released out into free water when cell wall broken from THP even at the low temperature.

Ammonia concentrations started to increase from 140C and got larger with increased reaction time. Wilson (2009) observed that the evolution of ammonia reached the maximum at 170℃, however, our results shows the ammonia reached the maximum at 200 ℃. And it is in agreement with Jeong [15] that they reported that ammonia gradually increased from 100 ℃ to 220 ℃.

Melanoidin concentrations increased rapidly after THP treatment, and the concentrations increased to maximum at 200℃. The Melanoidin concentration is related to solubility of both carbohydrates and proteins [31]. The main characteristic of Melanoidin is the brown color, and so it the color increasing meet the trend of THP temperature and reaction time. The color production is 3939 Pt-Co unit at 140C (60 min) and 5786 Pt-Co unit at 170℃ (60 min), the increments is much smaller than Dwyer that they found color increased to 12688 mg-PtCo/L from 3837 mg-PtCo/L as temperature from 140℃ to 165℃. This difference may be because of different sludge properties.

It has been widely known that the biogas production of THP-treated WAS can be improved compared with untreated WAS. The increment of biogas production of WAS THP at low temperature (65-70 ℃) is 28% - 50%, and the increment of THP at high temperature (165-180 ℃) is 42% - 100% [25,27]. Biogas production increased with treatment temperature that methane increased for about 28% after treatment of 70 ℃ and 121 ℃, for about 51% with THP of 172 ℃ [29]. The biogas production decreased from a pre-treatment temperature higher than 175 ℃ which is observed by Bougrier [27], and is explained by inhibitory compounds and recalcitrant formation. Similar results were obtained in the present study that the highest BMP was obtained at 170℃ THP (318 $mlCH_4\ gVS^{-1}$), and decreased to 301 $mlCH_4\ gVS^{-1}$ at 200 ℃ treatment.

Author Contributions: Conceptualization, R.B.; methodology, B.H. and R.B.; validation, B.H.; formal analysis, B.H. and R.B.; investigation, B.H.; writing—original draft preparation, B.H and R.B.; writing—review and editing, R.B.; visualization, B.H. and R.B.; funding acquisition, R.B.

Funding:.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Dwyer, J.; Starrenburg, D.; Tait, S.; Barr, K.; Batstone, D. J.; Lant, P. Decreasing Activated Sludge Thermal Hydrolysis Temperature Reduces Product Colour, Without Decreasing Degradability. *Water research*, **2008**, 42(18), 4699-4709.
2. Taş, N.G.; Gökmen, V. Maillard Reaction and Caramelization During Hazelnut Roasting: A Multiresponse Kinetic Study. *Food chemistry*, **2017**, 221, 1911-1922.
3. Wilson, C. A.; Novak, J. T. Hydrolysis of Macromolecular Components of Primary and Secondary Wastewater Sludge by Thermal Hydrolytic Pretreatment. *Water research*, **2009**, 43(18), 4489-4498.
4. Xue, Y.; Liu, H.; Chen, S.; Dichtl, N.; Dai, X.; Li, N. Effects of Thermal Hydrolysis on Organic Matter Solubilization and Anaerobic Digestion of High Solid Sludge. *Chemical Engineering Journal*, **2015**, 264, 174-180.
5. Dubois, M.; Gilles, K. A.; Hamilton, J. K.; Rebers, P. T.; Smith, F. Colorimetric Method for Determination of Sugars and Related Substances. *Analytical chemistry*, **1956**, 28(3), 350-356.
6. Dulley, J. R.; Grieve, P. A. A Simple Technique for Eliminating Interference by Detergents in the Lowry Method of Protein Determination. *Analytical biochemistry*, **1975**, 64(1), 136-141.
7. Banel, A.; Zygmunt, B. Application of Gas Chromatography-mass Spectrometry Preceded by Solvent Extraction to Determine Volatile Fatty Acids in Wastewater of Municipal, Animal Farm and Landfill Origin. *Water Science and Technology*, **2011**, 63(4), 590-597.
8. Wang, X.; Andrade, N.; Shekarchi, J.; Fischer, S. J.; Torrents, A.; Ramirez, M. Full scale study of Class A biosolids produced by thermal hydrolysis pretreatment and anaerobic digestion. *Waste Management*, **2018**, 78, 43-50.
9. Anjum, M.; Al-Makishah, N.H.; Barakat, M.A. Wastewater Sludge Stabilization Using Pre-treatment Methods. *Process Safety and Environmental Protection, **2016**, 102*, 615-632. doi: 10.1016/j.psep.2016.05.022
10. Ariunbaatar, J.; Panico, A.; Esposito, G.; Pirozzi, F.; Lens, P.N.L. Pretreatment Methods to Enhance Anaerobic Digestion of Organic Solid Waste. *Applied Energy*, **2014**, 123, 143-156.
11. Barber, W.P.F. Thermal Hydrolysis for Sewage Treatment: A Critical Review. *Water Res*, **2016**, 104, 53-71.
12. Cano, R.; Pérez-Elvira, S.I.; Fdz-Polanco, F. Energy Feasibility Study of Sludge Pretreatments: a Review. *Appl. Energy*, **2015**, 149, 176–185.
13. Choi, J.M.; Han, S.K.; Lee, C. Y. Enhancement of Methane Production in Anaerobic Digestion of Sewage Sludge by Thermal Hydrolysis Pretreatment. *Bioresour Technol*, **2018**, 259, 207-213.
14. Ennouri, H.; Miladi, B.; Diaz, S.Z.; Guelfo, L.A.; Solera, R.; Hamdi, M.; Bouallagui, H. Effect of Thermal Pretreatment on The Biogas Production and Microbial Communities Balance During Anaerobic Digestion of Urban and Industrial Waste Activated Sludge. *Bioresour Technol*, **2016**, 214, 184-191.
15. Jeong, S.Y.; Chang, S.W.; Ngo, H.H.; Guo, W.; Nghiem, L.D.; Banu, J.R.; . . . Nguyen, D.D. Influence of Thermal Hydrolysis Pretreatment on Physicochemical Properties and Anaerobic Biodegradability of Waste Activated Sludge with Different Solids Content. *Waste Manag*, **2019**, 85, 214-221.

16. Feng, G.; Tan, W.; Zhong, N.; Liu, L. Effects of Thermal Treatment on Physical and Expression Dewatering Characteristics of Municipal Sludge. *Chemical Engineering Journal*, **2014**, 247, 223-230.
17. Higgins, M.J.; Beightol, S.; Mandahar, U.; Suzuki, R.; Xiao, S.; Lu, H.W.; . . . Murthy, S.N. Pretreatment of A Primary and Secondary Sludge Blend at Different Thermal Hydrolysis Temperatures: Impacts on Anaerobic Digestion, Dewatering and Filtrate Characteristics. *Water Res*, **2017**, 122, 557-569.
18. Zhang, D.; Feng, Y.; Huang, H.; Khunjar, W.; Wang, Z.W. Recalcitrant Dissolved Organic Nitrogen Formation in Thermal Hydrolysis Pretreatment of Municipal Sludge. *Environment International*, **2020**, 138, 105629.
19. Ahuja, N.; Novak, J.T.; Higgins, M.J.; Le, T.; Murthy, S.N. Impact of Operating Temperature on Dissolved Organic Nitrogen and UV Absorbance in Thermal Hydrolysis Pretreated Digestion Return Liquor. *Proc. Water Environ. Federation*, **2015**, (10), 76–89.
20. Van Boekel, M.A.J.S. Formation of Flavour Compounds in the Maillard Reaction. *Biotechnology advances*, **2006**, 24(2), 230-233.
21. Hofmann, T. Studies on the Relationship Between Molecular Weight and the Color Potency of Fractions Obtained by Thermal Treatment of Glucose/Amino Acid and Glucose/Protein Solutions by Using Ultracentrifugation and Color Dilution Techniques. *Journal of Agricultural and Food Chemistry*, **1998**, 46(10), 3891-3895.
22. Hii, K.; Baroutian, S.; Parthasarathy, R.; Gapes, D. J.; Eshtiaghi, N. A Review of Wet Air Oxidation and Thermal Hydrolysis Technologies in Sludge Treatment. *Bioresource technology*, **2014**, 155, 289-299.
23. Pilli, S.; Yan, S.; Tyagi, R.D.; Surampalli, R.Y. Thermal Pretreatment of Sewage Sludge to Enhance Anaerobic Digestion: A Review. *Critical Reviews in Environmental Science and Technology*, **2015**, 45(6), 669-702.
24. Mottet, A.; Steyer, J.P.; Déléris, S.; Vedrenne, F.; Chauzy, J.; Carrère, H. Kinetics of Thermophilic Batch Anaerobic Digestion of Thermal Hydrolysed Waste Activated Sludge. *Biochemical Engineering Journal*, **2009**, 46(2), 169-175.
25. Carrère, H.; Dumas, C.; Battimelli, A.; Batstone, D.J.; Delgenes, J.P.; Steyer, J.P.; Ferrer, I. Pretreatment Methods to Improve Sludge Anaerobic Degradability: A Review. *Journal of hazardous materials*, **2010**, 183(1-3), 1-15.
26. Barber, B.; Nilsen, P.J.; Christy, P. Cambi SolidStream®: Thermal Hydrolysis as a Pre-treatment for Dewatering to Further Reduce Operating Costs. *Proceedings of the Water Environment Federation*, **2017**, (5), 5070-5083.
27. Bougrier, C.; Delgenès, J.P.; Carrère, H. Effects of Thermal Treatments on Five Different Waste Activated Sludge Samples Solubilisation, Physical Properties and Anaerobic Digestion. *Chemical Engineering Journal*, **2008**, 139(2), 236-244.
28. Chen, S.; Dong, B.; Dai, X.; Wang, H.; Li, N.; Yang, D. Effects of Thermal Hydrolysis on the Metabolism of Amino Acids in Sewage Sludge in Anaerobic Digestion. *Waste Management*, **2019**, 88, 309-318.
29. Lu, D.; Sun, F.; Zhou, Y. Insights into Anaerobic Transformation of Key Dissolved Organic Matters Produced by Thermal Hydrolysis Sludge Pretreatment. *Bioresource technology*, **2018**, 266, 60-67.
30. Farno, E.; Baudez, J.C.; Parthasarathy, R.; Eshtiaghi, N. Impact of Temperature and Duration of Thermal Treatment on Different Concentrations of Anaerobic Digested Sludge: Kinetic Similarity of Organic Matter Solubilisation and Sludge Rheology. *Chemical Engineering Journal*, **2015**, 273, 534-542.
31. Liu, X.; Wang, W.; Gao, X.; Zhou, Y.; Shen, R. Effect of Thermal Pretreatment on the Physical and Chemical Properties of Municipal Biomass Waste. *Waste Management*, **2012**, 32(2), 249-255.

