ENHANCEMENT OF KELOWNA'S BIOSOLIDS TO ENERGY CONVERSION WITH THERMAL PRETREATMENTS

by

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M.A.Sc., University of Tehran, 2009

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE COLLEGE OF GRADUATE STUDIES

(Civil Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Okanagan)

October 2012

Abstract

The potential of using biogas generated from organic waste as energy source is broadly recognized and anaerobic digestion has become a major part of modern wastewater treatment plants (WWTPs). Various pretreatment techniques have been recently developed to increase the quantity of biogas and reduce digester volume by enhancing the hydrolysis of waste material fed to the digesters. This study evaluates advanced anaerobic digestion incorporating thermal pretreatments (microwave at 2.45 GHz and conventional heating) as an alternative disposal method for the municipal biosolids generated by Kelowna WWTP (BC, Canada) which are currently composted.

To be able to compare microwave irradiation with conventional heating under identical conditions (temperature/ heating rates), a custom pressure vessel was built for conventional heating. Biosolids heated from room temperature up to pretreatment temperatures of 80, 120 and 160^{o}C at heating rate of (7.5^{o}C/min) in the closed vessel microwave unit and the pressure sealed vessel. Both conventional heating and microwave pretreatments indicated that in a pretreatment range of 80-160^{o}C, temperature was a statistically significant factor ($p<0.05$) for increasing solubilization of chemical oxygen demand (COD) and biopolymers of the biosolids. Fourteen lab-scale semi-continuous digesters were operated for digestion of the biosolids to optimize energy (methane) output and sludge retention time (SRT) requirements of untreated (control) and thermally pretreated digesters.

In general, relative (to control) organic removal efficiencies dramatically increased as SRT was shortened from 20 to 10 and 5 days, indicating that the control digesters were challenged as the organic loading was increased. Except the control digesters at the SRT of 5 days, all control and pretreated digesters achieved steady state at three SRTs, corresponding to volumetric organic loading rates of 1.74 to 6.96 g COD/L/d. At the SRT of 5 days, the controls stopped producing biogas after 20 days of operation while the pretreated digesters continued producing biogas. Energy analysis showed that all digesters had positive net energy productions except the digesters fed with sludge pretreated at 160^{o}C and operated at SRT of 20 and 5 days. Digesters operated at 10 days SRT were more favorable, and they produced net energy of 1.3 - 9.6 (GJ/d/Tonne total solids $_{added}$).

Preface

Some parts of this study were presented in 2012 British Columbia Water and Waste Association (BCWWA) Annual Conference (April 21-25, Penticton, BC, Canada). An abstract has been submitted for presentation in Water Environment Federation (WEF) Residuals and Biosolids 2013 Conference (May 5-8, Nashville, Tennessee). Also a summary of this research is under preparation to be sent to Water Research Journal.

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List of Abbreviations

BOD: biological oxygen demand

CH: conventional heating

COD: chemical oxygen demand

DWSC: dewatered sludge cake

ME: mesophilic

MW: microwave

MPN: most probable number

PS: primary sludge

TCOD: total chemical oxygen demand

TH: thermophilic

SCOD: soluble chemical oxygen demand

SRT: sludge retention time

SC: semi-continuous

VFAs: volatile fatty acids

WAS: waste activated sludge

WWTP: wastewater treatment plant

Acknowledgements

First and foremost I would like to thank God for giving me the power to believe in myself and pursue my dreams.

Next, I wish to express enduring gratitude to my supervisor, Dr. Cigdem Eskicioglu for her vast reserve of patience and knowledge in this field. She has been a great inspiration to me throughout my research. I sincerely acknowledge my committee members, Dr. Rehan Sadiq and Dr. Abbas Milani. Also, I am very grateful to the fellow students in our research team, Piero Galvagno, Hanna Hamid and Tim Abbot at UBC for their support during the experiments.

I owe special thanks to Dr. Thomas Johnson and Dr. Jake Bobowski, for their guides and also, providing pressure sealed vessel for conventional heating method and energy measurement apparatus for the microwave unit. I also thank NSERC Strategic Project Grant, City of Kelowna and BC Ministry of Environment for supporting this project.

At last but not least, I want to express special thanks to my family, specially my dear parents, for their unconditional love and support throughout my life.

To my Father and Mother

Chapter 1 Introduction

1.1 Background

The treatment of wastewater produces semi solid residuals that is commonly termed as "waste sludge" or simply "sludge" and must be disposed to the environment. The quantities of sludge produced in our modern society are astounding. According to Okuno (2007), annual production of sludge in Canada is at least 0.4 million dry metric tonnes and United States produced more than 7.5 million dry metric tonnes of sludge in 2010 (U.S.EPA, 1999; Sanin et al., 2011).

Sludge treatment and disposal accounts for more than 50% of a wastewater treatment plant (WWTP) operating cost (Canales et al., 1994). Sludge often contains substantial nutrients and organics that can be used beneficially after treatment. Therefore, it can be considered as a resource rather than a waste.

Sludge treatment aims for stabilization, pathogen removal, odour reduction and volume reduction. The first three goals can be achieved using anaerobic digesters. Sludge volume reduction proceeds disposal and is achieved through dewatering. Anaerobic digestion is a three-step process comprised of hydrolysis, acidogenesis and methanogenesis. It is a favoured stabilization method for treatment of organic waste due to biogas production and improvement agricultural practices by recycling of plant nutrients. Also, it has lower energy footprint compared to aerobic digestion (Carrere et al., 2010). Hydrolysis is the bottleneck of anaerobic digestion process and results in longer sludge retention time. Application of pretreatment methods prior to anaerobic digestion can accelerate the hydrolysis (Mottet et al., 2009; Zheng et al, 2009) and improve the degradability of the materials being fed to the digesters. These pretreatment methods can be categorized under physical, biological and chemical sludge pretreatment. Among different pretreatment studies, thermal pretreatments seem to achieve higher improvements in biogas productions. Furthermore, sludge sanitization and enhanced dewaterability are other advantages of thermal pretreatment. In general, no extra energy is needed for thermal pretreatment since the energy requirements can be covered by excess biogas production and positive energy balance (Kepp et al., 2000). Therefore, this study focused on thermal pretreatments to enhance anaerobic digestibility of municipal waste sludge.

