EVALUATION OF SOLUBILIZATION WITH THERMAL HYDROLYSIS PROCESS OF MUNICIPAL BIOSOLIDS

Hung-Wei Lu

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Gregory D. Boardman, Chair
Sudhir N. Murthy
John T. Novak

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ABSTRACT

The increased demand for advanced sludge stabilisation in wastewater treatment facilities over the past decade has led to the implementation of various pretreatment techniques prior to anaerobic digestion. In an attempt to reduce sludge volumes and improve sludge conditioning properties, the use of thermal hydrolysis process before anaerobic digestion has been adopted with an increase in solids destruction, COD removal, and methane gas. In this study, the evaluation of thermal hydrolysis process as a viable pretreatment strategy to anaerobic digestion has been conducted in order to assess its capacity for solids solubilisation. Solubilisation experiments were conducted at temperatures ranging from 130 to 170°C and reaction times between 10 and 60 min. Anaerobic biogas production by thermally pre-treated sludge was carried out through a mesophilic anaerobic digester. The results showed that solids solubilisation increased with increases in temperature and time, while temperatures above 160°C for 30 min strongly affected the sludge characteristics. Ammonia production via deamination by thermal hydrolysis was less significant than protein solubilisation at a temperature of 170°C. Both protein and carbohydrate solubilisation were more dependent on temperature than reaction time. The enhancement of the biogas production was achieved with increases in temperature as pretreatment of 170°C yielded 20% more biogas than at 130°C. However, it seems the enhancement was linked to the initial biodegradability of the sludge.
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CHAPTER 1

INTRODUCTION & OBJECTIVES

Sludge management is important due to the large amounts of sludge produced through the
treatment of municipal and industrial wastewaters. While biological processes serves as an
effective way of treating wastewater and enhancing nutrient removal before wastewaters are
discharged to receiving streams, they have the inherent drawback of producing large amounts of
biomass. The more efficient the process for removing contaminants, the more sludge is produced.
Many efforts have been made to reduce sludge volumes by treatments such as digestion and
dewatering (Bougrier et al., 2006; Higgins, 2006; Hii et al., 2014; Neyens et al., 2004; Pérez-
Elvira et al., 2006). Anaerobic digestion with thermal pretreatment shows promise as a means of
enhancing digester performance in terms of solids reduction, and is therefore of great interest to
many facility operators.

The Thermal Hydrolysis Process (THP) is a heat conditioning technique which is used for raw
sludge pretreatment before anaerobic digestion. It uses high temperature and pressure to
solubilize particulate matter, disrupt biopolymer structures, and release soluble contents. During
the anaerobic digestion of sewage sludge, the disintegration of organic materials is usually slow
and recognized as a rate-limiting step before microbes can assimilate those organic materials (Bougrier et al., 2008). By improving the hydrolysis step with THP, more food is available for microorganisms, resulting in increased biogas volumes and decreased amounts of sludge to be disposed.

The adoption of the commercialized THP, CAMBI™ process at several plants in Europe and in one, full-scale installation in the US, represents a growing trend for solids reduction. In the CAMBI process, high temperature (130 to 170°C) and pressure (2.5 to 8 bar; 1 bar = 100 kPa) steam are applied to the sludge in order to accelerate the degradation of organic and mineral matter. Carlsson et al. (2012) summarized the findings from various literature sources and suggested that COD solubilization is one of many factors most people used to characterize the performance of thermal hydrolysis. Other factors such as particle size reduction, organics removal, or recalcitrant compound formation have also been reported, but it appears that no direct indicator is available to assess solubilization by THP and the relationships between indicators are still ambiguous.

A focus of work at the Blue Plain, Advanced Wastewater Treatment Plant (AWTP) in Washington, DC, is to evaluate the impact of THP, at different temperature-time regimes, on the
performance of mesophilic anaerobic digestion (MSD). This study is divided into two area: (1) to characterize the solubilization of the combined primary and secondary sludge from Blue Plains using THP at different operational times and temperatures, and (2) to examine the effectiveness of a mesophilic digester to produce biogas from thermally hydrolyzed sludge. Therefore, this work is designed to enhance our understanding of how THP changes sludge properties and improves digester performance.

Assessment of a pilot-scale THP system as a sludge pretreatment step prior to anaerobic digestion was desirable for several reasons. First, the sludge type most frequently studied is the biosolids from a wastewater treatment plant (WWTP), but there is now no universal THP criterion. Results from the literature (Carlsson et al., 2012; Qiao et al., 2012) suggest that the characteristics of sludge differed from one study to another, so the performance of THP cannot be determined without preliminary testing. Second, the THP is often operated under specific temperature and time condition as this temperature-time variable is often linked to internal costs that must be included as part of an economic assessment before plant startup. Thus, a better understanding of how these variables affect THP is needed.
In this context, the scope of this study is to examine the effect of thermal pretreatment temperature and time on sludge solubilization to enhance anaerobic digestion and its potential biogas production. Data collected from the influent and effluent from a pilot-scale THP unit are used to assess the solubilization capacity of the process in terms of substrate COD and macromolecular components (i.e., proteins, carbohydrates, and lipids). This temperature-time testing regime may provide general guideline for plant operators to optimize their THP systems. Moreover, to characterize anaerobic biodegradability of the sludge, batch digesters coupled to respirometers with THP pre-treated sludge are tested over a long-term incubation period. The specific methane yield (expressed as mL/g VS destroyed or fed) in a batch anaerobic reactor is calculated in order to adequately characterize the effect of sludge combined with THP pretreatment.
The overall objectives of this study are:

- To evaluate THP performance fed with mixed sludge (mixed the dewatered primary sludge and WAS to a TS concentration of 16.5%) and operated at different temperatures (130, 140, 150, 160, and 170°C) and retention times (10, 20, 30, 40, and 60 min).

- To characterize the biodegradability of THP pre-treated sludge by means of respirometric analysis in a batch, anaerobic reactor.
2.1 Sludge Pretreatment prior to Anaerobic Digestion

The management of excessive sludge poses an increasing challenge for wastewater treatment facilities due to environmental, economic, and regulative aspects. In 2012, about 40,000 wet tons of municipal residuals were produced with an average of 26.7% dry solids content in DC Water’s Blue Plains Advanced Wastewater Treatment Plant (DC Water, 2012). Hauling biosolids to land application cost more than 5,000,000 U.S. Dollars (DC Water, 2012). However, excessive biosolids also gives an opportunity to recycle nutrients rich biosolids as a valuable fertilizer and soil conditioner since the production of sludge will be continuing as a result of population growth and industrial expansion. One of many strategies is to introduce a sludge pretreatment process (i.e., thermal, chemical, physical alternation, or a combination of them) before aerobic/anaerobic digestion process. The ultimate goal of these techniques is to alter sludge characteristics to increase the degree of organic degradation (Pérez-Elvira et al., 2006).
For wastewater treatment facilities using biological treatment process, waste activated sludge (WAS) is the most common technique to treat pollutants. The content of the biodegradable organic materials and water are high in primary sludge, whereas WAS retains extracellular polymeric substance (EPS) which is difficult to degrade (Devlin et al., 2011) and composed roughly 80% of total mass of WAS (Neyens et al., 2004). EPS is a complex mixture of biopolymer consisting of mainly carbohydrates and proteins (Carrère et al., 2010). Therefore, a number of researchers have focused on using thermal pretreatment to make EPS more bioavailable, leading to the enhancement of subsequent sludge stabilization processes (Bougrier et al., 2008; Eskicioglu et al., 2006; Morgan-Sagastume et al., 2011). Another factor related to digestibility of waste activated sludge is the presence of microbial cells with rigid wall structures, making WAS less biodegradable.

Sludge disintegration has been reported as a possible pathway to solubilize intracellular substance and release bioavailable organic contents through cell membrane (Neyens et al., 2004). It was estimated that more than 20% EPS degradation was achieved by using sludge pretreatment prior to anaerobic digestion (Neyens et al., 2004). Since anaerobic digestion has emerged as a potential solution for solids stabilization, several improvements have been proposed and implemented in both pilot- and full-scale installations (Morgan-Sagastume et al., 2011; B Wett et
al., 2009; Zhou et al., 2013). By means of efficient sludge conditioning, the substrate for anaerobic digestion can be made more accessible to microorganisms, accelerating enzymatic hydrolysis, increasing the degree of solids reduction, and consequently reducing the amounts of excessive sludge to be disposed of (Carlsson et al., 2012).