32. Oosterhuis, M.; Ringoot, D.; Hendriks, A.; Roeleveld, P. Thermal hydrolysis of waste activated sludge at Hengelo wastewater treatment plant, The Netherlands. *Water science and technology*, **2014**, 70(1), 1-7.
33. Liao, X.; Li, H.; Zhang, Y.; Liu, C.; Chen, Q. Accelerated high-solids anaerobic digestion of sewage sludge using low-temperature thermal pretreatment. *International Biodeterioration & Biodegradation*, **2016**, 106, 141-149.
34. Lopes GR, Ferreira AS, Pinto M, Passos CP, Coelho E, Rodrigues C, Figueira C, Rocha SM, Nunes FM, Coimbra, MA (2016) Carbohydrate content, dietary fibre and melanoidins: Composition of espresso from single-dose coffee capsules. Food Research International, 89: 989-996.

CHAPTER 4.

Article

Physical characteristics of thermal hydrolysis treated primary and secondary sewage sludge

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Received: date; Accepted: date; Published: date

Abstract: The effects of thermal hydrolysis process (THP) pre-treatment of primary sludge (PS), and waste activated sludge (WAS) on particle size distribution (PSD), apparent viscosity and dewaterability prior to and following anaerobic digestion (AD) were studied. Results showed that when THP there was a shift in particle size distribution during THP of WAS, with particles in the range of 10 to 40 μm decreasing and 2-3 μm particles increasing. The apparent viscosity of WAS at a shear rate of 5 s^{-1} and 15-min reaction time increased relative to a control (4071 cP) at lower temperatures (80-110°C) due to gelation (up to 5880 cP) and then decreased dramatically in proportion to temperature increases to 140, 170 and 200°C (2261, 1131 and 678 cP, respectively). Anaerobic digestion of the THP-treated mixed PS+WAS sludge further decreased the viscosity. The dewaterability of digestate from lab-scale ADs fed THP-treated mixed sludge improved compared to a control. The total solids (TS) of centrifuged sludge cake increased from 19.8 to 30.4% for pre-treated at 170°C THP treated sludge compared to non-THP-treated. This result suggests a lower energy usage in the downstream sludge drying process.

Keywords: Thermal hydrolysis pretreatment (THP), primary sludge (PS), waste activated sludge (WAS), digestate, particle size distribution (PSD), viscosity, dewaterability

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1. Introduction

Thermal hydrolysis process (THP) is a method to pre-treat wastewater sludges prior to anaerobic digestion (AD) or other stabilization processes. THP partially hydrolyzes the sludge which is the first and rate-limiting process in digestion, thereby making nutrients readily available, accelerating biodegradation and biogas production. THP changes the particle size distribution and the viscosity, converting non-Newtonian sludges into ones that flow more like water which is easier to pump and improves sludge dewaterability (allowing dryer cake). These characteristics reduce energy input for sludge pumping and especially when sludge drying processes are utilized for production of Class A biosolids (Barber, 2016; Carrere, 2010).

During THP and AD, sludge particulate matter is broken down into smaller pieces, bacteria cells are broken open, and some material is fully solubilized which modifies the particle size distribution (PSD) and enhances the biodegradability and dewaterability (Houghton, 2002b; Karr and Keinath, 1978). The mean particle size of municipal wastewater sludges have been

reported to decreased with ultrasonic pre-treatment and the particle size further decreased after AD of the treated sludge (Martinez, 2015). The mean particle size of waste activated sludge (WAS) decreased from 61 μm to 54 μm during ultrasonic pre-treatment and then further decreased to 31 μm after AD. The peak size of PSD was reduced from approximately 50 μm to 30 μm due to THP and then further to 20 μm following 30-days of AD (Zhang et al., 2018). They also found that dewaterability has an inverse relationship with mean particle size and that PSD can be correlated with the degree of digestion because a bimodal distribution (with peaks at approximately 50 and 500 μm) in raw sludge changes to a single peak at approximately 20-30 μm in fully digested sludge (Zhang, et al., 2018).

Decrease of viscosity following THP has been reported by Bougrier (2008), who found that apparent viscosity (at a shear rate of 50 s^{-1}) decreased from 110 cP (untreated sludge) with increasing THP temperature to 80 cP at 150°C, but did not decrease further at higher temperatures. The capillary suction time (CST) test can be used to determine filterability (and optimum polymer dose) and the gravity drainage test an be used to determine sludge drainability and both of these are affected by THP (Houghton, 2002a; Martinez, 2015; Na, 2007). A method was developed by Higgins et al. (2017) using CST and laboratory centrifugation to estimate the effects of THP and AD on dewaterability. They reported that the highest cake total solids (TS) was 33% when pre-treated at 170°C prior to AD, compared to 27% for non-pre-treated sludge.

In this research, the physical properties of THP-treated primary sludge (PS) and WAS prior to and following AD were studied. The PSD of WAS treated at different THP temperatures was evaluated, and also the PSD change during digester operation time. WAS viscosity changes were evaluated for different THP reaction times. Dewaterability and viscosity changes following AD with and without prior THP-treatment were evaluated.

2. Materials and Methods

Sludges from two different municipal wastewater plants (WWTPs) were utilized in this study. The PSD and viscosity studies utilized PS (gravity thickened) and WAS (gravity-belt thickeed) obtained from a trickling-filter-solids-contact (TF/SC) secondary WWTP that receives an average flow of 98 million liters per day (MLD)(26 million gallons per day, MGD) of municipal wastewater with no industrial component. The dewaterability studies utilized mixed PS+WAS (dissolved air flotation thickened - FS) from a conventional activated sludge (CAS) WWTP that receives an average flow of 2.5 MLD (0.65 MGD) of municipal wastewater with no industrial component. Collected samples were stored at 4°C and utilized within 24 hours. All samples were warmed up to room temperature (22°C) prior to evaluating viscosity and PSD.

The FS or FS treated by THP at 110, 140 and 170°C were used to feed separate 15-L completely-mixed ADs. A fifth AD was fed a mixture of 170°C THP-treated WAS and untreated PS. The AD working volume was 10 L and the stirrer speed was 60 rpm. Heat tape was used to maintain AD contents at 37°C. Biogas production and methane content were monitored. The organic loading rate was 0.8 kgVS d^{-1} m^{-3} and the retention time was 30 days. The average steady-state AD characteristics are listed in Table 1, including TS, VS, pH, alkalinity, volatile fatty acid (VFA) (AWWA, 2005; Dilallo and Albertson, 1961).

Particle size distribution (PSD) of PS, WAS, THP treated sludge, and the digested sludges were measured on a Mettler Toledo FBRM S400A (Columbus, OH). Viscosity was measured on a BROOKFIELD DV-II+Pro M03-165-F0612 viscometer (Middleboro, MA) at different shear rate ranges. Spindle SC4-21 was used for shear rates of 2 to 97 s^{-1}, and spindle SC4-25 was used for

shear rates of 0.5 - 23 s^{-1}. Dewaterability was measured via a laboratory centrifuge process (Chu, 2019) which was a modified version of Higgins et al, (2017).

Table 1. Laboratory 15-L Complete-Mixed Anaerobic Digester Sludge Characteristics

Lab Digester	TS (mg L^{-1})	VS (mg L^{-1})	pH	Alkalinity (mg L^{-1} as $CaCO_3$)	VFA (mg L^{-1})
Control	29.4	24.5	6.82	2500	600
FS 110°C THP	22.2	18.5	7.25	2750	471
FS 140°C THP	22.9	20.5	7.01	2500	429
FS 170°C THP	22.5	19.5	7.42	2950	446
WAS 170°C THP + untreated PS	16.4	14.2	7.50	3100	403

3. Results

Figure 1 shows the change in particle size distribution after THP treatment of WAS between 80 and 200°C. Compared to untreated WAS, there is a pronounced increase in very small particles of size 2 to 3 µm with a concomitant decrease in particles in the size range of 6 to 35 µm. The extent of this shift in particle size generally correlates with increasing THP temperature (Figure 1).

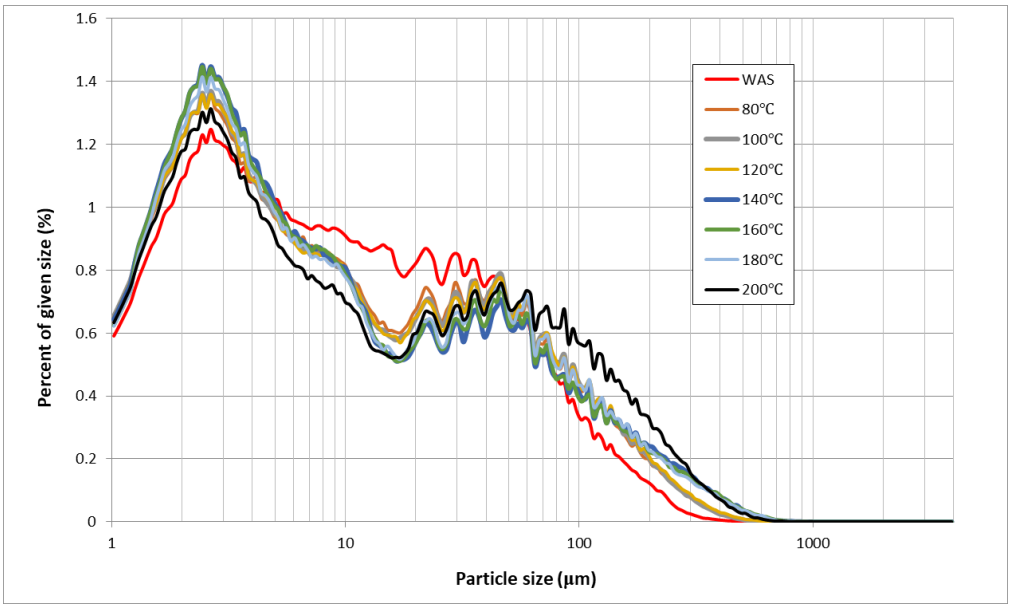

Figure 1. PSD of THP-treated WAS and the Digested Sludge.