1.2 Motivation for research

This research is part of an NSERC Strategic Project in collaboration with City of Kelowna, BC Ministry of Environment and Paradigm Environmental Inc. The overall objective is to find a more sustainable alternative to current disposal scenario (Figure 1.1) for municipal waste sludge or “biosolids” generated in the Kelowna’s WWTP.

The City of Kelowna (with a population of ~150,000) in Okanagan Valley operates a WWTP (Kelowna Pollution Prevention Center) for wastewater and a landfill (Glenmore Landfill) for solid waste treatment and disposal. Kelowna Pollution Prevention Center (KPPC) has a tertiary treatment with a Bardenpho unit to eliminate carbon, nitrogen and phosphorous compounds from wastewater and to protect Okanagan Lake from eutrophication. The waste activated sludge from the WWTP is thickened and centrifuged with the fermented primary sludge (PS) to produce dewatered biosolids with 18% solid concentration. The dewatered biosolids are produced at an average rate of 2.5 truckloads (~ 66 tonnes) per day and are hauled to a composting facility located near the City of Vernon which is 46 km away from KPPC. The by-product of the composting facility is Ogogrow™ which is sold as soil amendment.

The City also operates Glenmore Landfill. The leachate (liquid that drains from landfill) has been collected and pumped to the City sewer system for several years. In recent years, City has installed perforated piping in the landfill pile to allow for circulation of the leachate to increase the moisture content of the pile and accelerate the decomposition of the organic solid waste. Perforated pipes are also used to collect the methane gas generated within the landfill.

The composting facility has limited capacity and KPPC have to send the extra biosolids to the landfill occasionally when conditions are not ideal (mostly during the cold months of the year). Although anaerobic digestion (conversion of biosolids to methane and organic rich fertilizer in an oxygen free bioreactor) is an attractive alternative to compost biosolids, the City has not pursued this method for two principal reasons. First, the treatment plant has a limited space for expansion and is contained by adjacent development. In addition, there is a concern that the potential odour from anaerobic digesters may affect nearby residents. Therefore the City continues composting of its biosolids.

In recent years, with the alignment of BC's Energy Plan for reducing greenhouse emissions and for the goal of obtaining energy self-sufficiency by 2020 (The BC Energy Plan, 2010), the City has begun looking for alternative biosolids disposal options. The option under consideration in this study is the implementation of an anaerobic digester at the Glenmore Landfill instead of Kelowna's WWTP (Figure 1.2). Under this scenario, dewatered biosolids would be transported for 15 km from the WWTP to the Glenmore Landfill for anaerobic digestion. Methane recovered from the biosolids can be connected and utilized as part of landfill biogas system for electricity generation. The digester would achieve 35-55% organic removal efficiencies depending on the operating conditions (assessed experimentally as part of this thesis). In general, longer sludge retention time (SRT) and under-loading of the digester enables stable operation, but it results in larger reactor volume, low productivity, and therefore low economic profit. On the other hand, increased organic loading (corresponding to shorter SRTs) increases biogas production rate but can lead to overloading, extended recovery times, consequent loss of biogas production, and significant restart expenses (Boe, 2006). Therefore determination of an optimum SRT and organic loading rate is crucial for a healthy anaerobic digestion operation. In this study, the performance of a potential full-scale anaerobic digester for Kelowna biosolids is simulated in bench-scale anaerobic digesters under different operating conditions (i.e., digester temperature, organic loading and SRT) to optimize the removal efficiency and biogas potential. Furthermore, in order to enhance the rate limiting step of hydrolysis and reduce the digester volume requirement, the effects of thermal pretreatments on bench-scale digesters utilizing Kelowna biosolids are studied.

The novelty, in this study, lies in the ability to compare two different thermal pretreatments (microwave irradiation and conventional heating) under <u>identical heating profiles</u> at <u>above and below boiling temperatures</u>. Although previous studies intended to compare the conventional and microwave heating for enhanced biogas production, these studies could not be performed under the identical heating rates over a wide temperature range due to the nature of heating equipment used. In this study, a custom pressure vessel was built for conventional heating. This pressure vessel was able to achieve identical pretreatment temperatures (80, 120 and 160^{o}C) at identical heating rates (7.5^{o}C/min) to the reference vessel of a programmable MW unit able to operate under pressure. Therefore, for the first time, this set-up has allowed for a systematic comparison of the thermal and athermal effects of the electromagnetic pretreatments at both under and above boiling temperatures. The knowledge gained in this study fills an important gap in advanced anaerobic digestion field.

1.3 Objectives

The main objective of this project is to assess the performance of a potential anaerobic digester, located at Glenmore landfill and utilizing Kelowna biosolids at bench-scale, and to investigate the effect of thermal hydrolysis of municipal biosolids prior to digestion. The effects of microwave and conventional heating pretreatments at different temperatures (below and above boiling point) were studied systematically by investigating:

1. Biosolids particulate chemical oxygen demand (COD) solubilization and mineralization
2. Biosolids biopolymers (protein, sugar and humic acid) solubilization
3. Mesophilic and thermophilic anaerobic digestion of pretreated and untreated biosolids at different sludge retention times (20, 10 and 5 days) to evaluate:
    - Organic removal efficiencies
    - Biogas production and methane recovery
    - Net energy generation assessment
    - Volatile fatty acids accumulation and ammonia inhibition
    - Coliform and metal content of digested biosolids (digestate) to assess fertilizer reuse.