2.2 Anaerobic Digestion

Anaerobic digestion (AD), an effective method that converts organic matter to methane, is a biochemical process involving both the Bacteria and the Archaea in an oxygen-free (anaerobic) environment. The microbial communities fundamental to successful functioning of anaerobic digestion are acidogenesis bacteria (including acetogens) and methanogenesis archaea (Grady Jr et al., 2011). As shown in Figure 1, the decomposition of organic materials by AD occurs in three major steps: particulate hydrolysis, acidogenesis, and methanogenesis (Grady Jr et al., 2011). Furthermore, AD is a complex and multistep process, which requires strict anaerobic conditions, and dependent on balance between different microbial communities.
Particulate hydrolysis is the first of three steps used to describe the anaerobic digestion process and methane gas production. Particulate hydrolysis involves: (1) The disintegration of particulate solids into proteins, carbohydrates, lipids, and nucleic acids, which are further degraded into soluble components (solubilization), and (2) The enzymatic hydrolysis via extracellular enzymes of those high molecular weight compounds into sugars, amino acids, and long chain fatty acids (hydrolysis) (Strong et al., 2011). The components formed during hydrolysis are subsequently utilized by acidogenesis bacteria in the second step, acidogenesis.
During acidogenesis, hydrolyzed compounds such as sugars and amino acids are decomposed to form volatile fatty acids (VFAs), ammonia (NH$_3$), carbon dioxide (CO$_2$), hydrogen sulfide (H$_2$S), and other by-products. The intermediate organic acids, like VFAs and other organic matter, are then digested by acetogens and serve as electron donors to produce true methane precursors, acetate and hydrogen gas (Grady Jr et al., 2011). The partial pressure of hydrogen gas generated from acidogenesis affects the proper functioning of the AD system, according to Grady Jr et al. (2011). Not only is hydrogen gas the primary electron donor from which methane is formed, but also the final reduced product which escapes from liquid phase leading to a favorable energy environment for methanogenesis to occur.

The final step of AD is to produce biogas by methanogenesis (methane and carbon dioxide) (Batstone et al., 2002). There are two groups of methanogens involved: aceticlastic methanogens that reduce acetic acid into methane and carbon dioxide, and H$_2$-oxidizing methanogens that oxidize hydrogen gas to produce methane. The decomposition of the complex compounds or insoluble matter via hydrolysis is usually slow and considered a rate-limiting step; whereas, in systems where soluble substances are dominant, methanogenesis becomes the rate-limiting step because of slow cell growth rates (Siegert & Banks, 2005).
2.3 Anaerobic Digestion Performance Parameters

For an effective AD system, the understanding of the key factors affecting process efficiency and stability is important. The essential parameters include pH, temperature, solids retention time (SRT), and presence of inhibitory and toxic compounds. A stable anaerobic reactor should be operated under nearly steady-state conditions; i.e., the unchanging conditions remaining throughout the digestion process. Otherwise, AD subjected to sudden changes, like the introduction of toxic substances or inhibitors, will result in the accumulation of intermediate products and slow degradation efficiency.

2.3.1 pH

The maintenance of the proper digestion pH is critical and in the range of 6.5 to 7.6 to ensure an efficient degradation. Methanogens are known among the most sensitive species to pH shocks in AD system (Leitão et al., 2006). Because of the narrow pH range of methanogens, any pH shift below 6.3 or above 7.8 will result in inhibitory effects on methanogens as long as the changes are of sufficient magnitude and duration (Leitão et al., 2006; Parkin & Owen, 1986). This system imbalance is mainly caused by the slow growth rate of methanogens as a consequence of excessive volatile acids accumulation by acidogenesis.
2.3.2 Temperature

Temperature greatly affects the growth rate of microorganisms and thus determines the microbial communities in AD. It is generally believed that the optimum temperature is around 35°C for mesophilic environment and in the range of 55 to 60°C for thermophilic condition. The adoption of higher temperature is beneficial to AD design because of superior metabolic and reaction rate and, therefore, better organic matters destruction efficiency and higher methane production (Bruce & Perry, 2001). However, Cha and Noike (1997) have pointed out that unstable factors such as VFAs accumulation, ammonia toxicity, foaming and odor issues were detrimental to anaerobic digestion, especially for thermophilic digestion.

2.3.3 Solids Retention Time

The use of solids retention time (SRT) is the most important design factor which provided insights into how environment changed affect digestion performance. To ensure efficient conversion of biodegradable particulate matters into methane and carbon dioxide, microorganisms, especially methanogens, must be of sufficient population and functioning time to maintain maximum specific growth rate of the biomass. In reality, the selection of the SRT for AD design must be greater than the minimum SRT required by the associated microbes to properly perform their biochemical functions. In this case, aceticlastic and H₂-oxidizing
methanogens are the species with the slowest growth rate among other prevalent microorganisms in anaerobic digestion. Therefore, conventional mesophilic AD is generally operated with a SRT of 15 to 20 days, which is above the minimum SRT for methanogens, to achieve a solid removal of 50% in a continuously-flow stirred-tank reactor (Bruce & Perry, 2001).

2.3.4 Inhibitory and Toxic Compounds

Compounds most commonly cited as inhibitory to anaerobic digestion are inorganics such as metal cations, ammonia-nitrogen, sulfide, and many other organic chemicals. Ammonia toxicity is of great concern during digestion of the organics containing nitrogen and protein. It was generally believed that free ammonia (NH₃), not ammonium ion, was responsible for the toxicity to methanogens above concentration of 100 mg/L as N (McCarty & McKinney, 1961). Bruce and Perry (2001) described that ammonia may be presented in the form of the ammonium ion (NH₄⁺), or the dissolved ammonia gas depending on pH as shown by the following equilibrium:
\[ NH_4^+ = H^+ + NH_3 \]  

Equation 1

where

\[ K_a = 5.56 \times 10^{-10} \text{ (at 35°C)} \]

and

\[ \text{pH} = 9.26 + \log \left( \frac{[NH_3]}{[NH_4^+]^+} \right) \]  

Equation 2

From Equation 2 it implies that controlling pH below 7.4 can lessen the severity of ammonia toxicant to anaerobic digestion. Nevertheless, many studies have reported that operating AD with ammonia concentration in excess of 1,500 mg/L as N and with the pH in the range of 7.5 to 8.0 were satisfactory in terms of reactor performance. This was probably due to the acclimation of high ammonia concentration by methanogens given a longer solids retention time (Van Velsen, 1979).

### 2.4 Thermal Hydrolysis Process (THP)

Thermal Hydrolysis have been implemented for decades and proven a viable strategy for biosolids management in wastewater treatment facilities. Brooks (1970) provided the earlier
reference describing the benefits of thermal treatment of sewage sludge for the subsequent anaerobic digestion. Conventionally, sludge produced from biological wastewater treatment plant were simply disposed after dewatering. This resulted in the increases in operational costs associated with sludge storage, polymer dosing, biosolids transportation, and landfill site limitation. Thermal pretreatment was first applied for sludge conditioning and dewaterability improvement of either primary sludge or WAS (Haug et al., 1978), and thus achieving significant solid-liquid separation. Early studies have also examined the effect of thermal pretreatment on settleability and filterability of sludge by changing sludge’s physical characteristics (Neyens & Baeyens, 2003; Neyens et al., 2004). In addition to sludge dewatering, THP improved the disintegration of both organic substances and cell integrity (cell lysis) in the sludge leading to the release of cell contents. Higher temperatures and longer reaction durations caused sludge composition undergo particulate transformation into more water-soluble state during THP (Donoso-Bravo et al., 2011; Li & Noike, 1992). Later, it was realized that anaerobic digestion of sludge combined with thermal hydrolysis as a sludge pretreatment method can dramatically improve digestion performance for better solids removal, an increase in organic loading capacity, and the promotion of biogas production. According to several authors (Appels et al., 2008; Kim et al., 2003; Zhou et al., 2013), anaerobic digestion has become an essential treatment process to wastewater treatment plants for solid stabilization, and thermal pretreatment followed by
anaerobic digestion of the sludge accelerated the digestion efficiency, especially for WAS degradation (Carrère et al., 2010). Moreover, THP provided the benefits associated with sanitation and sterilization by killing microorganisms through high temperature and pressure.