Figure 2 and 3 show the effects of THP and AD on PSD in the lab-scale, semi-contnuous, 15-L ADs. Figure two shows the effect of AD approaching equilibrium, with the quantity of particles in the range of 20-60 µm gradually decreasing between 1 and 2 and 3 SRTs (30, 60, and 90-days).

The control (untreated WAS+PS) did not show any changes during the approach to equilibrium. After 3 SRT, the highest temperature (170°C THP) had a little more small particles than 110 and 140°C, and the AD treating 170°C THP WAS + untreated PS had the most small particles. Figure 3 allows comparisons of the effects of THP temperature at a given point in time (SRT). Initially, the control had the most small particles and then there was a shift such that 170-THP and 170-THP + PS have more small particles over time. There are smaller changes for 110 and 140°C.

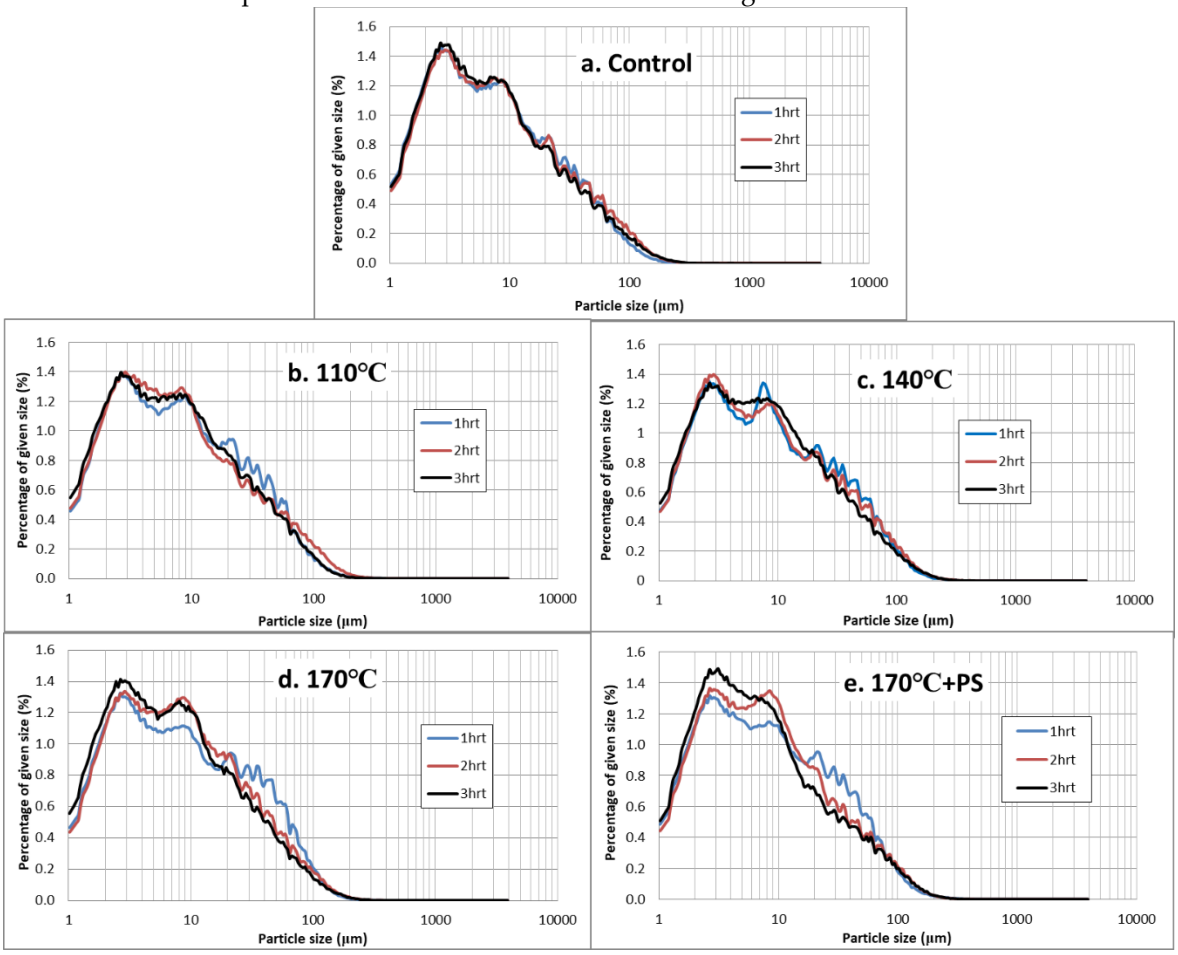

Figure 2. Effects of THP pre-treatment temperatures from 110 to 170°C on the PSD of anaerobically digested WAS+PS. Control (a) received no THP, while (b), (c), and (d) received THP treatment at 110, 140, and 170 C, respectively, and (e) received 170-THP WAS plus untreated PS.

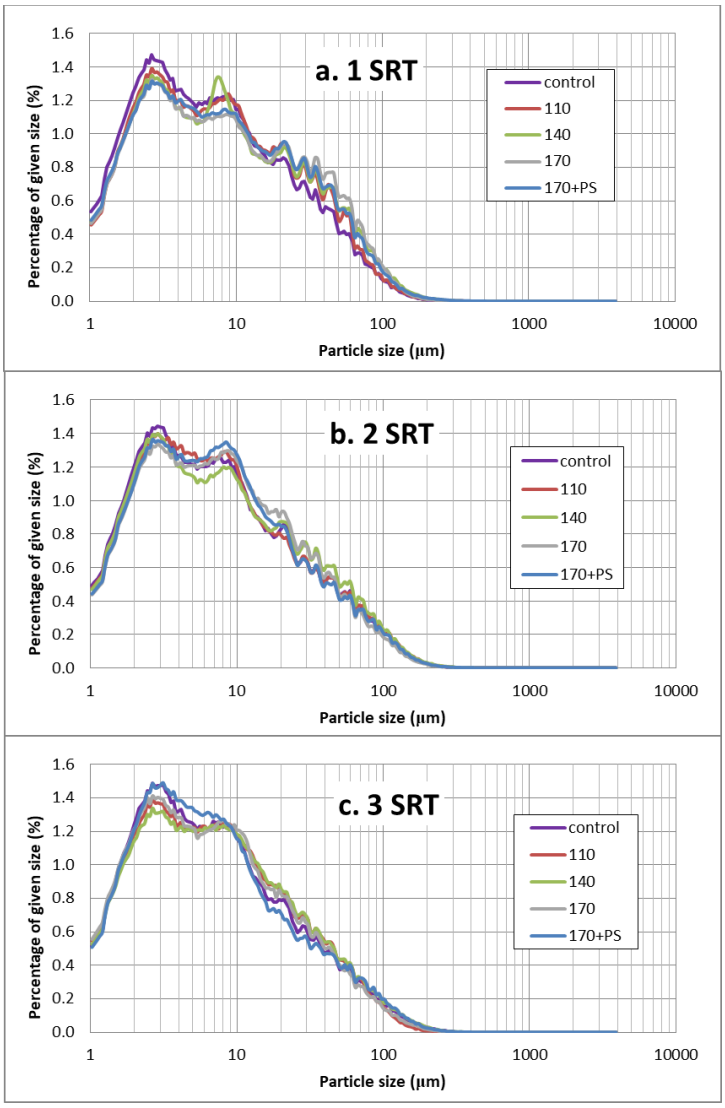

Figure 3. Effects of SRT on PSD of anaerobically digested WAS+PS with and without THP pre-treatment at 110 to 170°C, as the ADs approached equilibrium from 1 SRT (a) to 2 SRT (b) and 3 SRT (c).

Figure 4 shows the effects of 15-min duration THP at 80, 110, 140, 170, and 200C on apparent viscosity of mixed WAS+PS. Figure 4a shows low shear rates between 0.5 to 23 s^{-1}; and 4b shows higher shear rates of 50 to 186 s^{-1}. The viscosity curves show that the sludge viscosity increases when treated at 80 and 110°C at low shear rates (Figure 4a) compared to the un-treated control, but decreases when treated at 140, 170 and 200°C. For the high shear rates, the viscosity is too high to measure with the (out of range or the spindle) at 80, 110, and 140°C compared to the control and then decreases significantly at 170 and 200°C. This phenomenon occurs due to the release of inter-cellular molecules that form of a gel-like material that is stable at temperatures of 80 and 110°C, but which melts into liquid at higher temperatures (14-200°C). This change and the effect of reaction time is also shown in Table 2, where the bolded viscosities are larger than the control. This result indicated that only sludge treated under high enough temperatures or with long enough durations can avoid the gel-formation issue and have the benefit of reduced viscosity. Similar results were observed by Bougrier's group when THP-treating sewage sludge

to 200°C, the apparent viscosity decreased to 75 cP from 110cP at 50 s-1 shear rate (Bougrier et al., 2008). The viscosities in the study herein are larger because the initial viscosity of the untreated sludge is also higher than their study.