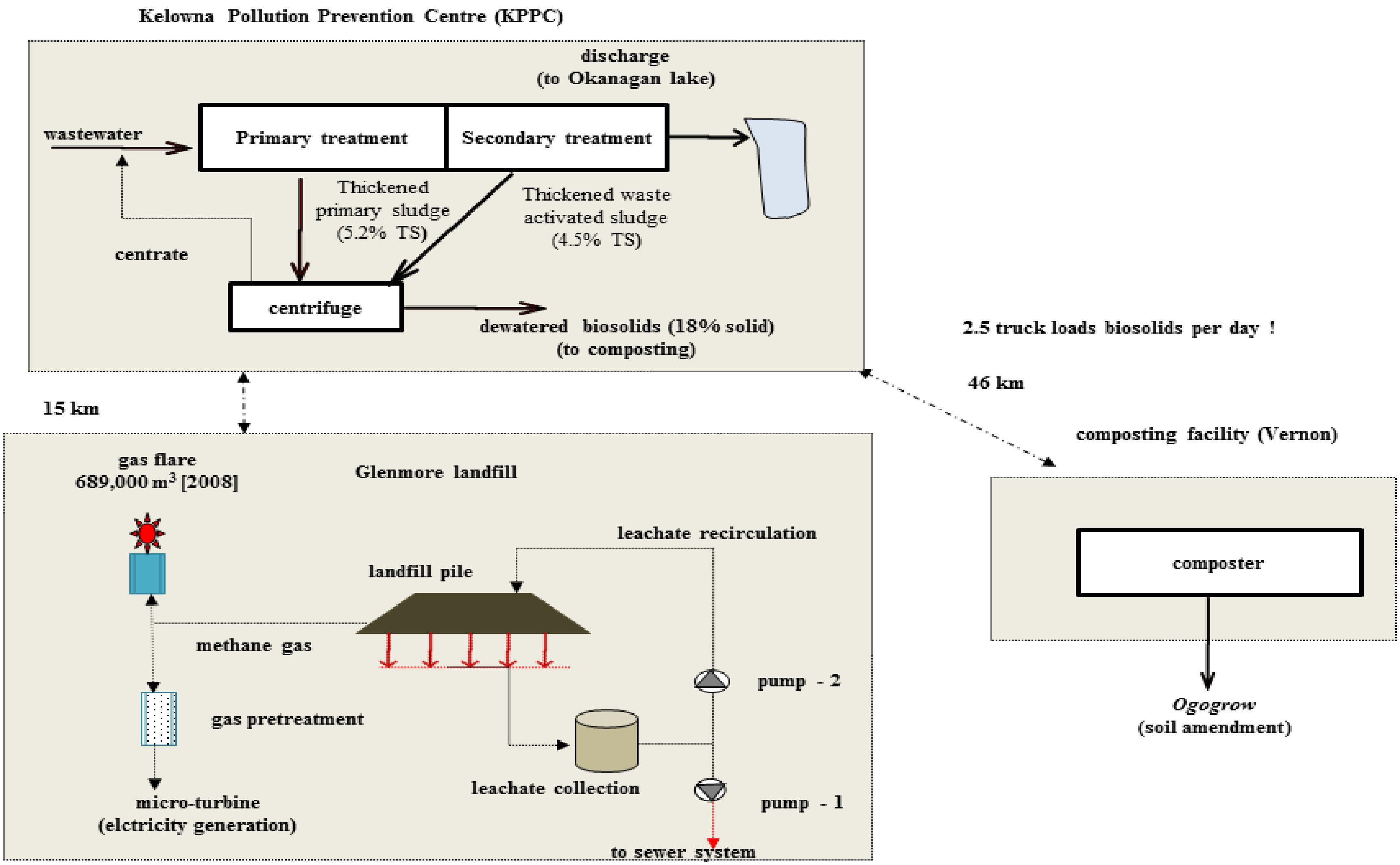

Figure 1.1 Diagram of current waste disposal process

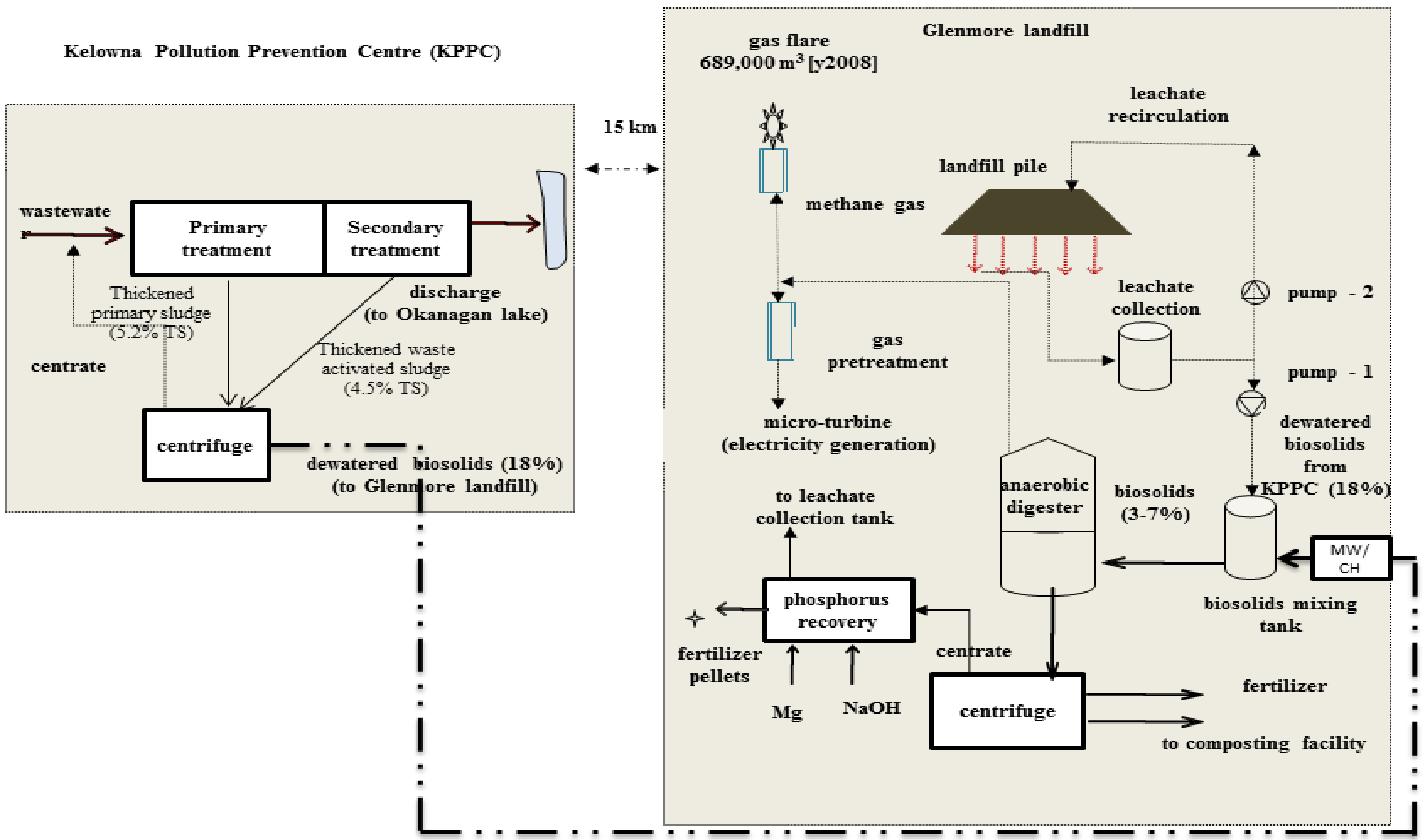

Figure 1.2 Diagram of proposed biosolids disposal process involved anaerobic digester (MW: microwave, CH: conventional heating)

1.4 Thesis outline

This thesis is organized into five chapters. The first chapter, presented above, was a brief introduction to anaerobic digestion of municipal biosolids, background and motivation and objectives of the study. The second chapter provides an overview about wastewater treatment, sludge features, thermal hydrolysis and anaerobic digestion. Materials and methods are explained in Chapter 3. Equipment and instrumentation used in this study, characterization methods and experimental procedures are discussed in this chapter. Chapter 4 presents the results and discussion. The experimental data from lab-scale digesters are justified and compared with the results presented in the literature. Finally, Chapter 5 concludes the thesis with a summary of the results obtained in this study, as well as recommendations for future work.

Chapter 2 Literature Review

2.1 Introduction

New technologies in wastewater treatment are being sought to pursuit a sustainable and healthy society. Treatment of wastewater produces different organic and inorganic residuals. One of the residuals is commonly termed as “waste sludge”. This sludge must be disposed to the environment. Although, sludge is usually semi-solid, pathogenic and putrid, it has considerable amount of organics and nutrients that can be used beneficially.

Although many methods are available for sludge treatment, most of them are expensive and suffer from lack of efficiency. The common goals of different sludge treatment methods are to dewater the raw waste sludge, transform it into a relatively stable residue, and condition the residue to meet disposal acceptance regulations. Therefore sludge treatment generally consists of thermal, chemical or biological stabilization, pathogen removal, odour/putrefaction reduction and volume reduction.

Due to biogas production, which can reduce the cost of treatment, anaerobic digestion of waste sludge is drawing more attention compared to various sludge treatment methods. In recent years, anaerobic digestion process has become a major part of modern WWTPs. Also, anaerobic digestion yields less sludge volume compared to aerobic or chemical stabilization due to slow growth rate of anaerobic microorganisms. Sludge volume reduction proceeds disposal and is achieved through dewatering of digestate.