2.5 Determination of THP Pretreatment Conditions

In thermal hydrolysis process, pretreatment time and temperature are the most two important variables to determine the performance of THP. In order to identify the best condition of THP, several laboratory and pilot-scale thermal experiments have been performed based on a wide range of temperatures and reaction times (Bougrier et al., 2007; Ferrer et al., 2008).

Li and Noike (1992) investigated the impact of thermal pretreatment on the degradation of WAS in anaerobic digestion with temperatures ranging from 62 to 175°C and reaction times between 15 and 120 min. They observed the fraction of organic particulates in the sludge decreased as the temperature was increased to above 120°C indicating that better disintegration occurred as THP temperature increased. More specifically, the concentration of soluble proteins, carbohydrates, and lipids increased as the temperature was increased from 120 to 175°C due to particulate solubilization. Reaction times less than 30 min showed little influence on solids disintegration. Considerable efforts to identify the factors for efficient solubilization have shown that elevated
temperatures (120 to 275°C) promoted cellular disintegration and organics breakdown, thereby changing the characteristics of sludge (Bougrier et al., 2008; Muller, 2001). Therefore, the degree of sludge solubilization depended on the properties of mineral and organic components presented in the sludge.

Similar to Li and Noike (1992), Donoso-Bravo et al. (2011) examined the influence of THP pretreatment time on WAS decomposition and its anaerobic biodegradability. Pretreatment times were in the range of 0 to 30 min with 5 min increments and temperature was set up at 170°C. Despite a marginal increase in solubilization of WAS, he observed both the improvement of the dewaterability and the biodegradability of pre-treated sludge as pretreatment time increased.

Furthermore, a rapid thermal hydrolysis with reaction time of 1 min was proposed in a rapid thermal reactor (RTR) showing an effective solubilization at the temperature between 120 to 170 ºC (Dohnyos et al., 2004). Skiadas et al. (2005) and Ferrer et al. (2008) also have indicated that using thermal pretreatment of low-temperature 70°C, as compared with high-temperature phase, was advantageous in terms of biogas production but lower temperature required an extended reaction time, usually over 9 hours periods, to achieve substantial solubilization.
2.6 Effect of Sludge Pretreatment on Biogas Production

Previous THP investigations have mostly focused on the effects of thermal pretreatment on substrate solubilization and its biodegradability in order to enhance anaerobic biogas production. Carlsson et al. (2012) summarized the findings from various literatures and suggested that COD solubilization was one of many factors most people used to identify the performance of THP. Other factors such as particle size reduction, organics removal, or recalcitrant compound formation have also been reported, but it appeared that no direct indicator was available to assess THP solubilization and the relationships between indicators were still ambiguous. Table 1 shown below is a list of multiple expressions of COD solubilization as described by Carlsson et al. (2012). In addition to COD solubilization, other authors have defined particulate solubilization based on the TS, VS, or proteins, carbohydrates, and lipids measurements (Bougrier et al., 2008; Elbeshbishy et al., 2011).
Table 1. Expressions of solubilization based on COD measurements

<table>
<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD Solubilization</td>
<td>$S_{COD} = \frac{COD_s - COD_{SO}}{COD_{PO}} \times 100%$</td>
<td>(Bougrier et al., 2007; Bougrier et al., 2008; Elliott &amp; Mahmood, 2007)</td>
</tr>
<tr>
<td></td>
<td>$S_{COD} = \frac{COD_s - COD_{SO}}{COD_T} \times 100%$</td>
<td>(Appels et al., 2010)</td>
</tr>
<tr>
<td></td>
<td>$S_{COD} = \frac{COD_s}{COD_T} \times 100%$</td>
<td>(Kianmehr et al., 2010; B. Wett et al., 2010)</td>
</tr>
</tbody>
</table>

- $COD_s$: COD measured from supernatants or filtrates after thermal treatment
- $COD_{SO}$: COD measured from supernatants or filtrates before thermal treatment
- $COD_{PO}$: COD measured on particulate fractions of the raw sludge
- $COD_T$: total COD of raw sludge, often assumed unchanged during thermal treatment

In a study of examining 14 different types of sludge from industrial, household sewage, and treatment plant, Qiao et al. (2012) demonstrated that the thermal pretreatment effects were heavily dependent on sludge types that were studied, especially the amounts of organic content in the sludge, thereby evaluation for the influence of THP on different sludge sources was needed.

Residuals such as WAS from wastewater treatment plants represented the materials frequently studied in recent year, followed by food waste, municipal biowastes, and manures (Qiao et al., 2012). Most of studies reported that the optimal temperatures for thermal treatment of WAS were in the range from 160°C to 170°C while reaction times were between 30 and 60 min (Bougrier et
The particulate organic contents of the sludge, which was rich in lipids or carbohydrates, usually resulted in a slow hydrolysis during anaerobic digestion (Liu et al., 2012).

The increases of biogas and methane production from anaerobic digestion are beneficial as methane represented energy recovery from wastes and served as fuel substitutes for heat, electricity, and transportation gas. In addition, more methane by thermal pretreatment can be used to compensate for the energy consumption and thus whole treatment processes are energy-neutral technologies. It has been reported that thermal hydrolysis as a sludge pre-conditioning process can retrofit for a mesophilic digestion plant up to 40% of its revenue, which could lead to significant economic savings (Cano et al., 2014). Moreover, Haug et al. (1978) calculated a net increase of 14% and 60% methane yield by thermal treatment of WAS at 100°C and 175°C, respectively, and concluded that THP prior to anaerobic digestion had a positive energy production since more biogas was produced. However, above temperature 175°C inhibitory materials were produced to interfere with biogas production and thus decrease the efficiency of anaerobic digestion. Melanoidins, formed via Maillard Reaction, was mainly responsible for the lower degradation efficiency of organic compounds according to most of studies (Bougrier et al., 2007; Eskicioglu et al., 2006).
2.7 Commercialized THP Examples

As the THP has been developed since 1960s, there are several commercialized THP used in full-installation plants, especially in the Europe. The CAMBI™ process, developed by a Norwegian company, offers a sustainable solution to biosolids management where one of the earlier full-scale CAMBI™ implementation was tested at the Hamar wastewater treatment plant in Norway. Figure 2 provides a schematic of the CAMBI™ process. Elliott and Mahmood (2007) described the process of the CAMBI™ as beginning by dewatering the raw sludge to a dry solids of about 16 to 18% and stored in a silo. Then the sludge went through the CAMBI™ plant, which was consisted of a pulper, a thermal reactor, and a flashing tank, with high pressure steam addition (4.5bar, 1bar = 100 kPa) at temperatures between 150°C and 180°C to undergo solubilization. Once reached 30 min reaction time, the hydrolyzed sludge will be sent to the flashing tank at the flashing set point to allow steam explosion. The processed sludge will be directed to the downstream anaerobic digestion for organic degradation and biogas production.
The advantages of the CAMBI™ treatment coupled with anaerobic digestion involve the reduced digester volume up to 50% as solid loadings to digester double, enhanced biogas production since high VS destruction (55 to 70%) is achieved, and Class A Biosolids production for economic land application. Moreover, the use of steam as a heating source avoids the issues of heat exchanger corrosion and the waste steam can be recycled to preheat the sludge and thus the energy input for the CAMBI™ process is neutral. Recently, another commercialized THP is developed by Veolia Water which provides either batch or continuous THP operations in a number of wastewater treatment plants with typical temperature of 165°C and reaction time of 30 min (Hii et al., 2014).
CHAPTER 3