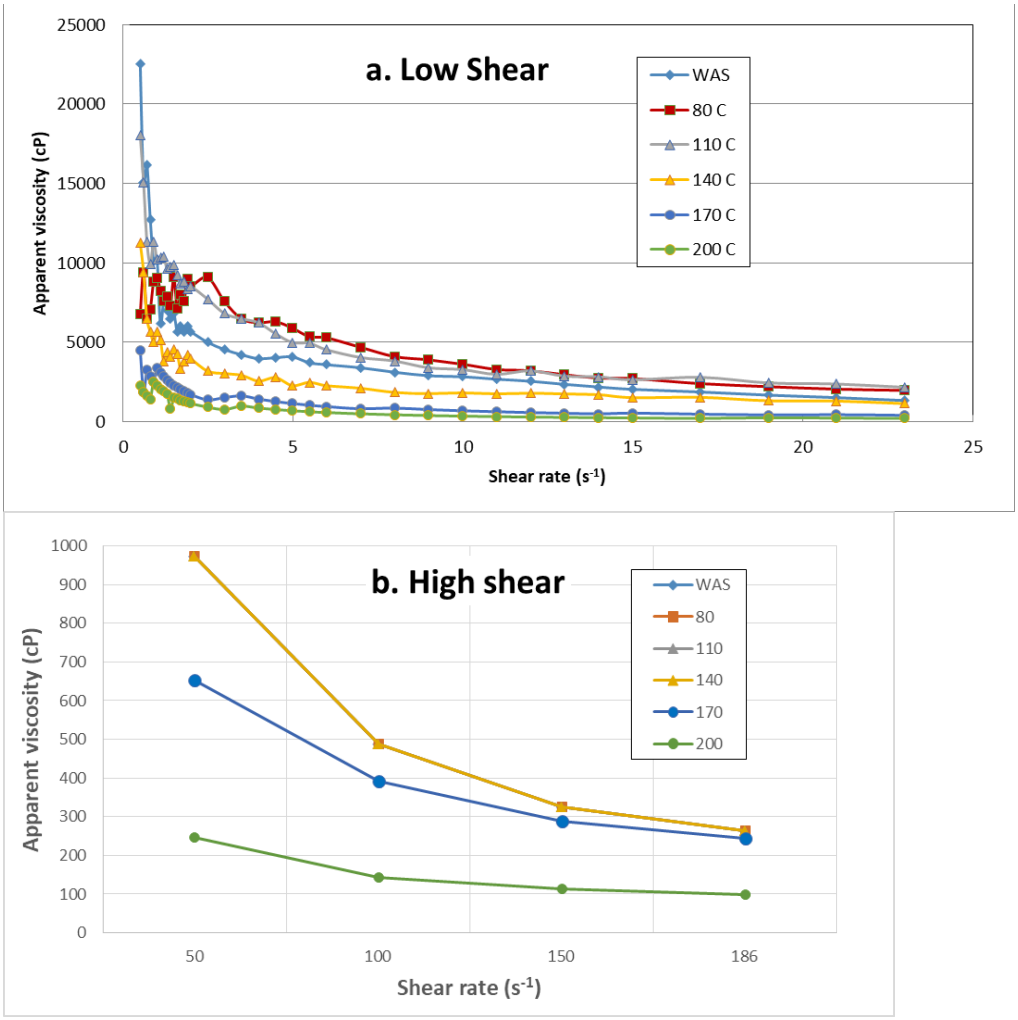

Figure 4. Apparent viscosity at low (a) and high (b) shear rates of WAS+PS sludge treated via THP at 80 to 200°C for 15 min.

Table 2. Apparent viscosity at 5 s^{-1} shear rate of Different Temperature and Reaction Time Treated Sludge

Apparent Viscosity at 5 s^{-1} Shear Rate (cP)		THP Reaction Temperature (°C)					Untreated sludge
		80	110	140	170	200	
THP Reaction Time (min)	0	**5201**	**5428**	3392	2035	905	4071
	15	**5880**	**4975**	2261	1131	678	
	30	**5201**	**4523**	2887	452	< 1	
	60	**4749**	2714	904	226	< 1	

The viscosity decreased significantly after AD, as shown in Figure 5, where the viscosity of the untreated and THP-treated sludges were much larger than the digested sludges. The viscosity of the THP-treated feed sludges decreases with temperature increases; the AD-treated sludges have lower viscosities than the THP-treated feed sludges and are lower by temperature increases; and there is a further decrease in viscosity observed from 1 SRT to 3 SRT for 140 and 170°C but not for 110°C.

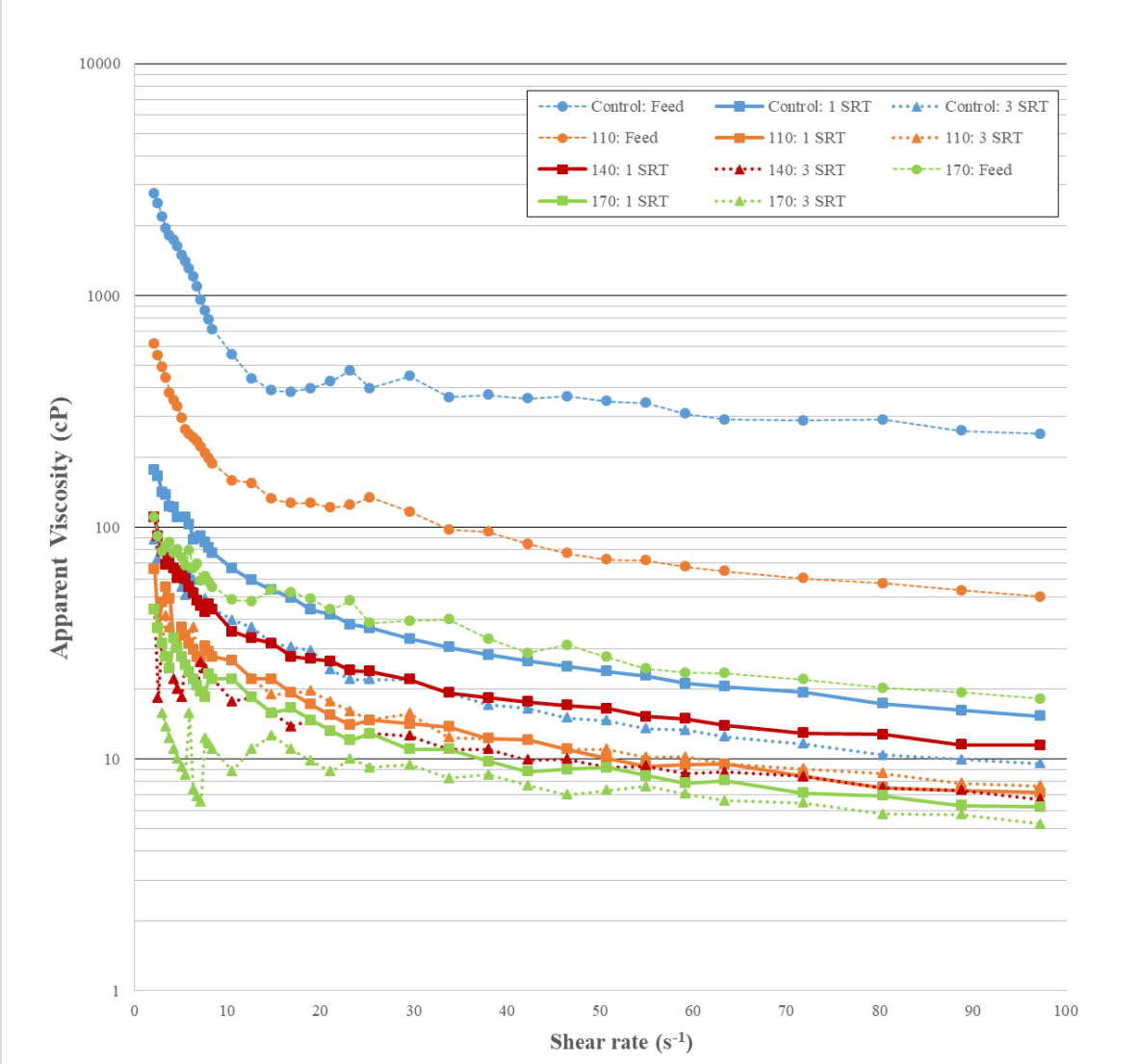

Figure 5. Apparent viscosity of THP-treated WAS+PS mixed sludge prior to and after anaerobic digestion for 1 to 3 SRTs.

Figure 6 shows the dewaterability of digested sludges as the ADs approached equilibrium. The non-THP treated control had the lowest TS values, but they did increase from 16.8 to 20.6%. The TS in the 110C THP-treated digested sludge steadily increased from 20.5 to 23.7% between 1 and 3 SRT. The TS of digested sludge for 140 and 170°C increased a lot from 1 to 2 SRT but then were reduced at 3 SRT, but still higher than 1 SRT. The partially-treated feed sludge (WAS only at 170°C) showed viscosities that were always less than 170 for WAS and PS and were even less

than 140-THP at 2 and 3 SRTs. Thus, in terms of improved (reduced) viscosity, the data shows that it is better to THP the combined sludge.

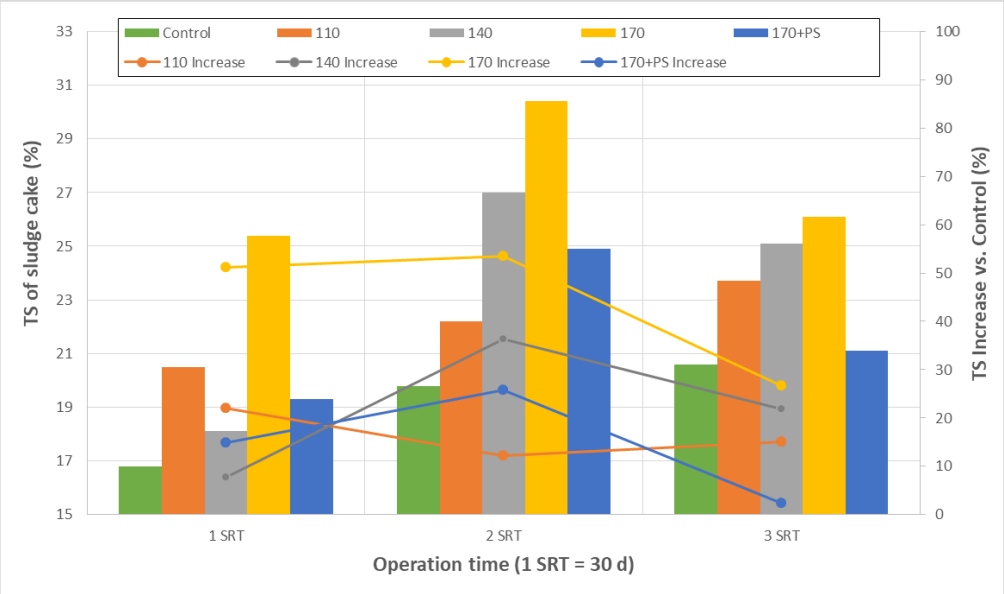

Figure 6. TS of Dewatered Sludge Cake

4. Discussion

The PSD peak of THP-treated WAS are at 1-100 μm and the highest percentage was located at 2-20 μm. This result is similar with data reported by Martinez (2015) that the particle size peak is at 3-100 μm, but their highest point is near 50μm which is larger than the data presented herein. Similarly, the sludge particle size peak is at 10-500 μm with highest point at 30 μm reported by Houghton (2002 a); and the peak is 50-200 μm with 90μm as the highest point by Na (2007). In general, the particle size of sludges used in this research is smaller than other reports.