Anaerobic digestion process consists of three phases: hydrolysis, acidogenesis, and methanogenesis. Hydrolysis is the rate limiting step (Bougrier et al., 2005) and results in longer retention time, and therefore require larger reactors. Pretreatment methods, applied to waste sludge prior to anaerobic digestion, have recently been used to accelerate the hydrolysis and improve the degradability of the waste materials being fed to the digesters. These pretreatment methods can be categorized under physical, biological and chemical sludge pretreatment with examples of mechanical, thermal, thermo-chemical, thermo-mechanical, ultrasound, chemical oxidation, enzymatic, and electrolysis. Among these different pretreatment studies, thermal pretreatments seem to achieve higher improvements in both biogas production as well as dewaterability of the digested sludge. However, issues around the specific energy required to achieve similar levels of improvement with different methods are not well emphasized or investigated extensively.

In recent years, microwave pretreatment has also gained interest as an attractive alternative to conventional heating due to much faster heating for the samples with high organic content. Many researchers have postulated that due to this advantage, microwave heating should also be more energy efficient. However, there is lack of information from controlled studies conducted with same waste sludge with identical heating profiles (above and below sample boiling points) achieved with conventional and microwave heating systems. Therefore this study focused on the assessment of thermal pretreatments (conventional heating and microwave irradiation) to enhance hydrolysis of waste sludges before anaerobic digestion at modern WWTPs. A review of research conducted on the subject is presented. Emphasis is put on the impact of pretreatment on sludge volume reduction, potential biogas (renewable energy) production, the resulting sludge properties, and their application at industrial scale.

2.2 Wastewater treatment

Wastewater contains a high load of dissolved and suspended organics which are mostly reported as biochemical oxygen demand (BOD) or COD, inorganic sediments and minerals (nitrogen, phosphorous and sulphur compounds) and pathogenic microorganisms. In addition, heavy metals exist in wastewater generated by industries are well known for toxic and carcinogenic effects to living organisms when discharged to environment without treatment. Wastewater treatment systems are designed to reduce the adverse effects of these constituents. Treatment removes solids in wastewater and change the decomposition of highly complex, putrescible, organic solids to mineral or relatively stable organic solids (Sonune and Ghate, 2004).