MANUSCRIPT 1: EVALUATION OF SOLUBILIZATION CHARACTERISTICS OF THERMAL HYDROLYSIS PROCESS

Abstract

An evaluation of the thermal hydrolysis process as a viable pretreatment strategy for anaerobic digestion was conducted in order to assess its capacity for solids solubilization. Solubilization experiments were conducted at temperatures ranging from 130 to 170°C and reaction times between 10 and 60 min. Biogas production from thermally pre-treated sludge was carried out with a mesophilic anaerobic digester. The results showed that solids solubilization increased with increases in temperature and time, while temperature above 160°C with reaction time above 30 min strongly affected the sludge characteristics. The soluble ammonia production via protein deamination by thermal hydrolysis was less dependent on pretreatment temperature, while protein solubilization was greatly increased at temperature above 160°C. The enhancement of the biogas production by thermal pretreatments was achieved with increase in temperature as compared to the control. However, it seemed the enhancement was linked to the initial biodegradability of the sludge.
3.1 Introduction

Sludge management is important due to the large amounts of sludge produced through the treatment of municipal and industrial wastewaters. While biological processes serves as an effective way of treating wastewater and enhancing nutrient removal before wastewaters are discharged to receiving streams, they have the inherent drawback of producing large amounts of biomass. The more efficient the process for removing contaminants, the more sludge is produced. Many efforts have been made to reduce sludge volumes by treatments such as digestion and dewatering (Bougrier et al., 2006; Higgins, 2006; Hii et al., 2014; Neyens et al., 2004; Pérez-Elvira et al., 2006). Anaerobic digestion with thermal pretreatment shows promise as a means of enhancing digester performance in terms of solids reduction, and is therefore of great interest to many facility operators.

The Thermal Hydrolysis Process (THP) is a heat conditioning technique which is used for raw sludge pretreatment before anaerobic digestion. It uses high temperature and pressure to solubilize particulate matter, disrupt biopolymer structures, and release soluble contents. During the anaerobic digestion of sewage sludge, the disintegration of organic materials is usually slow and recognized as a rate-limiting step before microbes can assimilate those organic materials (Bougrier et al., 2008). By improving the hydrolysis step with the THP, more food is available
for microorganisms, resulting in increased biogas volumes and decreased amounts of sludge to be disposed.

Li and Noike (1992) investigate the impact of thermal pretreatment on the degradation of waste activated sludge (WAS) in anaerobic digestion with temperatures ranging from 62 to 175°C and reaction times between 15 and 120 min. They observe the fraction of organic particulates in the sludge decreased as the temperature is increased to above 120°C indicating that more disintegration occurs as THP temperature increases. More specifically, the concentration of soluble proteins, carbohydrates, and lipids increases as the temperature is increased from 120 to 175°C due to the solubilization of particulates. Reaction times less than 30 min shows little influence on solids disintegration. Considerable efforts to identify the factors for the solubilization process have shown elevated temperatures (120 to 275°C) promote cellular disintegration and organics breakdown, thereby changing the characteristics of sludge (Bougrier et al., 2008; Muller, 2001). Therefore, this implies that the degree of sludge solubilization depends on the different sludge properties and organic components present in the sludge.

The adoption of the commercialized THP, CAMBI™ process at several plants in Europe and in one, full-scale installation in the US, represents a growing trend for solids reduction. In the
CAMBI process, high temperature (130 to 170°C) and pressure (2.5 to 8 bar; 1 bar = 100 kPa) steam is applied to the sludge in order to accelerate the degradation of organic and mineral matter. Carlsson et al. (2012) summarized the findings from various literature sources and suggested that COD solubilization is one of many factors most people used to characterize the performance of thermal hydrolysis. Other factors such as particle size reduction, organics removal, or recalcitrant compound formation have also been reported, but it appears that no direct indicator is available to assess solubilization by THP and the relationships between indicators are still ambiguous.

A focus of work at the Blue Plain, Advanced Wastewater Treatment Plant (AWTP) in Washington, DC, is to evaluate the impact of THP, at different temperature-time regimes, on the performance of mesophilic anaerobic digestion (MSD). This study is divided into two area: (1) to characterize the solubilization of the combined primary and secondary sludge from Blue Plains using THP at different operational times and temperatures, and (2) to examine the effectiveness of a mesophilic digester to produce biogas from thermally hydrolyzed sludge. Therefore, this work is designed to enhance our understanding of how THP changes sludge properties and improves digester performance.
Assessment of a pilot-scale THP system as a sludge pretreatment step prior to anaerobic
digestion was desirable for several reasons. First, the sludge type most frequently studied is the
biosolids from a wastewater treatment plant (WWTP), but there is now no universal THP
criterion. Results from the literature (Carlsson et al., 2012; Qiao et al., 2012) suggest that the
characteristics of sludge differed from one study to another, so the performance of THP cannot
be determined without preliminary testing. Second, the THP is often operated under specific
temperature and time condition as this temperature-time variable is often linked to internal costs
that must be included as part of an economic assessment before plant startup. Thus, a better
understanding of how these variables affect THP is needed.

In this context, the scope of this study is to examine the effect of thermal pretreatment
temperature and time on sludge solubilization to enhance anaerobic digestion and its potential
biogas production. Data collected from the influent and effluent from a pilot-scale THP unit are
used to assess the solubilization capacity of the process in terms of substrate COD and
macromolecular components (i.e., proteins, carbohydrates, and lipids). This temperature-time
testing regime may provide general guideline for plant operators to optimize their THP systems.
Moreover, to characterize anaerobic biodegradability of the sludge, batch digesters coupled to
respirometers with THP pre-treated sludge are tested over a long-term incubation period. The
specific methane yield (expressed as mL/g VS destroyed or fed) in a batch anaerobic reactor is calculated in order to adequately characterize the effect of sludge combined with THP pretreatment.

The overall objectives of this study are:

- To evaluate THP performance fed with mixed sludge (mixed the dewatered primary sludge and WAS with a TS concentration of 16.5%) and operated at different temperatures (130, 140, 150, 160, and 170°C) and retention times (10, 20, 30, 40, and 60 min).

- To characterize the biodegradability of THP pre-treated sludge by means of respirometric analysis in a batch, anaerobic reactor.

3.2 Materials and Methods

3.2.1 Thermal Hydrolysis Pilot Setup

In this study a batch thermal hydrolysis pilot unit, supplied by CAMBI™, Norway, is operated in order to evaluate solids solubilization before anaerobic digestion. A schematic of the THP pilot system with direct steam injection is shown in Figure 3. This pilot unit, located at DC Water’s Blue Plains AWTP, consists of a 15 L stainless steel hydrolysis vessel covered with thermal
insulation, a 40 L flashing tank used for the “steam explosion” where the steam is quickly released into the flashing tank, and a steam boiler with capacity of 15 horsepower (1 horsepower = 0.7457 kW) as a heating source.

Before running the THP, about 5 kg of thickened sludge is transferred into hydrolysis reactor and then the steam valve is opened to heat the reactor. The temperature ramping up time is 6 min.

Once the target temperature is reached, samples are hydrolyzed under the desired reaction time, and then the steam explosion is achieved at pressure of 25 psig. As shown in Table 2, the tested temperatures range from 130 to 170°C with 10 degree increments and reaction times of 10 to 60
min are considered for each temperature. At the end of each reaction cycle, the hydrolysis vessel is decompressed by gradually opening the breeding valve to 25 psig (flashing set point) before sending the sludge to the flashing tank. Between each batch process water is applied to both the hydrolysis reactor and flashing tank, thus the residual solids stuck inside the reactor are flushed out for collection and analysis.