It has been reported that digestate from THP-treated sludge gives a homogeneous result of PSD with smaller particle size, indicating that the digestion is thorough (Zhang, 2018). The lab-scale ADs used in our research agree with is in that after 3 SRT duration of use, the digestates have uniformly smaller particle distributions in the range of 20-80 μm and larger amounts at around 2-3 μm. Houghton (2002 a) reported a new peak occurred at 110-140 μm (in addition to the peak at 22-32 μm) when a digester was fed with both WAS and PS instead of 100% PS, indicating that the peak would be due to WAS. Comparison of Figure 1 (THP of WAS only) with Figures 2 and 3 (THP of WAS+PS) indicates that THP of WAS doe create many more larger particles in the range of 100-300 μm in agreement with Houghton.

The viscosity of THP-treated WAS increased at temperatures of 80 and 110°C due to formation of a gel that was observed to melt at a long reaction time (for 110°C) and not to form at higher temperatures (140-200°C). The gelation behavior during thermal pretreatment on WAS has been reported with high thermal doses above 7425 min-°C and the cause of gelation is protein structures change from liquid to gel and eventually solid on a macro-level caused by formation of intermolecular bonds (Rasel, et al., 2019). However, the gelation described by Rasel is possibly different from the gelation phenomenon of this paper which were generated under low thermal dose (here: 15-60 min at 80-110C, which gives doses of 1,200 to 3,300) and were not stable (they melted) with higher thermal doses herein (3,000 to 12,000)..

Viscosity of all the sludge samples exhibited non-Newtonian, shear shining behavior as they showed a decreasing viscosity with the shear rate increasing. The whole range of the apparent viscosity of digestate decreased when THP treatment temperature increased. This result agrees with the findings of Higgins et al. (2017) who found the 130-170°C THP digestate viscosity decreased with treatment temperature nicely. The viscosity of their digestate samples was about 200-600 cP which is much higher than the values for our samples (less than 100 cP); presumably because the TS concentration in their samples (6.3-6.5%) was much higher than that herein (2.3-2.9%).

The dewaterability of digested sludge improved by 4.1-5.1% when THP pretreatment was applied to the feed sludge (compared to non-pre-treated). This is due to a breaking down of the porous network structure by THP and further biochemical/enzymatic weakening during AD (Zhang, 2018). Dewaterability is also improved by lower specific surface area of sludge particulates and thus, the THP-related increase in smaller particles which are preferential removed in the digester enhances dewaterability (Lawler, 1986). The extracellular polymer content is another factor influencing dewaterability; when the level of extracellular polymer increased it is harder to remove water from sludge (Houghton, 2002 b).

5. Conclusions

When THP is applied to sewage sludge, the physical properties are modified. The PSD, viscosity and dewaterability of THP-treated sludges before and after AD were studied in this research. For the digestate of FS (WAS+PS), both the THP treated and untreated ones all showed a particle size decrease at 30-70 μm. And the particle size changed gradually with the operation time of the digesters. The viscosity of THP WAS decreased at mid-high temperature (140-200 °C). Because of a gelation phenomenon happened at low temperature (80 °C) and short reaction time (110°C for 0-30 min), the viscosity increased but then decreased when the gelation metled. The best viscosity results were at 200°C THP for 15 min with an apparent viscosity of 678 cP (untreated WAS = 4017 cP) at 5 s^{-1} shear rate. Decreasing viscosity was also observed in the long-term, lab-scale ADs fed with 110-170°C THP-treated FS. Like particle size, the viscosity also decreased with increasing digester operation time. The dewaterability of THP-treated FS digestate improved from 19.8 to 30.4% TS centrifuge cake when pre-treated at 170°C. However, when the AD was fed a mixture of 170°C THP WAS and untreated PS, the sludge cake TS was 24.9%, indicating that THP of both PS and WAS contributed to the dewaterability improvement.

Author Contributions: Conceptualization, R.B.; methodology, B.H. and R.B.; validation, B.H.; formal analysis, B.H. and R.B.; investigation, B.H.; writing—original draft preparation, B.H. and R.B.; writing—review and editing, R.B.; visualization, B.H. and R.B.; funding acquisition, R.B.

Funding:.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Houghton, J.I.; Burgess, J.E.; Stephenson, T. Off-line particle size analysis of digested sludge. *Water Research*, **2002a**, 36(18), 4643-4647.
2. Martínez, E.J.; Rosas, J.G.; Morán, A.; Gómez, X. Effect of ultrasound pretreatment on sludge digestion and dewatering characteristics: Application of particle size analysis. *Water*, **2015**, 7(11), 6483-6495.

3. Na, S.; Kim, Y.U.; Khim, J. Physiochemical properties of digested sewage sludge with ultrasonic treatment. *Ultrasonics sonochemistry*, **2007**, 14(3), 281-285.
4. Zhang, J.; Li, N.; Dai, X.; Tao, W.; Jenkinson, I.R.; Li, Z. Enhanced dewaterability of sludge during anaerobic digestion with thermal hydrolysis pretreatment: new insights through structure evolution. *Water Research*, **2018**, 131, 177-185.
5. Houghton, J.I.; Stephenson, T. Effect of influent organic content on digested sludge extracellular polymer content and dewaterability. *Water Research*, **2002b**, 36(14), 3620-3628.
6. Lawler, D.F.; Chung, Y.J.; Hwang, S.J.; Hull, B.A. Anaerobic digestion: effects on particle size and dewaterability. *Journal (Water Pollution Control Federation)*, **1986**, 1107-1117.
7. Higgins, M.J.; Beightol, S.; Mandahar, U.; Suzuki, R.; Xiao, S.; Lu, H.W.; ... Novak, J.T. Pretreatment of a primary and secondary sludge blend at different thermal hydrolysis temperatures: Impacts on anaerobic digestion, dewatering and filtrate characteristics. *Water research*, **2017**, 122, 557-569.
8. Bougrier, C.; Delgenès, J.P.; Carrère, H. Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion. *Chemical Engineering Journal*, **2008**, 139(2), 236-244.
9. Rasel, M.M.; Mitchell, M.; Manning, E.; Riffat, R.; Higgins, M.; Bott, C.; … Clippeleir, H.D. Gelation factor as potential indicator of overcooking solids in thermal hydrolysis process. *WEFTEC*, **2019**, 375-383.
10. DiLallo, R.; Albertson, O.E. Volatile acids by direct titration. *Journal (Water Pollution Control Federation)*, **1961**, 356-365.
11. APHA. Standard Methods for the Examination of Water and Water Water. 21th ed. Washington DC, USA: American Public Health Association/American Water Works Association/Water Environment Federation, **2005**
12. Barber, W.P.F. Thermal hydrolysis for sewage treatment: A critical review. *Water Res*, 2016, 104: 53-71.
13. Carrère, H.; Dumas, C.; Battimelli, A.; Batstone, D.J.; Delgenes, J.P.; Steyer, J.P.; Ferrer, I. Pretreatment methods to improve sludge anaerobic degradability: a review. *Journal of hazardous materials*, **2010**, 183(1-3), 1-15.
14. Karr P.R.; Keinath T.M. Influence of particle size on sludge dewaterability. *J Water Pollut Control Fed*, **1978**, 50, 1911–30.

CHAPTER 5.

Energy Considerations for Sewage Sludge Treatment via Thermal Hydrolysis Pretreatment, Anaerobic Digestion, Thermal Drying and CHP

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ABSTRACT: Thermal hydrolysis process (THP) has been used prior to anaerobic digestion (AD) in sewage sludge treatment to increase anaerobic digestion (AD) reaction rate, methane generation, and digested sludge dewaterability. All of these benefits point toward energy savings and the potential for net zero energy. Energy simulations were performed for a medium-sized municipal wastewater treatment plant (WWTP) that is in the process of adding THP, co-digestion of high energy wastes, thermal sludge drying, and combined heat and power (CHP). Laboratory experiments were conducted to determine site-specific efficiencies for THP, AD and biomethane potential (BMP) as inputs to the model. Historic and future projected facility energy use was also incorporated. The electricity energy input for sludge treatment decreased when applying THP to secondary sludge at 140°C (421 kW input when flow rate is 509 kg hr^{-1}) and 170°C (258 kW input) compared to no THP treatment (463 kW). THP has little effect on the energy balance for primary sludge (PS) because the methane yield improvement is minimal compared to secondary sludge (WAS). Energy input for PS without THP is 537

kW when the flow rate is 927 kg hr^{-1}, which decreased to 327 kW with THP at 170°C. Net zero energy can be achieved only by conducting co-digestion with a high-energy substrate such as 20% of volatile solids (VS) loading added as fats oils and grease (FOG).

KEYWORDS: Energy savings, net zero energy, thermal hydrolysis process (THP), anaerobic digestion (AD), dewaterability, co-digestion.

Introduction

One of the main reasons of introducing THP in sludge treatment process is because of energy benefits. The advantages of saving energy include improve of biogas production, reducing sludge viscosity, and dewaterability increase. However, the drawback of extremely high energy input to do THP cannot be overlooked.

Anaerobic digestion is a suitable alternative to reduce both environmental and economic burdens because this approach reduced dry mass volume and applied energy recovery (Xu, et al., 2014). The energy usage here includes electrical for feeding and mixing, and thermal to maintain the digestion temperature. Electrical requirements are approximately 0.1-0.2kWh/m^3d, and thermal requirements are the thermal capacity of sludge plus 10% loss in mesophilic condition, or 20% loss in thermophilic condition (Carrere, et al., 2010). Biogas energy can be recovered when apply a combined heat and power plant (CHP). The gas energy can be split to 30-40% of electricity, and 40-50% of thermal energy. Generally, both mesophilic and thermophilic produce biogas at rates well in excess of that required for self-heating (Carrere, et al., 2010).

Thermal hydrolysis processes require a huge input of energy to maintain the reactor high temperature and pressure, and an increase in gas production rate in the following AD (Hii et al., 2014). The feeding sludge to THP need to be concentrated

(from 3% to 7% total solids) in order to produce enough biogas in THP-AD system to be energetically self-sufficient (Perez-Elvira, et al., 2008). Another point is to exploitation of high enthalpy streams like vapor produced in the hydrolyzed sludge, exhaust gases and hot water will help with net energy recovery (Fdz-Polanco et al., 2008).

Some energy integration studies have been done. A mass and energy balance study based on pilot plant experimental data found that using 8% dry solid of secondary sludge is able to be energetically self-sufficient, and a combined THP + AD is profitable in terms of green energy and higher waste removal (Perez-Elvira, et al., 2012). The electricity production balance of THP + AD scenario is 0.86 kWh/kg DS fed (8% improvement). In another study from Cano's group (2014), THP combined with AD of 7% total solid sewage sludge required much more steam than produced, turned out input is -24% than no THP process (Cano et al., 2014).