Municipal (domestic) and industrial wastewaters are two main categories of wastewaters. Wastewaters differ greatly, so do their treatment methods. Municipal wastewater treatment can be classified into three steps: 1- Primary treatment, i.e., grit removal, screening, grinding, and primary sedimentation. 2- Secondary treatment, which entails oxidation of dissolved organic matter by means of using biologically active sludge. 3- Tertiary treatment, in which advanced biological methods of nitrogen removal as well as chemical and physical methods such as granular filtration and activated carbon absorption are employed.

Primary and secondary treatment removes the majority of the BOD and suspended solids found in wastewaters. Figure 2.1 shows a typical WWTP with primary and secondary treatment processes. The main goal of the primary treatment is to remove mainly inorganic materials, i.e. sand, silt, rags that can damage the equipment and also settle in the pipes and basins prior to secondary treatment. During primary treatment, while no attempt is deliberately made to remove oxygen demanding or organic pollutants, some of the BOD is removed as a result of solid removal. Raw primary sludge (PS) that can settle at the bottom of the primary clarifier is highly putrescible with 97% to 99% water content, along with high concentration of pathogenic microorganisms. These characteristics of PS make the further handling difficult. This sludge is often digested (aerobically or anaerobically) to make it less unpleasant and is known as primary digested sludge. Figure 2.1 also illustrates the secondary wastewater treatment processes designed to remove BOD as well as remaining solids. In a typical activated sludge process, a mixed culture of microorganisms (mixed liquor suspended solids or MLSS) degrades the oxygen demanding materials in the aeration tank (Figure 2.1). Air is driven into mixed liquor by air diffusers, surface aerators or by other means such as aspirators. The MLSS in the aeration tank is settled out in the secondary clarifier and returned to the head of the aeration system to maintain the concentration of the microorganisms at the required level.

The amount of microorganisms generated in the activated sludge process exceeds the amount required by the system and some of the excess amount must be disposed. This residue, comprised of excess microbial cells and extracellular polymeric compounds, is called waste activated sludge (WAS). In a typical WWTP, WAS is often mixed with PS and sent to the anaerobic digestion for its abilities to further transform organic matter into biogas. The effluent of the digester is called mixed digested sludge or digestate and usually dewatered before disposal (Tchobanoglous et al., 2003).

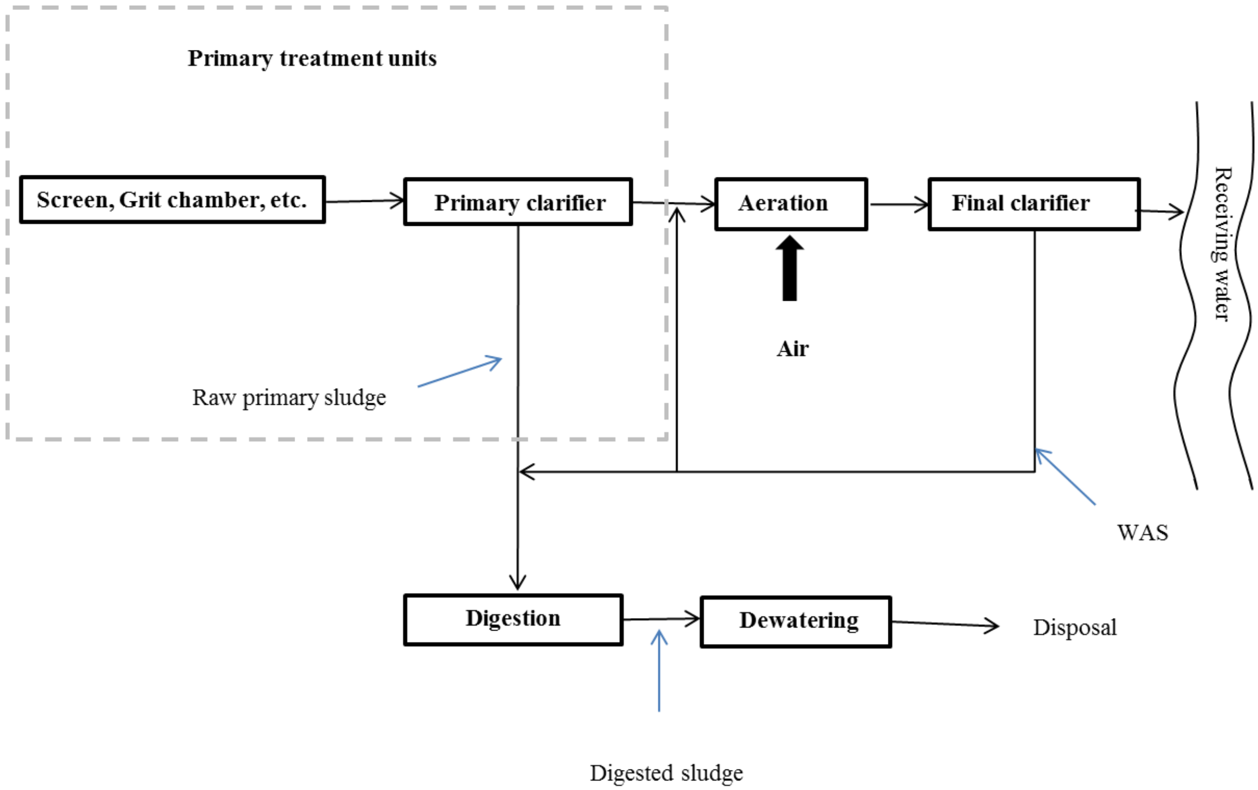

Figure 2.1 Typical primary and secondary wastewater treatment processes (WAS: waste activated sludge)

In recent years the removal of nutrients such as nitrogen and phosphorous has been considered as an important issue and there are stringent regulations for their quantities in the effluent of WWTPs. Nutrient removal systems, are also called tertiary or advanced treatments, are now being used globally. Biological aerobic and anoxic processes are used to convert nitrogenous materials into nitrogen gas. Phosphorous in the wastewater stimulates algal and aquatic growth and interferes with coagulation and lime/soda softening. Phosphorous can be removed from wastewater by phosphorus accumulating organisms (PAOs) and then removed with WAS. Another means of removing nutrient is addition of chemicals such as iron or aluminum salts (Sanin et al., 2011).