Table 2. Operational parameters of THP study (a total of 25 batches)

<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>130</th>
<th>140</th>
<th>150</th>
<th>160</th>
<th>170</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Pressure (psig)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (min)</td>
<td>30</td>
<td>40</td>
<td>55</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>Total five batches</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Total five batches</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Total five batches</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Total five batches</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Total five batches</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.2 Sludge Sampling and Characteristics

The dewatered solids cakes of the primary sludge (TPS) and waste activated sludge (TWAS) are collected from DC Water’s Blue Plains Treatment Plant. Raw sludge samples are collected for each tested temperature [130℃ (RW130), 140℃ (RW140), 150℃ (RW150), 160℃ (RW160),
and 170°C (RW170)] adjusted to around 16.0 ~ 16.5% by using the formula shown below. The
general sludge characteristics for these experiments are listed in Table 3.

\[ X_b = X_c \times \frac{TSc - TSt}{TSc - TSb} \]  
Equation 3

where

\( TSc = \) Cake total solids (%)
\( TSt = \) Target total solids (%)
\( TSb = \) Blend total solids (%)
\( Xc = \) Cake weight (kg)
\( Xb = \) Blend weight (kg)
Table 3. General properties of mixed sludge (PS + WAS) used in THP test

<table>
<thead>
<tr>
<th>Property</th>
<th>RW130</th>
<th>RW140</th>
<th>RW150</th>
<th>RW160</th>
<th>RW170</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (%)</td>
<td>16.2</td>
<td>16.5</td>
<td>16.4</td>
<td>16.2</td>
<td>16.5</td>
</tr>
<tr>
<td>VS (%)</td>
<td>12.7</td>
<td>13.2</td>
<td>12.7</td>
<td>12.8</td>
<td>13.4</td>
</tr>
<tr>
<td>Total COD (g/L)</td>
<td>232</td>
<td>278</td>
<td>272</td>
<td>269</td>
<td>240</td>
</tr>
<tr>
<td>Soluble COD (g/L)</td>
<td>23</td>
<td>24</td>
<td>17</td>
<td>25</td>
<td>28</td>
</tr>
<tr>
<td>Soluble Protein (g BSA/L)</td>
<td>2.6</td>
<td>3.3</td>
<td>3.1</td>
<td>2.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Soluble Polysaccharide (g D-glucose/L)</td>
<td>0.9</td>
<td>0.8</td>
<td>0.8</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>235</td>
<td>287</td>
<td>205</td>
<td>224</td>
<td>254</td>
</tr>
<tr>
<td>Acetic Acid (mg/L)</td>
<td>19</td>
<td>626</td>
<td>411</td>
<td>473</td>
<td>720</td>
</tr>
<tr>
<td>Propionic Acid (mg/L)</td>
<td>98</td>
<td>321</td>
<td>205</td>
<td>249</td>
<td>386</td>
</tr>
<tr>
<td>Volatile Fatty Acids (as HAc mg/L)</td>
<td>350</td>
<td>1,465</td>
<td>995</td>
<td>1190</td>
<td>1570</td>
</tr>
<tr>
<td>Total Lipids (g/g TS)</td>
<td>0.14</td>
<td>0.15</td>
<td>0.16</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
<td>6.2</td>
<td>5.93</td>
<td>5.94</td>
<td>5.98</td>
</tr>
</tbody>
</table>

HAc: Acetic Acid; BSA: Bovine Serum Albumin
3.2.3 Anaerobic Digester

The pilot-scale mesophilic anaerobic digestion (MAD) used in this experiment has an active volume of 60 L. The digester is maintained in a mesophilic state by recirculating hot water (38.5 °C ± 1°C) through pipes in a sealed space where the digester is placed and operated with daily manual feeding and sludge maintains a solids retention time (SRT) of 15 days. The MAD is fed with THP pre-treated (at 160°C, 30min) sludge, with a TS concentration of about 10.5% and a VS concentration of about 8.2%, for three months to reach a steady-state condition. The reactor is continuously and mechanically mixed at a speed of 250 rpm (Lightnin, New York).

3.2.4 Respirometer System

The respirometer utilized to automatically measure biogas production is supplied by Challenge Technology (Challenge Technology, Arkansas). Inocula obtained from the MAD pilot described above is transferred to 700 mL serum bottles. The bottle is then set up on a magnetic stirrer (200 rpm) in a temperature controlled incubator at 38.5 ± 1°C. Each bottle contains approximately 400 mL inoculum and 80 gm of THP pre-treated substrate to meet a (food to inoculum) ratio of 0.14±0.04 g COD/g VS_{added}. For an experimental control, a blank treatment with only inoculum is used to estimate the biogas production due to the microbial endogenous respiration.
Performance is assessed by measuring accumulative gas production and converting the data to terms of biogas production rate ($L_{\text{biogas}}/L_{\text{bottle}}/\text{hr}$), and gas yield ($g \text{ COD}_{\text{CH}_4}/g \text{ VS}$).

### 3.2.5 Analytic Methods

The performance of the THP reactor is evaluated by characterizing influent and effluent samples. To avoid microbial activity, samples are immediately stored at $4^\circ\text{C}$ until further analyses. Figure 4 and Figure 5 depict the overall analyses performed on solid and soluble fractions for the THP and anaerobically digested sludge test.

![Figure 4. Analysis overview of the THP test](image-url)
The solids content of sludge, total solids (TS) and volatile solids (VS) are determined as per Standard Methods (APHA, 2012), procedure 2540-G. The soluble components of the sludge (i.e. protein, NH₃) are determined by first centrifuging at 10,000 G (Beckman, California) and 20°C for 30 min and then passing the supernatant through a 0.45 µm syringe filter. A 1.0 µm glass fiber filter is used for soluble COD. The chemical oxygen demand is determined on the total sludge and on the supernatant after centrifugation by using the HACH digestion method (HACH, Colorado). In this experiment, the difference between total and soluble COD is referred to as particulate COD. The pH is measured on fresh samples.
In order to better understand the effect of thermal pretreatment on sludge solubilization, proteins, polysaccharides, and lipids were measured. Soluble protein was determined by using the modified Lowry method (Hartree, 1972) with bovine serum albumin (BSA) as a standard. D-glucose, according to DuBois et al. (1956), is used as standard for polysaccharide measurements. A spectrophotometer (HACH, Colorado) at 750 and 485 nm wavelengths is used to measure soluble protein and polysaccharide, respectively. Lipid concentration is determined according to (Smedes, 1999).

For measuring volatile fatty acids (VFAs), sludge samples are centrifuged. The supernatants are filtered by 0.45 µm filter, diluted (1:20), and acidified with methanesulfonic acid (MSA) to lower the pH below 3. VFAs, including acetic, propionic, iso-butyric, butyric, iso-valeric, and valeric acids, are measured by means of a gas chromatograph (Shimadzu, Japan) equipped with an autosampler, a capillary column (Stabilwax-DA, 30m x 0.32mm x 1µm), and a flame ionization detector (FID). The chromatograph is calibrated with a dilution of commercial VFA mixed standard (Sigma-Aldrich, Missouri) in the range of 0 – 200 mg L⁻¹. Helium is the carrier gas at 2.76 mL L⁻¹ and both the injector and FID temperature are 250°C. The oven temperature is held at 60°C for 0.5 min, and then ramped at 10°C min L⁻¹ to the final temperature of 230°C.
3.3 Results and Discussion

Samples are collected a few weeks apart resulting in variations in raw sludge composition. Analyses are performed for all the pilot-scale influent and effluent sludge samples. Because steam is supplied to hydrolyze the solids, which may dilute the concentrations, mass ratios of sludge output to feed are conducted for most of the results. Parameters like total and volatile solids and total COD demand should conserved throughout the process. To examine the effects of temperature on substrate biodegradability, batch anaerobic digesters are fed with thermally pre-treated sludge followed by respirometric analysis. Different characteristics of the sludge including total and volatile solids and COD are measured.

3.3.1 Raw sludge variations

As previously described and noted in Table 3, the characteristics of the raw sludge vary from batch to batch due to the plant treatment process and the sampling duration. Also, as described by Bougrier et al. (2008), untreated (raw) sludge can spontaneously undergo variations in its characteristics because of storage or due to a high level of soluble components within raw sludge. An increase of soluble COD by more than 300\% occurs for untreated raw sludge after 75 days of storage (Bougrier et al., 2008). A similar result of soluble COD with pre-treated sludge is obtained from a preliminary study conducted at DC Water as shown in Figure 6. Raw sludge
with the TS of about 16.5% is hydrolyzed with treatment at 160°C and 30 min. Treated sludge is then stored at room temperature and 4°C. Result shows that soluble COD increases by 20% and 50% after 25 days of storage under 4°C and room temperature, respectively. Therefore, to avoid the issue of the sludge storage leading to unreliable results, storage at 4°C is limited to 3 days.

Figure 6. Soluble COD profile over storage periods.