To achieve an optimized energy scenario, a good design of Cambi system, which is the most successful commercial THP system, was used in this study for net energy calculation. Three different THP temperatures (110℃, 170℃ and 200℃) were evaluated in summer and winter environment temperatures. For a better net energy result, co-digestion of sewage sludge with fat oil and grease (FOG), food waste (FW) and bio-plastics were studied.

Methodology

DWSIM, a multiplatform CAPE-OPEN compliant chemical process simulator developed and maintained by Daniel Wagner Oliveira de Medeiros [16], was used for this work. The thermodynamic models and unit operations (steady-state) were used for built up the THP-AD-centrifuge-dryer process. With assumptions and equipment's parameter

obtained from vendors, energy requirements in each unit were calculated. For getting the substrate dewaterability and methane yield in the AD process, biochemical methane potential (BMP) and total solid (TS) of dewatered sludge cake were measured in the lab.

Result

The THP model built from material stream, energy stream, stream mixer, stream splitter, heater, valve, gas-liquid separator and recycle block is shown in Figure 1. This THP process is built up based on a Cambi system (https://www.cambi.com/what-we-do/thermal-hydrolysis/how-does-thermal-hydrolysis-work/) that consists of pulper to pre-heat the feeding sludge, steam boiler (or steam from biogas CHP), reactor where the reaction happens, flash tank that release the high pressure and decrease the temperature of sludge, and steam recycle. And a recycle block was added into the recycle line to help acceleration the calculation to the steady-state. Because of the limitation of the software, only the mass and energy balance were calculated but not the biomass hydrolysis reaction. All the mass flow data is listed in Table 1. The feeding sludge is pre-dewatered to TS concentration of 15% in 25℃, and the heating steam needed is 183℃ in 7.9 bar. When the sludge flow is 2250 kg/h, the initial steam flow need to be 624 kg/h to reach the 170℃ in reactor; with recycle steam generated and input to pulper, steam flow decreased to 405 kg/h and sludge in pulper would be heated to 98℃. The recycle/waste steam temperature is 105.6℃ in 1.2 bar, and 68% (280 kg/h) of the total generated steam is recycled (recl 3). The THP condition in Table 1 is 170℃ at 7.9 bar, and the sludge effluent from THP process is 105.6℃ in 1.2bar. When using the recycled hot water in 93℃ to feed the steam boiler, the energy requirement is 276 kW. However, in the reality, the CHP provides 75-95% of total steam energy requirements. The THP condition with

their steam energy requirements were listed in Table 2. The energy requirements in steady states are less than the initial period when just start the process that none recycle steam is used to preheat the sludge. The 110℃ THP does not need any recycle steam so that the energy requirements are the same in the two conditions. The THP reaction time was used for 15 mins to calculate the heat loss. To calculate the thermal energy compensation, we assume that for every minute 0.5% of total heat is dissipated to atmosphere from reactor wall.

Table 1. Mass flow in THP process in steady state

Parameter	Unit	Sludge	Water	Heat Steam	Pulper Out	React Out	Recycle 3	Waste Steam	THP Out
Temperature	C	25	93	183	98.	170.721	105.6	105.6	105.6
Pressure	bar	1.01325	1.01325	7.91325	1	7.9	1.2	1.2	1.2
Mass Flow	kg/h	2250	405	405	2530	2935	280	132	2523
Mass Fraction of Water		0.85	1.0	1.0	0.86	0.88	0.96	0.96	0.87
Mass Fraction of biomass		0.15	0	0	0.14	0.12	0.04	0.04	0.13

Table 2. THP conditions and their steam boiler energy requirements

THP temperature (℃)	Steam boiler energy with recycle steam at steady state (kW)	Steam boiler energy without recycle steam (initial period when start the process) (kW)
170	276	425
140	208	306
110	208	208

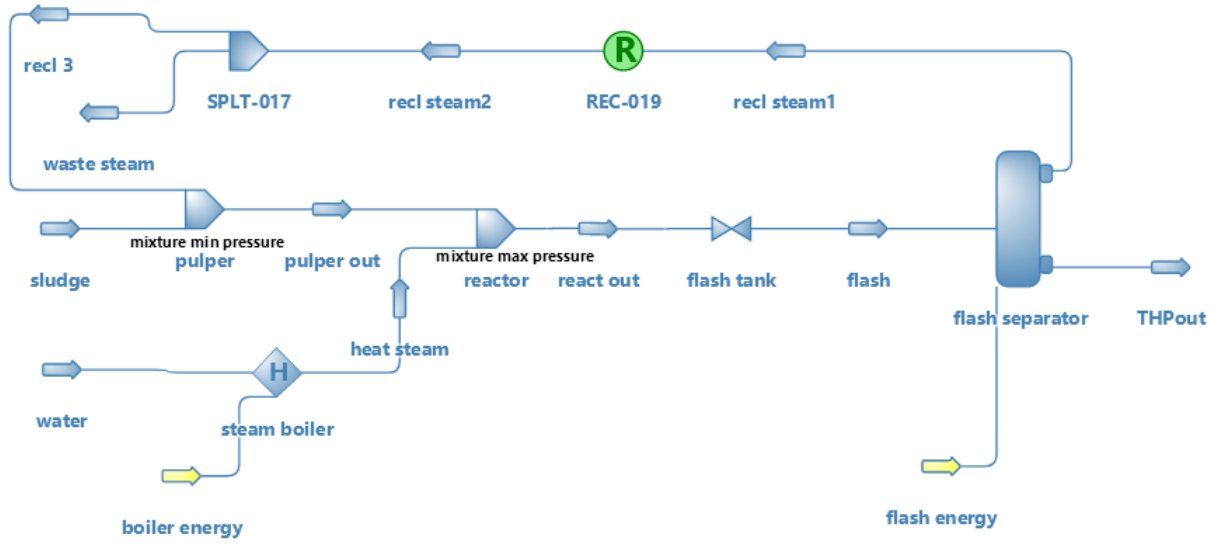

Figure 1. THP model in DWSIM

The process next to THP is the cooling system, dilution, and the AD digester, as the THP sludge was much thicker and hotter than the AD feeding requirements. Shown in Figure 2, the hot THP sludge was firstly cool off by cold water in a heat exchanger. Then the hot water generated can be reuse for steam generator, heat digester or elsewhere. Then the warm THP sludge was further cooled off when mixed with cold water for

dilution which was chilled by refrigeration. Finally, the digester feed sludge was diluted to 10% of TS and temperature was 44℃. The mass flow parameters are listed in Table 3.

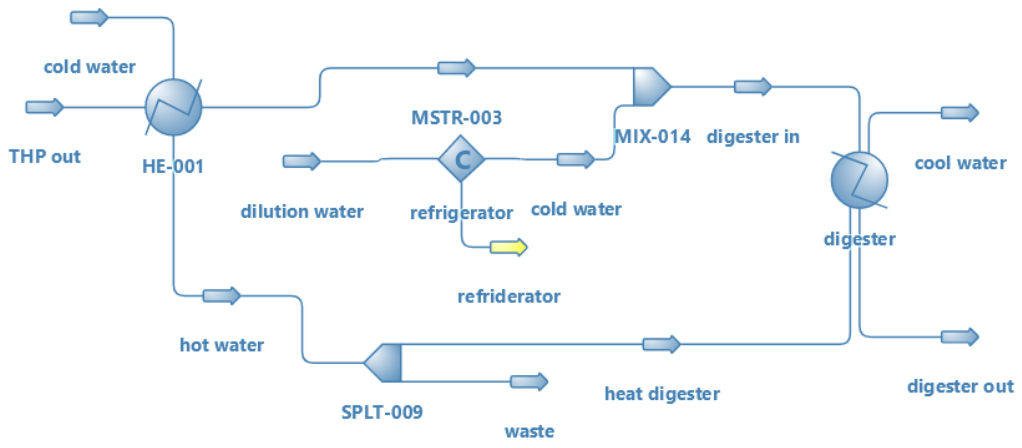

Figure 2. Cooling process and AD digester

Table 3. Mass flow in cooling system and AD digester.

Parameter	Unit	THP out	Cold water	Hot water	Dilution Water	Digester In
Temperature	°C	105.6	25	73	25	44.2
Pressure	bar	1.2	1.0	1.0	1.0	1.0
Mass Flow	kg hr^{-1}	2523	2000	2000	1125	3669
Mass Fraction of Water		0.87	1.0	1.0	1.0	0.90
Mass Fraction of biomass		0.13	0	0	0	0.10

The biogas produced in AD was calculated using BMP measured in lab (Holliger, et al., 2017). WAS, PS and their THP treated sludge at different temperatures were measured using AMPTS II (Bioprocess Control, Sweden). The results are listed in Table 4. The BMP of WAS was improved by THP but BMP of PS kept in the similar range as PS is a good digestible substrate. The BMP data was used for calculating the methane flow and energy recovery in CHP. The biogas CHP plant efficiency of usable electrical energy is 40% of gas supply, and usable thermal energy is 50% (https://www.clarke-energy.com/2013/chp-cogen-efficiency-biogas/).

Table 4. BMP of WAS, PS and THP treated sludges

BMP ($mlCH_4\ gVS^{-1}$)	Control	170°C THP	140°C THP	110°C THP
WAS	270	318	305	278
PS	370	370	N/A	N/A

Dewater and drying process is the last step in the sludge treatment shown in Figure 3. The digested sludge from AD digester was mixed with polymers then water was removed in centrifuge. The TS of centrifuged sludge when THP combined previous to AD was measured in lab (Chu, 2019). All the TS of dewatered sludge were tested using digested sludge fed by the THP sludge for 3 hydrolysis detention time (HRT). The dewatered TS of 170℃, 140℃ and 110℃ THP sludge fed digested sludge are 32%, 27% and 25%, respectively. The energy usage of centrifuge is based on the power of suitable

model of centrifuge and dryer (https://www.west-petro.com/equipment/high-speed-decanter-centrifuge/).