2.3 Waste sludge characteristics

The waste sludge production by municipal WWTPs is increasing worldwide in proportion to population growth. Sludge treatment and management is a complex and challenging problem for environmental engineers and researchers. The characteristics of sludge depend heavily on the type of sludge. Each type of sludge has certain physical, chemical and biological properties.

Primary sludge consists of settleable organic and inorganic matter. Solids are coarser and contain pathogenic organisms of human and animal faeces. It is readily degradable and biogas production and dewaterability following digestion is generally not problematic (Kropp and Ditchtl, 2001). Secondary sludge or WAS consists of a variety of organic and inorganic material, wound up in extracellular polymeric substances (EPS). EPS contain lipids, polysaccharides and proteins. They are hydrated, and capable of adsorbing significant amounts of organic molecules and heavy metals (Dewil et al., 2006). The biodegradability and dewaterability of WAS are highly dependent on the sludge age as well as design/operational features of the biological treatment process where sludge is generated. As WAS contains large quantities of both free and bound water, it is more difficult to dewater (Yin et al., 2004).

2.3.1 Physical features of sludge

The physical features of sludge are used to predict the performance of the sludge in treatment operations such as dewatering, conditioning and settlement. Physical features include particle size distribution, density, water distribution, rheology and viscosity. Sludge volume index (SVI) and the zone settling rate (ZSR) or zone settling velocity (ZSV) describe settling properties. The capillary suction time (CST), the specific filter resistance (SFR) and the zeta potential are used to describe the dewaterability of the sludge (Yin et al., 2004).

Dewatered sludge is much easier and cheaper to handle. Dewatering of the sludge increases the calorific value for incineration and also makes it suitable for land application. Dewatering can also reduce the odour of the sludge (Tchobanoglous et al., 2003). The distribution of water in sludge can be categorised into four groups (Yin et al, 2004; Kropp & Dichtl, 2001): free water: this water moves freely and it is unaffected by the forces among the particles. Free water can be removed by filtration, centrifugation or other mechanical means. Interstitial water: this water is trapped within the flocs and can be removed when the floc is broken. Surface water: it covers the surface of particles and bounded by adhesive and absorptive forces; therefore cannot be removed by mechanical forces. Intracellular or bound water: it has chemical bounds to particles and can only be released by thermo-chemical destruction of particles.

Capillary suction time (CST) is widely used in the laboratory to measure the dewaterability. It is based on the ease of filtration after coagulant addition. It is a simple, fast and inexpensive method to compare the effects of different agents and dosages on dewaterability of sludge (Scholz, 2005). In this method, two concentric electrodes placed at a diameter d_1 and d_2 from a cylindrical sludge sample vessel. The CST is the time taken for water to travel from the inner electrode to the outer electrode (Yin et al., 2004). Digested sludge and activated sludge are much harder to dewater than raw sludge and mineral sludge. Yin et al. (2004) reported the mean CST values of different types of sludge as follows: digested sludge > activated sludge > raw sludge > mineral sludge. The sludge with CST less than 20 seconds is known as a good dewaterable sludge. The main critique of CST method is filter clogging which makes the results un-representative of sludge dewaterability (Pino-Jelcic et al., 2006). In addition, as CST is a function of total solids (TS) concentration of samples, the results need to be normalized according to the TS.

2.3.2 Chemical features of sludge

Chemical features such as pH, alkalinity and VFAs are used to evaluate the digestibility of sludge. Nutrients, such as phosphorous, nitrogen, potassium and toxicity level, most related to heavy metals and toxic organics, are important parameters in sludge treatment engineering (Kropp and Dichtl, 2001). The pH of sludge is a good indicator of digestion conditions. Typical pH values for different types of sludge are listed in Table 2.1.

Volatile fatty acids are important early intermediates of biogas production. Acetic and propionic acids are most often used to characterize VFAs. Nutrients levels of sludge are also important when land applications of sludges are considered. Sewage sludge usually has high amount of nitrogen (N) and phosphorous (P) and low amounts of potassium (Kropp and Dichtl, 2001). Table 2.2 shows the typical values of N and P in different types of sludge.

Table 2.1 pH values for different types of sludge (Tchobanoglous et al., 2003)

Sludge type	Typical pH
Sewage sludge	7.0
Primary sludge	6.0
Digested sludge	7.0- 7.5
Sludge in methanogenic phase	7.0-7.5
Sludge in acidogenic phase	6.0

Table 2.2 Nitrogen (N) and phosphorous (P) levels in sludge (Tchobanoglous et al., 2003)

Nutrient	Untreated primary sludge	Untreated WAS
N (% of TS)	1.5-4	2.4-5
P (% of TS)	0.8-2.8	2.8-11

2.3.3 Biological features of sludge

Biological features describe the biological stability and pathogenic characteristics of the sludge. These features depend heavily on the type and age of the sludge. The bacterial shape and type present in the sludge is sometimes important and should be monitored for applications such as dewatering. Biological stability is a measure of the remaining potential of biological activity and is linked to COD, BOD and volatile (organic) fraction of sludge. Sludge stabilization is done by processes such as composting, anaerobic digestion, aerobic digestion and alkaline (lime) stabilization. Sludge from anaerobic digestion is very stable and post-biogas production is very low (Kropp and Dichtl, 2001). The degree of solubilization (soluble COD or SCOD) is an important parameter in assessment of pretreatments before anaerobic digestion process. It is often used as monitoring parameter for treatments involving cell lysis.