3.3.2 Effects of Time and Temperature on Solubilization

During thermal pretreatment, organic solids are subjected to reaction temperature and time variations. Several studies (Donoso-Bravo et al., 2011; Li & Noike, 1992) indicate that temperatures over 150°C and treatment times above 30 min can efficiently destroy cell
structures and release organic contents which are further degraded into lower molecule weight organic compounds such as amino acids and sugars. The COD demand of the soluble fraction of the hydrolyzed sludge therefore increases. Eskicioglu et al. (2006) found that thermal hydrolysis at high temperatures is responsible for the formation of refractory dissolved organic compounds, which cause a brown color in the solution. Figure 7 provides a comparison of the supernatants taken after centrifugation of pre-treated and untreated sludge samples and shows the color changes in accordance with reaction time and temperature.

![Figure 7. Comparisons of the centrifuged supernatant characteristics before and after filtering](image-url)
3.3.2.1 COD solubilization

The COD is used to express the pollutant strength of the waste stream and is the most common method used to describe the effects of thermal hydrolysis on solids solubilization. According to Bougrier et al. (2006); Elbeshbishy et al. (2011), the extend of COD solubilization can be used to evaluate if or how much the particulate matter is converted into soluble organic compounds. The calculation for the degree of COD solubilization expressed as a percentage is shown below:

\[
S_{COD\%} = \frac{COD_S - COD_{SO}}{COD_O - COD_{SO}} \times 100\% = \frac{COD_S - COD_{SO}}{COD_{PO}} \times 100\%
\]

Equation 4

where

\( S_{COD\%} \) solubilization degree of COD (%)

\( COD_S \) soluble COD in pre-treated sludge (gram O\(_2\) )

\( COD_{SO} \) soluble COD in untreated sludge (gram O\(_2\) )

\( COD_O \) total COD before in untreated sludge (gram O\(_2\) )

\( COD_{PO} \) particulate COD in untreated sludge (gram O\(_2\) )
Figure 8 and Figure 9 represent the degree of COD solubilization with increases in reaction time and temperature, respectively.

Figure 8. The effects of thermal treatment time on COD solubilization
Table 4 shows that the average solubilization of COD is in the range of about -1 to 10%, with standard deviations less than 1% for all the samples. A negative COD solubilization is due to the errors associated with COD measurements. For a reaction time lower than 30 min thermal hydrolysis seems to be less significant for COD solubilization, whereas for samples with temperature above 160°C, the solubilization level greatly increases with increase in temperature, reaching a maximum of 8 to 10%. Thus, pretreatment accelerated solubilization of the particulate organic matter. Once the thermal temperature and reaction time exceed both the 160°C and 30 min thresholds, the disintegration of organic matters is more effective.
Considering the absolute magnitude of COD solubilization compared with literature values (Bougrier et al., 2008; Elbeshbishy et al., 2011), the amount of COD solubilization is relatively low for all the tests. The highest COD solubilization is slightly above 10% while most samples have solubilization levels below 6%. This is probably because of the nature of the solids and the solids concentration within the sludge structure. By using the combined sludge with a TS concentration of around 16.0% for feeding the reactor, the active surface area of the solids in contact with high temperature and pressure steam is less than TWAS or TPS alone.
Table 4. COD solubilization degree of pre-treated sludge with temperature and time

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reaction Time (min)</th>
<th>Percent Solubilization of COD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>-1.1±0.3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.4±0.9</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.4±0.4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>4.1±0.1</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>4.4±0.8</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140</td>
<td></td>
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<tr>
<td></td>
<td>150</td>
<td></td>
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<td></td>
<td>160</td>
<td></td>
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<tr>
<td></td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>

Figure 10 shows the soluble COD concentration for the different pretreatment temperature (from 130 to 170°C) and time (from 10 to 60 min). The average COD concentrations for raw and pre-treated sludge are generally about 24,000 mg/L and 23,000 mg/L, respectively, but a much lower COD level is observed for all 150°C batches. For the samples below 30 min reaction time, the overall COD concentration of the effluent samples is lower than the influent COD. It should again be noted that the steam vapor is used as the heating source and may have condensed during the reaction to dilute the pre-treated sludge concentration. Therefore, a marginal increment in soluble COD concentration is obtained via the increase of reaction time at the same temperature.
To have a better understanding of COD solubilization by thermal hydrolysis, the soluble COD mass ratios of pre-treated to untreated samples are used and showed in Figure 11. In general, a continuous soluble COD increase is attained as time and temperature increase. The 170°C temperature increases soluble COD by approximately 70% for the combined sludge at a 25 psig flashing condition.
3.3.2.2 Soluble protein and carbohydrates

Proteins and carbohydrates comprise the largest fraction of the municipal wastewater sludge and are subjected to thermal pretreatment temperature and time influences (Bougrier et al., 2008). The increase in protein by thermal hydrolysis is beneficial and desirable for the downstream MAD to increase VS destruction and to improve biogas production. Nevertheless, the higher protein destruction also results in higher unionized ammonia level, which could cause inhibition of the methanogens. Li and Noike (1992) find that the hydrolysis effect by thermal pretreatment of WAS is greater for proteins and carbohydrates than lipids.
Bougrier et al. (2008) conducts THP experiments with WAS in the temperature range of 95 to 210°C and finds an increase in the concentration of soluble carbohydrates after 130°C treatment; however, a decrease in soluble carbohydrate level is observed in the sludge treated at 170°C. One possible explanation for the declining carbohydrate level is that carbohydrates react with other carbohydrates or proteins to form soluble refractory compounds which cannot be detected by the method (Bougrier et al., 2008).

The mass ratio of effluent to influent soluble protein is shown in Figure 12. The results indicate that soluble protein is continuously produced throughout the batch tests. However, a sharp increase in soluble protein mass, by up to 600%, is achieved by treatment at 170°C and 30 min, as compared to untreated sludge. Only about 450% is achieved by treatment at 160°C with a 30 min reaction time.
Similar to Figure 12, a plot of NH$_3$-N as a function of reaction time and temperature (Figure 13) reveals that there is a marginal increase with increasing reaction time and temperature. The small increase of NH$_3$-N at increasing reaction time and temperature likely indicates that a small portion of protein is hydrolyzed followed by deamination to produce soluble ammonia compounds in this experiment. Moreover, the increase in NH$_3$-N mass ratio is not significant between treatment at 160 and 170°C while soluble protein is greatly produced by treatment in the same temperature range. This result combined with the protein data, shown in Figure 14, indicates proteins are solubilized by THP, leading to small ammonia increase with increasing
temperature, but proteins are barely damaged to produce soluble ammonia at a temperature higher than 160°C.

Figure 13. The mass ratio of soluble ammonia-nitrogen with reaction time and temperature
Figure 14. Relationship of protein and ammonia nitrogen with reaction time and temperature

Figure 15 presents the mass ratio of effluent to influent soluble carbohydrate. For temperatures 130, 150, and 170°C, a distinct increase in carbohydrate is seen, up to a 30 min reaction time, followed by a constant amount up to 60 min. Moreover, the ratio of carbohydrate treated at 130, 150, and 170°C increased as THP temperature altered particulate characteristics to disintegrate biopolymer compounds and release more nutrients rich in carbon into solution.
3.3.2.3 Lipids and VFAs

The lipid concentrations are determined by using the gravimetric extraction method combined with organic solvent (cyclohexane and ethanol) as per Smedes (1999). An investigation done by Bougrier et al. (2008) shows that thermal pretreatment of WAS has little effect on lipids solubilization. For example, Bougrier et al. (2008) found the total lipid concentration increased with thermal treatment. This increase could be explained by the better extractability by the method, as the flocs are decomposed by thermal treatment, which increases the contact surfaces for efficient lipid transfer from solids to solvent. Thus, an increase in lipids content is achieved.
Due to high hydrophobicity, lipids are barely solubilized in aqueous phase. However, VFAs levels strongly increase as a consequence of thermal pretreatment. The increase in VFAs is linked to the degradation of long chain fatty acids and/or protein.