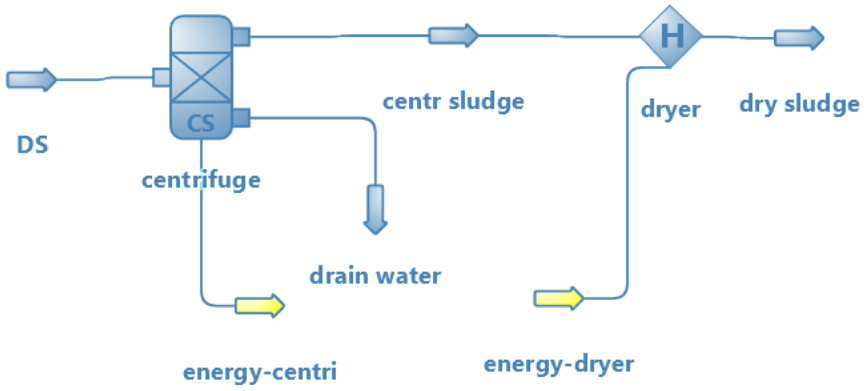

Figure 3. Dewater and drying process

Besides of all the main energy consume and generator processes, there are some other necessary assumptions fulfill net energy calculation. With the thermal energy recovery from CHP, assuming 15% of THP steam boiler energy required is the energy input for THP. There is no recycle steam in the starting stage of THP reaction but only for a short time. With the first batch reaction finish and recycle steam flow into pulper, the system transfer to S.S, so is the energy input. Thus, the average energy input is calculated as 15% of the maximum and 85% of the minimum. For the refrigerator to chill the dilution water, 1 kW of electricity can drag 5.4 kW of heat out. The power of solid pump to delivery sludge is 51 kWh/1000 m^3 of sludge (Kato, et al., 2019). The energy consumptions in each process are listed in Table 5.

Table 5. Energy consumption in each process based on assumptions (170℃ THP).

Process Description	**Energy consumption (kW)**
Centrifuged prior to THP	13
Boiler to produce heating steam	276
THP reactor heat loss (summer, winter)	32, 36
Refrigerator to cool off dilution water	6
Digester heat loss (summer, winter)	4, 11
Biogas chemical energy	887
Biogas combine CHP recovered heat	444
Biogas combine CHP recovered electricity	355
Dewater centrifuge	24
Sludge dryer	407
Sludge pump	1

Finally with all these assumptions, net energy results of WAS, PS and some other co-digestion candidates in AD with sewage sludge shown in Table 6 (Benn, et al., 2018; Davidsson, et al., 2008; Zhang, et al., 2014). Positive number means energy is produced in form of electricity, negative means need energy input to fulfill sludge treatment process. Results are calculated in summer conditions when environmental average temperature is 25℃. Winter condition which average temperature is 5℃ is also been calculated, however, in this scenario the extra heat loss in the cold weather is ignorable (about extra 5 kW heat loss).

Table 6. Net energy results in different treatment conditions.

Net energy (kW)	**Untreated**	**170°C THP**	**140°C THP**	**110°C THP**
WAS only (509 kg hr^{-1})	-463	-258	-421	-535
PS only (927 kg hr^{-1})	-537	-327	-582	-733
THP WAS + PS	-1000	-795	-955	-1072
THP WAS + THP PS	-1000	-585	-1003	-1268

% (VS) co-digestion with 170°C THPWAS + THPPS	5%	10%	15%	20%	25%
Fat oil and grease (FOG)	-433	-272	-111	50	211
Food waste (FW)	-556	-518	-479	-441	-403
Polyhydroxybutyrate (PHB)	-588	-582	-576	-570	-564

The co-digestion with mixed sludge helps with net energy recovery. The PS and WAS solid flow rate used for co-digestion calculation were 927 kg hr^{-1} and 509 kg hr^{-1}, respectively. The results shown in Figure 4 indicated that when no co-digestion was implied, the net energy was negative no matter with or without THP treatment. When applying THP or co-digestion portion increased, the net energy input decreased. Finally, when the THP sewage sludge co-digestion with 20% (VS) of FOG, the net energy is close to zero, and 3144 kWh d^{-1} of electricity can be generated when FOG portion is 25%.

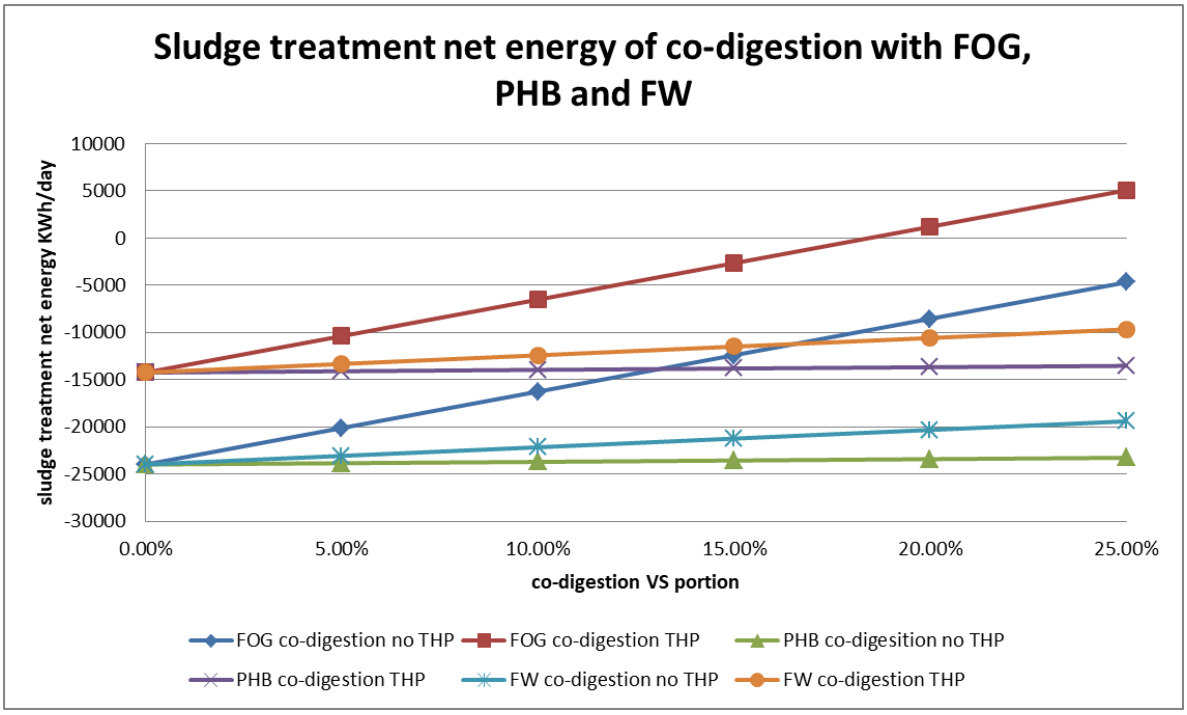

Figure 4. Sludge treatment net energy of co-digestion FOG, PHB and FW with untreated/170C THP mixed sewage sludge

Two of the parameters influence the net energy directly are BMP of the combined substrate and dewaterability. With higher BMP, more methane can be recovered and with higher TS of dewatered sludge, less energy input are needed for fully drying the sludge (Figure 5). The cut points in Figure 6 indicate the minimum of the mixture substrate BMP to satisfy zero net energy when a certain dewaterability was achieved.

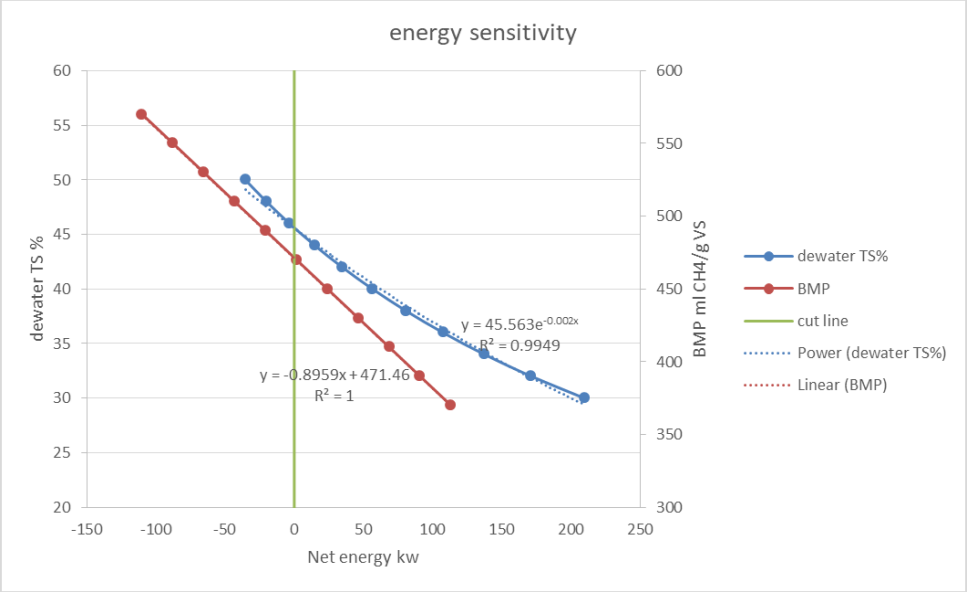

Figure 5. Net energy sensitivity

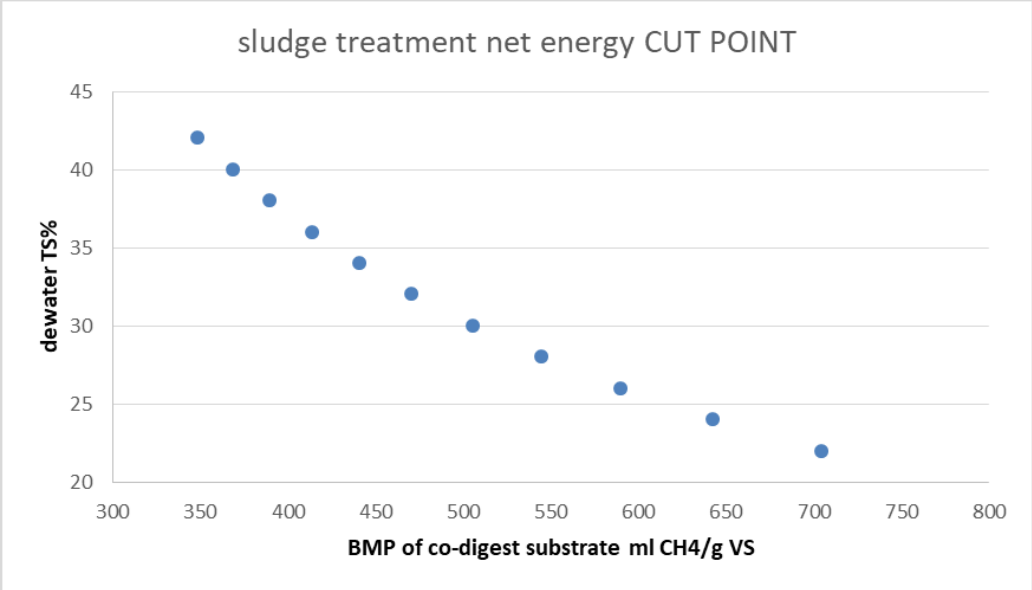

Figure 6. Net zero energy cut point.