A reduction of pathogens is often coupled with a reduction of odours and potential for putrefaction. Complete pasteurisation of sludge is achieved by drying sludge at temperatures more than 70˚C. The ideal result is to obtain Class A sludge. Class A sludge has a coliform density less than 1000 most probable number (MPN) per gram of total dried solids (1000 MPN/g TS), or *Salmonella sp*. bacteria less than 3 MPN/4 g TS (U.S.EPA, 1999b). Pathogenic microorganisms are weakened or killed during anaerobic digestion depending on the reaction time and temperature. Composting reduces the pathogens due to the temperature and microbial competition in the process (Kropp and Dichtl, 2001).

2.4 Anaerobic digestion

In recent years a worldwide movement has started towards the reuse of the energy and organic materials (Spinosa and Vesilind, 2001). Among different types of sludge treatment, anaerobic digestion is the favoured stabilisation method due to its lower cost, lower energy foot print and production of biogas (Apples et al., 2008). The flow chart of the sludge processing steps is presented in Figure 2.2. The benefit of anaerobic digestion is that the volume of the biosolids is reduced by conversion to valuable biogas and dewaterability and the quality of the final product are improved.

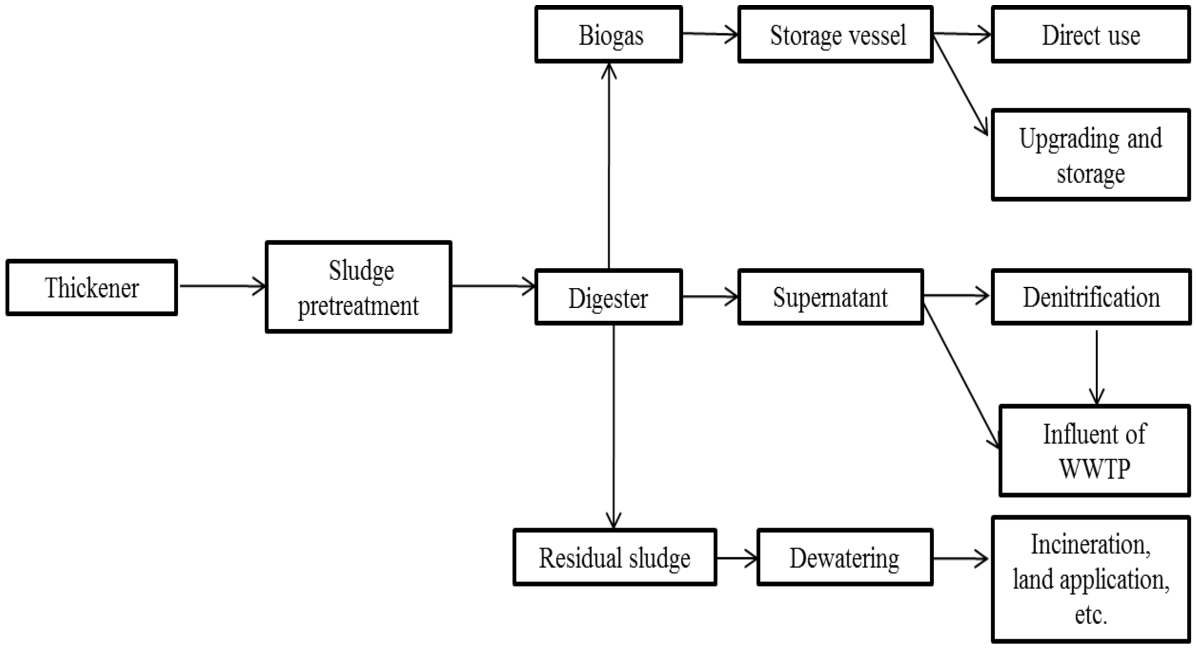

Figure 2.2 Flow chart of sludge processing incorporating an anaerobic digester

Anaerobic digestion of organic material follows these steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis as shown in Figure 2.3. Anaerobic digestion requires strict anaerobic condition to transform organic material into mostly methane (CH_4) and carbon dioxide (CO_2). Hydrolysis is generally recognised as the rate limiting step in complex anaerobic digestion process (Tiehm et al., 2001; Vavilin et al., 2002). During hydrolysis, high molecular weight organics, such as proteins, polysaccharides, lipids and nucleic acids, turn into low molecular weight soluble organics (e.g. amino acids and fatty acids). The hydrolysed components split during acidogenesis. Higher organic acids and alcohols produced are transformed into VFAs by acid producing bacteria in the next step.