Figure 16 shows the total lipid concentrations based on total solids in the samples treated at different temperature and reaction time. The total lipids of the treated samples are greater than of the untreated samples for all the temperature and reaction times. A small increase between the treated and untreated samples with increasing temperature is observed.
VFAs are measured in both the feed and the effluent to evaluate the performance of the THP unit. Because of thermal pretreatment, the hydrolyzed sludge results in higher VFAs as reaction time increases. However, as shown in Figure 17, the feed VFAs shows a higher concentration than the output regardless of increases in reaction time at temperature higher than 130°C. Individual VFAs for samples pretreated at 130°C are shown in Figure 18. VFA concentrations in untreated sludge are 300 mg/L for a batch at 130°C, to 1,000 mg/L for batches at 150°C, and 1,500 mg/L for batches at 170°C.

Strong et al. (2011) observe from thermal treatment of municipal biosolids that VFA concentration increases when the temperature increases from 140 to 165°C. In this study, the amount of VFAs in the effluent changes little with temperature. The thermal hydrolysis time seems to be more important than the temperature with regard to VFA production. Some loss of VFAs are observed at higher temperatures due to the lack of a gas recirculation system, and VFAs vaporize during the reaction and escape after decompressing the reactor. The main VFA components for municipal sludge are acetic acid and propionic acid, which have boiling points around 120 and 142°C, respectively. The increased concentrations of acetic acid and propionic acid with increased reaction time from 10 to 60 min at 130°C are shown in Figure 18.
Figure 17. Feed and output VFAs (as HAc) concentration with different reaction time and temperature

Figure 18. VFAs concentration after 130°C treatment with different reaction time
The pHs for untreated sludge are consistently around 6.0. Decreases in pH for treated samples are thought to be due to VFAs production by thermal pretreatment. Volatile fatty acids are weak acids that dissociate at neutral pH (Grady et al., 1999). Figure 19 illustrates the pH decreases after thermal hydrolysis at 130, 150, and 170°C, and different reaction times. Thermal pretreatment results in slight decreases in pH as reaction time increases.
3.3.3 Anaerobic Biodegradability

![Graph showing gas production over time for different temperatures](image)

Figure 20. Results of respirometer with 130, 150, and 170°C THP pre-treated sludge

(pretreatment time = 30 min)

Similar thermal experiments are further conducted to evaluate the impacts of reaction temperature on anaerobic biogas production. Figure 20 shows the total gas production from thermally pre-treated sludge during a 12 days assay. The “Control” represents the inoculum which is incubated over 12 days, and the sludge treated with 130°C (30min), 150°C (30min), and 170°C (30min), but with the same pretreatment time of 30 min are added and mixed with the inoculum. The final methane potential yields and COD mass balance for all sample types are
presented in Figure 21. As the reaction time is kept at 30 min, increasing the temperature
generally improves total gas production. The results of gas yield shown in Figure 21 are slightly
higher than the findings that have been reported by other authors (Strong et al., 2011). Strong et
al. (2011) conduct a series of experiment at 140 and 165°C thermal pretreatment of municipal
biosolids from a local WWTP. Their ultimate methane yields for the THP pre-treated samples
varied widely compared to some literature values. The optimal pretreatment temperature
supported by the literature is in the range of 160 to 180°C (Bougrier et al., 2007; Li & Noike,
1992). This variances from one study to another are probably because of the different treatment
processes, the sludge characteristics, and the microbial communities adapting to a specific
environment. However, it should also be noted that the increase in temperature by thermal
pretreatment usually results in biogas enhancement. The formation of refractory compounds by
high temperature that caused inhibitory effects to anaerobic biodegradability seemed to be less
important in this study where the temperatures are all below 180°C.
3.4 Conclusion

Overall, thermal pretreatments are efficient at solubilizing sludge in the range of temperatures and times considered. The data also indicate that solubilization increases as reaction time and temperature are increased. For temperatures higher than 160°C, COD solubilization is found to be strongly dependent on the temperature. However, reaction time seems to attribute to COD solubilization once the temperature reaches above 160°C. This suggests that temperatures above 160°C with sufficient contact time (30 min) greatly affect the disintegration of particulates disintegration. For temperatures higher than 170°C, microbial cells release protein-rich cell contents which are further solubilized into soluble protein. The soluble NH3-N production via...
deamination by thermal hydrolysis is less significant than protein solubilization. However, at the temperatures below 150°C, carbohydrates solubilization is more important than proteins solubilization.

The enhancement of the biogas production by thermal pretreatments is achieved with increase in temperature as compared to the control during the batch anaerobic digestion. The enhancement is likely somewhat linked to initial biodegradability of the sludge, as the total biogas yields are slightly higher than reports by others using the same reaction time and temperature.

3.5 Acknowledgement

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CHAPTER 4

ANAEROBIC RESPIROMETRIC ANALYSIS

4.1 Introduction

During conventional anaerobic digestion, hydrolysis of particulates, including cell mass, is a slow and rate-limiting step. Most of the time incomplete disintegration lowers the potential for biogas production. The intercellular content of biological cells is biodegradable and has potential for producing biogas. However, the cell wall that protects the cellular content from physical and chemical stress is made up of D-amino acid, cross-linked polysaccharide chains that are resistant to biodegradation. Use of thermal hydrolysis process (THP) (i.e., CAMBI™) as a sludge pretreatment prior to anaerobic digestion has proven to be promising means for improving biogas production. Exposure of sludge to specific temperatures (of 130 to 170°C) for a brief period of time, 30 to 60 min, has been effective. THP disintegrates WAS cells, excreting cellular biodegradable content for digestion and solubilizing particulate organic matter to more soluble biodegradable organics. The biodegradability of sludge using respirometry test as a means to assess particulate solubilization has been reported where the biodegradability can be evaluated in
terms of specific biogas yield (mL biogas/g VS destructed or added) (Carlsson et al., 2012). The goal of this study is to investigate the impact of different THP temperatures on biodegradability by using respirometry tests.

4.2 Methods and Materials

THP was carried out in a 4 gallon hydrolysis vessel with a direct steam injection unit supplied by CAMBI™, Norway (Figure 22). The combined primary and waste activated sludge collected from Blue Plains Advanced Wastewater Treatment Plant was used as raw sludge. Batch hydrolysis trials with temperatures of 130, 150, and 170°C and with 30 min reaction times were performed. For respirometry tests, inoculum (seed sludge) were collected from a 60 L mesophilic anaerobic digester (38.5°C) with a solids retention time of 15 days, which was previously fed with thermally hydrolyzed sludge (160°C, 30 min). Duplicate serum bottles where the hydrolyzed substrate was mixed with inoculum by a magnetic stirrer (250 rpm) were incubated at a temperature of 38.5°C; and, anaerobic biogas was measured over time by a calibrated respirometer (Challenge Technology, Arkansas) connected to each serum bottle (Figure 23).

Inoculum obtained from the MAD pilot described above were transferred to 700 mL serum bottles. Each bottle contained approximately 400 gm of inoculum and 80 gm of THP pre-treated substrate to meet a food to inoculum ratio of $0.14 \pm 0.04$ g sCOD$_{substrate}$/g VS$_{inoculum}$. For an
experimental control, a blank treatment with only inoculum was used to estimate the biogas production due to microbial endogenous respiration. Performance was assessed by measuring accumulative gas production and converted the data in terms of biogas production rate \( (\text{mL}_{\text{biogas}}/\text{hr}) \), and specific gas yield \( (\text{mL}_{\text{biogas}}/\text{g VS}) \).

Figure 22. Thermal Hydrolysis Process unit in DC Water

The influent and effluent of the batch reactor were collected for analysis of total solids (TS), volatile solids (VS), total/soluble chemical oxygen demand (tCOD/sCOD), protein, \( \text{NH}_3-N \), pH and alkalinity. Figure 24 depicts the overall analysis performed on samples for batch anaerobic digester. Measures of TS and VS contents were determined as per Standard Methods, procedure
2540-G (APHA, 2012). The soluble components of the sludge (i.e., protein, NH₃) were determined by first centrifuging at 10,000 G (Beckman, California) and 20°C for 30 min, and then passing the supernatant through a 0.45 µm syringe filter. A 1.0 µm glass fiber filter was used for soluble COD. The chemical oxygen demand was determined on the total sludge and on the supernatant after centrifugation by using the HACH digestion method (HACH, Colorado). In this experiment, the difference between total and soluble COD was referred to as particulate COD. The pH was measured on fresh samples. The alkalinity of samples (as mg CaCO₃/L) was determined by titration with 0.2 N sulfuric acid to an end point of pH 5.0. Soluble protein was determined by using the modified Lowry method (Hartree, 1972) with bovine serum albumin (BSA) as a standard. A spectrophotometer (HACH, Colorado) at 750 nm wavelengths was used to measure soluble protein.