Discussion

The energy and process model helped with net energy calculation, but the dynamic simulation and S.S give different results. As mentioned before, the S.S is considering the sludge (140°C and 170°C THP) well preheated in pulper which is the

optimistical case, whereas the startup of each process of THP that no recycle steam for preheating and can be considered as the worst case. The energy difference is between 149 kW for 170℃ THP and 102 kW for 140℃ THP, 28% and 16% of the energy input, respectively.

Aichiger (2019) did the energy calculation as well but in the open environment of SUMO© simulator platform with established process model. Their energy model describes heat, electricity and chemical bound energy. It has been confirmed that the heat loss of hot surfaces of each unit (THP reactors, digesters) is relatively small compared to the main energy usage units (steam boiler and sludge dryer). They also highlighted that the annual average CHP heat supply is enough to serve steam production, but short term effects affects the total energy balance when compared with their study THP system in Blue Plains. The weather environment is another variability in energy mimic that warm climate inhibits heat loss. However, compared with the main energy utilizing processes, the environmental temperature influence is micro.

The substrate be treated in THP should be cautious decide in a view of energy benefit. The sludge VS is a key parameter that a low VS substrate leads to poor treatment efficacy as huge heat lost on useless material in the substrate, and this is the reason that sludge need to be prior thickened to THP (Cano, et al., 2014). And also the well biodegradable substrate (PS, FOG, FW and PHB) need to be considered carefully because they maybe cannot recovery more biogas from AD, whereas it's possible to improve dewaterability as a benefit of THP.

Energy integration based on biogas-CHP is a key factor for THP-AD process economic viability. Fdz-Polanco (2008) claimed that 170℃ THP with 30 minutes

residence time at 7 bar produce methane increases more than 50% and can be fulfill the sludge heating requirements. Even through the heat energy recovery from CHP is sufficient for sludge heating, the heat density is not high enough to produce 183℃ at 7.9 bar heating steam in our scenario (book). Therefore, to achieve net energy zero, we need to either improve biogas production by introduce co-digestion, or improve sludge dewaterability by using more powerful centrifudge.

Conclusion

A sludge treatment model including THP, AD, dewatering and drying processes was built in DWSIM in order to calculate the energy usage. The THP treatment temperatures, treated sludge type, and co-digestion with other energy-rich substrates were evaluated. Using the BMP and dewaterability results data collected from laboratory experiments, the energy benefit created from THP applying on PS is not as much as WAS, and the best energy input reduction is achieved at 170℃ THP. Low-middle temperature THP should be avoided applying on PS treatment. Total energy input for PS (solid flow rate is 927 kg hr^{-1}) treatment without THP is 537 kW, but increased to 733 kW with 110℃ THP, 582 kW with 140℃ THP, then decreased to 327 kW at 170℃ THP. For WAS, the energy benefit showed up from 140℃ THP that energy input is 463kW without THP, decreased to 421kW at 140℃ THP, 258 kW at 170℃ THP, but increased to 535kW at 110℃ THP. The total energy saving when applying 170℃ THP to WAS and PS is 41.5% (decreased to 585 kW from 1000 kW). More energy can be saved with co-digestion in AD, and extra energy can be produced from CHP with 20% (VS) co-digestion with FOG. 50kW and 211 kW of electricity energy can be created by 20% and 25% of FOG co-digestion, respectively. The key factor to influence total energy affected

from THP-AD-CHP is THP temperature as the energy input, and BMP, dewaterability improvement as the energy recovery/saving. For example, to meet net zero energy, the BMP should be high as 506 $mlCH_4$ gVS^{-1} when TS of sludge cake is 40%.

References

1. Aichinger, P., DeBarbadillo, C., Al-Omari, A., & Wett, B. (2019). 'Hot topic'–combined energy and process modeling in thermal hydrolysis systems. *Water Science and Technology*, *79*(1), 84-92.
2. Mills, N., Pearce, P., Farrow, J., Thorpe, R. B., & Kirkby, N. F. (2014). Environmental & economic life cycle assessment of current & future sewage sludge to energy technologies. *Waste management*, *34*(1), 185-195.
3. 4.Carrère, H., Dumas, C., Battimelli, A., Batstone, D. J., Delgenes, J. P., Steyer, J. P., & Ferrer, I. (2010). Pretreatment methods to improve sludge anaerobic degradability: a review. Journal of hazardous materials, 183(1-3), 1-15.
4. 20 Hii, K., Baroutian, S., Parthasarathy, R., Gapes, D. J., & Eshtiaghi, N. (2014). A review of wet air oxidation and thermal hydrolysis technologies in sludge treatment. Bioresource technology, 155, 289-299.
5. Xu, C., Chen, W., & Hong, J. (2014). Life-cycle environmental and economic assessment of sewage sludge treatment in China. *Journal of Cleaner Production*, 67, 79-87.
6. Fdz-Polanco, F., Velazquez, R., Perez-Elvira, S. I., Casas, C., Del Barrio, D., Cantero, F. J., ... & Rouge, P. (2008). Continuous thermal hydrolysis and energy

integration in sludge anaerobic digestion plants. *Water Science and Technology*, 57(8), 1221-1226.

7. Cano, R., Nielfa, A., & Fdz-Polanco, M. (2014). Thermal hydrolysis integration in the anaerobic digestion process of different solid wastes: energy and economic feasibility study. *Bioresource technology*, 168, 14-22.
8. Pérez-Elvira, S. I., & Fdz-Polanco, F. (2012). Continuous thermal hydrolysis and anaerobic digestion of sludge. Energy integration study. *Water Science and Technology*, 65(10), 1839-1846.
9. Pérez-Elvira, S. I., Fernández-Polanco, F., Fernández-Polanco, M., Rodríguez, P., & Rouge, P. (2008). Hydrothermal multivariable approach: Full-scale feasibility study. *Electronic Journal of Biotechnology*, 11(4), 7-8.
10. Holliger, C., Alves, M., Andrade, D., Angelidaki, I., Astals, S., Baier, U., ... & Ebertseder, F. (2016). Towards a standardization of biomethane potential tests. *Water Science and Technology*, 74(11), 2515-2522.
11. Kato, H., Fujimoto, H., & Yamashina, K. (2019). Operational Improvement of Main Pumps for Energy-Saving in Wastewater Treatment Plants. *Water*, 11(12), 2438.
12. Benn, N., & Zitomer, D. (2018). Pretreatment and anaerobic co-digestion of selected PHB and PLA bioplastics. *Frontiers in Environmental Science*, 5, 93.
13. Davidsson, Å., Lövstedt, C., la Cour Jansen, J., Gruvberger, C., & Aspegren, H. (2008). Co-digestion of grease trap sludge and sewage sludge. *Waste Management*, 28(6), 986-992.

14. Zhang, C., Su, H., Baeyens, J., & Tan, T. (2014). Reviewing the anaerobic digestion of food waste for biogas production. *Renewable and Sustainable Energy Reviews*, 38, 383-392.
15. Chu, M. (2019) Bench-scale simulation of dewatering digested sludge using CST and high-speed centrifugation. MS Thesis, Civil Engineering, University of Hawaii, Honolulu, HI.
16. Medeiros, D. DWSIM technical document; available via the Internet at: http://dwsim.inforside.com.br/, 2018; last accessed on Oct. 1, 2018.

CHAPTER 6. CONCLUSIONS

In this dissertation, the effects of THP on sewage sludge based on reaction temperature and time were studies, including the sludge property changes, impacts in the following AD process and the contribute to energy input of the sludge treatment. Here are the summaries of major findings throughout this dissertation and suggestions for further research.

In chapter 2, low temperature between 44 and 121℃ THP was applied to PS and WAS to investigated the benefits of solubilizing VS and producing of FDS, carbohydrates and proteins. The VS solubilization of PS is not as much as WAS at all temperatures, and there are proteins for the FDS than carbohydrates. Even though the recalcitrant compounds, Melanoidins are produced that increase the brown color in the fluids, the BMP of WAS is increased for around 50%. However, the methane yield of low temperature THP treated PS is not influenced much, indicated that THP of PS is not necessary aiming to enhance bigoas production.

In chapter 3, the production speciation was studied of THP treated WAS from 80-200 ℃ with treatment time 0-60mins. Most of the soluble compounds concentration is increased after THP in both HMW and LMW, including COD, TOC, carbohydrate, VFA, TN, protein, and ammonium, and the increase shows a positive correlation with the reaction temperature and time, but a decreasing is observed in amino acids because of decomposition at high temperature. The producing rate of carbohydrate and protein for COD gradually decreased with temperature indicated that the decomposition conducted faster than formation. Finally, the color (in unit Pt Co) and Melanoidin concentration

increased with THP temperature/time. And digestion results showed a increment of 32-51% of BMP in THP treated WAS.

The sludge physical properties changes according to THP was investigated in chapter 4. With THP the particle size treated PS and WAS both decreased, and the digestate produced from AD of THP sludge present a lower viscosity and a better dewaterability. The viscosity of THP WAS is firstly increased when the treatment temperature is lower than 110℃ with the treatment time is as short as 30min because of gelation of sludge accrues. When this phenomenon disappears at high temperature and long reaction time, viscosity decreases rapidly as well.

The net energy simulation on sludge treatment method of THP - AD - CHP was studied in chapter 5. The results show that when THP applied on PS and WAS at a high temperature of 170℃ and 140℃ or higher respectively, the energy input can be saved. With a co-digestion with FOG in AD, the zero net energy can be achieved. The two key factors that influence the energy input are BMP of substrate in AD, and the degestate dewaterability. With a higher methane yield, more energy can be recovered from CHP, and for a lower water content in dewatered sludge cake, the heat input for drying is mush less.

The THP of sewage sludge has shown a series of benefits in sludge treatment process, but there are more gaps need to be filled. The correlation of THP WAS gelation and biomass property (extracellular polymeric substance) at low temperature is unclear. The applying of THP on other biomass substrates need to be investigated of the benefits

in THP-AD process. Dewaterability changes of digestate from co-digestion THP sludge with other substrate is also need to be find out.