![Image](Image.png)

Figure 23. Batch anaerobic digestion (right) connected with respirometer (left)
4.3 Results

Respirometry tests with sludge pretreated with THP were conducted to evaluate the impacts of reaction temperature on anaerobic biogas production. Figure 25 presents the total biogas production during a 12-day assay with sludge pretreated at 130°C (130°C, 30 min), 150°C (150°C, 30 min), and 170°C (170°C, 30 min), and without treated sludge addition (Control). The average gas production rates with different THP pretreated sludge are shown in Figure 26. Figure 27 shows the biogas yield based on total VS (g) added, destructed, and COD balance (%) for each reactor. The characteristics of sludge before and after respirometry tests are shown in Figure 28. Increasing the THP temperature improved total gas production and the pretreatment of 170°C resulted in the highest total gas production which was about 20% higher as compared to sludge pretreated with 130°C after 7.5 days. The results of gas yield based on either VS added and
destruction showed continuous improvements in biogas production as temperature increased.

However, the overall improvements on gas yield seemed to be less dependent on pretreatment temperature as the highest temperature usually led to greatest particulate solubilization. Moreover, the VS destructions after 12 days remained 60.7±0.1%, 62.4±0.1%, and 62.7±0.1% for temperatures of 130°C, 150°C, and 170°C, respectively. Such small improvements of gas yield and VS destruction with increased temperature may be due to the fact that most of the readily biodegradable contents produced by THP were consumed in respirometry tests, regardless of different temperatures. To further identify the overall impact of temperature on the substrate biodegradability, a comprehensive study on the kinetics such as biogas production rates along with macromolecular analyses needs to be performed.
Figure 25. Results of respirometry with THP pre-treated sludge (pretreatment time = 30 min)

Figure 26. Biogas production rate for the (1) control, (2) 130°C, 30 min, (3) 150°C, 30 min, and (4) 170°C, 30 min.
Figure 27. Results of specific biogas yield and COD balance

Figure 28. Characteristics of feed, influent, and effluent in batch anaerobic digesters of the control and sludge pretreated with 130C, 150C, and 170C.
Table 5. Specific gas yield, COD removal, and solids removal for the batch reactors.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control</th>
<th>130°C, 30 min</th>
<th>150°C, 30 min</th>
<th>170°C, 30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate to Inoculum Ratio (g sCOD_{substrate}/g VS_{inoculum})</td>
<td>-</td>
<td>0.13</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>VS Removal (%)</td>
<td>13.7 ± 0.8</td>
<td>60.7 ± 0.1</td>
<td>62.4 ± 0.1</td>
<td>62.7 ± 0.1</td>
</tr>
<tr>
<td>COD Removal (%)</td>
<td>11.4 ± 2.3</td>
<td>59.5 ± 2.6</td>
<td>61.7 ± 3.6</td>
<td>70.9 ± 0.4</td>
</tr>
<tr>
<td>Specific Gas Yield (mL/g VS_{added})</td>
<td>-</td>
<td>692</td>
<td>849</td>
<td>886</td>
</tr>
<tr>
<td>Specific Gas Yield (mL/g VS_{destructed})</td>
<td>106</td>
<td>1021</td>
<td>1097</td>
<td>1223</td>
</tr>
<tr>
<td>Specific Gas Yield (mL/g sCOD_{added})</td>
<td>-</td>
<td>3331</td>
<td>2338</td>
<td>2197</td>
</tr>
</tbody>
</table>
CHAPTER 5

OVERALL CONCLUSIONS, ENGINEERING SIGNIFICANCE AND RECOMMENDATIONS FOR FUTURE STUDY

5.1 Conclusions

In general, thermal hydrolysis greatly affected sludge characteristics with increases in reaction time and temperature. Higher temperatures usually resulted in better solubilization of COD, proteins, and carbohydrates, whereas reaction time had less influence on particulate disintegration. Nevertheless, high temperatures (above 160°C) with sufficient contact time (over 30 min) were required to achieve 10% increase in COD solubilization as compared with 4% at a shorter reaction time.

At temperatures higher than 160°C, proteins solubilization was heavily dependent on pretreatment temperature, due to cell disintegration, while little increases in carbohydrate solubilization were obtained as reaction times increased. Therefore, pretreatment temperature greatly affected sludge characteristics. However, the use of THP did not improve ammonia release from protein at 170°C.
Higher temperature facilitated lipid extraction leading to a slightly higher output lipid concentration. Due to their high hydrophobicity, lipids were barely solubilized in the aqueous phase. However, in contrast with lipids solubilization, VFAs were strongly increased as a consequence of thermal pretreatment. The increase in VFAs was linked to the degradation of long chain fatty acids or protein decomposition.

Thermal hydrolysis systems, such as the CAMBI™ process, are increasingly used in large plants for the benefits of energy recovery throughout increasing methane production. Biogas production after thermal treatments up to 170°C was improved by 20 to 25% in contrast with a lower temperature of 130°C at a solids retention time of 7.5 days. The enhancement appeared to be linked to the initial biodegradability of the sludge, as the total biogas yields in this study were slightly higher than in other references where similar reaction times and temperatures were used.

5.2 Engineering Significances

Thermal hydrolysis is operated with exposure of sludge to specific temperatures and times as this temperature-time variable is associated with process efficiency, as well as part of an economic assessment for the plant startup. Thus, this research may provide general guidelines for plant
operators to design or optimize their thermal hydrolysis systems. Second, the characteristics of sludge differ from place to place, so there seems no universal THP standard procedure is available. However, this study serves as a preliminary test for treatment plants with a specific type of sludge. Third, biogas improvements shown in this study enabled anaerobic reactors to perform more efficiently with high THP temperature for stabilizing municipal biosolids.

5.3 Suggestions for Future Works

A number of problems must be solved to allow the development of more efficient THP system. These problems would suggest a variety of research directions that need to be pursued to make such a system feasible.

As CAMBI™ is enclosed by stainless steel hydrolysis vessel with steam circulation, one strategy to simulate the real process is to use a closed vessel, such as an autoclave or a “bomb”. The data collected by closing the THP system may be more reliable and representative. More comprehensive research involving the studies of individual sludge (i.e., primary sludge or WAS alone) should be completed in order to compare the THP efficiency with respect to diversified substrate sources.
VFAs are a very important index for both the thermal hydrolysis efficiency and the stability of the digestion process. It would be preferable to study the effects of long chain fatty acids degradation for substrate rich in fatty acids contents (i.e., food waste), especially for a co-digestion process with thermal pretreatment.

A better understanding of the elementary stoichiometry, which allowed the development of the general stoichiometric formulae for each substrate type, should be helpful in terms of knowing energy flow and nutrient balance for monitoring digester performance and applying for future digester modeling.

The study of biodegradability, as well as bioavailable organic contents from biogas production profile, is of great interest due to various applications for modeling and process control. Therefore, one future emphasis should be placed on the use of the biochemical methane potential (BMP) test that allows for a tracking of changes of target chemicals based on a daily monitoring process. A comparison of lab-scale BMP tests with data from full scale systems should be conducted to recognize the differences.
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APPENDIX A: SUPPLEMENTARY MATERIALS

Figure A - 1. Total solids mass balance with different reaction time and temperature

Figure A - 2. Volatile solids mass balance with different reaction time and temperature
Figure A - 3. Total COD concentration with different reaction time and temperature

Figure A - 4. Total COD mass balance with different reaction time and temperature
Figure A - 5. Soluble protein with different reaction time and temperature

Figure A - 6. Soluble polysaccharide with different reaction time and temperature
Figure A - 7. Soluble ammonia-nitrogen with different reaction time and temperature