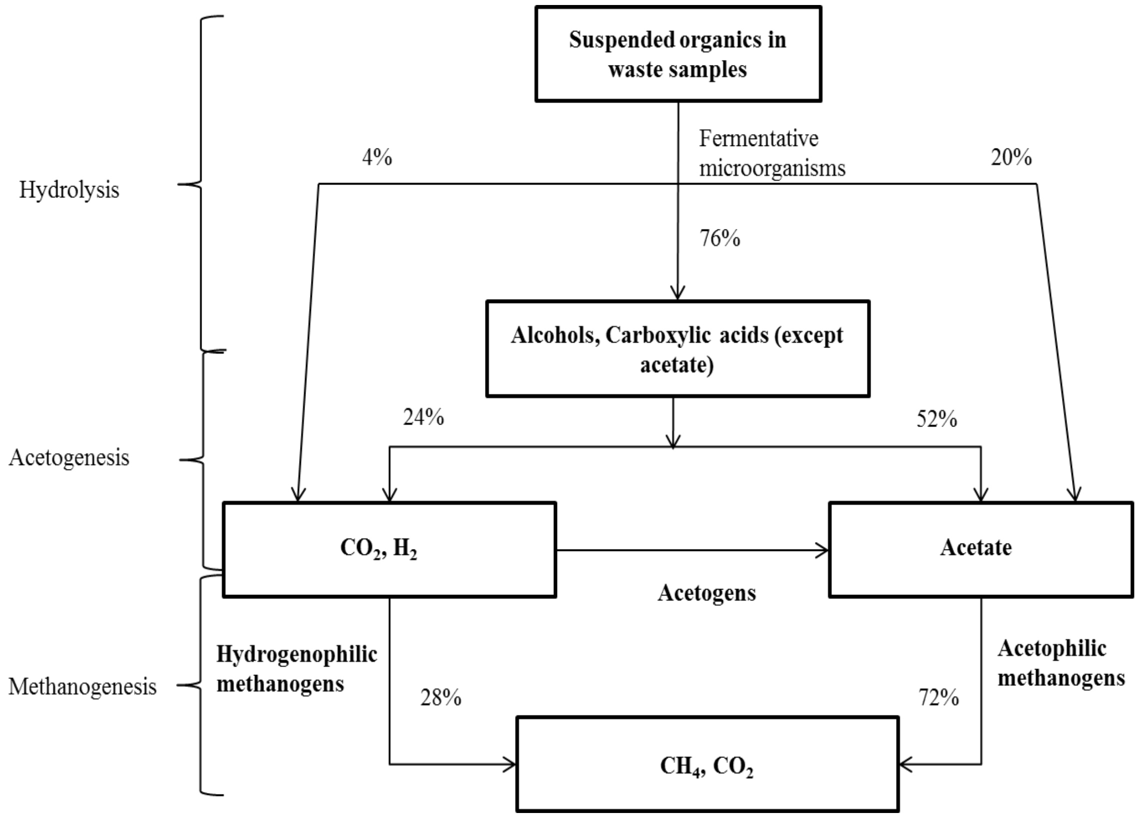

Figure 2.3 Multi-step nature of anaerobic digestion (Droste, 1997)

Volatile fatty acids are transformed into acetate, CO_2 and H_2O in the acetogenesis phase of anaerobic digestion. This step is followed by methanogenesis phase in which acetate splits and H_2O and CO_2 are utilised to produce methane (Mechichi and Sayadi, 2005). High concentration of VFAs can be toxic to microorganisms, especially to methanogens. High VFA concentrations are result of variation in temperature, high organic loading (Kropp and Dichtl, 2001), and presence of toxic compounds (Mechichi and Sayadi, 2005). Volatile fatty acid accumulation causes inhibitory effects on VFA degradation and subsequent drop in pH (<6) and biogas production (Siegert and Bank, 2005). During digestion, alkalinity of several hundred mg $CaCO_3$/L higher than the amount of VFA is generally an indication that the digestion process is not endangered (Kropp and Dichtl, 2001). At the third stage, acetogenic bacteria produce acetic acid as well as CO_2 and H_2O. This conversion is controlled to a large extent by the partial pressure of H_2 in the mixture. When hydrogen is formed, it represents a gaseous product which escapes from the medium and causing a reduction in the energy content and thus the COD of the liquid. The final stage of methanogenesis produces methane by two groups of methanogenic bacteria: the first group splits acetate into methane and carbon dioxide and the second group uses hydrogen as electron donor and carbon dioxide as acceptor to produce methane (Droste, 1997).

In the last decade, emerging pretreatment methods have been used to enhance the rate limiting hydrolysis step and accelerate the digestion. All pretreatment methods result in partial or complete lysis of microorganisms and disintegration of flocs. They release and solubilize intracellular material into the water phase and help transformation of refractory organic materials into biodegradable species. Materials become more bio-available after pretreatment, and biogas generation increases. Accelerated degradation rate of digestion results in reduced volume requirement of the digester and capital cost for a given organic load (Carrere et al., 2010).

2.5 Environmental parameters affecting digestion

Characteristics of the microorganisms and features of their metabolic pathway must be considered in the design and operation of anaerobic digestion. Each bacterial group has its own optimum working conditions. They are sensitive to several physical and chemical process parameters, such as pH, alkalinity, digestion retention time, digester temperature, concentration of free ammonia, hydrogen, and VFAs, etc. several parameters can be inhibiting factors to some or all bacteria employed in anaerobic digestion for biogas production (Weemaes et al., 1998).

2.5.1 Temperature

Temperature influences the growth rate and metabolism of bacterial population in the anaerobic digestion process. Reaction rate increases with an increase in digestion temperature. It is more important to maintain a stable operating condition in a digester. Fluctuation in temperature highly affects the methanogenic bacteria. There are two optimal ranges for process operation to produce methane: 30-40^{o}C (mesophilic range) and 50-60^{o}C (thermophilic range). Production rate of methane approximately doubles for each 10^{o}C increase in the mesophilic range (Droste, 1997). At thermophilic conditions, increase of temperature enhances the death rate of pathogens, which is an advantage when digested material is utilized as soil amendment or fertilizer. On the other hand, it increases the free ammonia fraction, which has inhibiting effect on methanogenic microorganisms. Furthermore, increase in VFA formation can make the process more prone to inhibition (Boe, 2006). Therefore, control of the temperature is more essential in thermophilic digesters compared to mesophilic ones.

2.5.2 pH

The most important parameter in the anaerobic digestion process is pH. Each group of microorganisms has different optimum pH range, but neutral pH (~7) is the optimum value for the entire bacterial population (Droste, 1997). Methanogenic bacteria have an optimum pH of 6.5 -7.2 (Boe, 2006). The fermentative bacteria are less sensitive and can function in a wider range of pH between 4.0 and 8.5. At low pH, the main products are acetic and butyric acid and at pH>7 acetic and propionic acid are produced (Boe, 2006). VFAs tend to reduce the pH. There must be enough buffering capacity or excess alkalinity in the system to protect it against the accumulation of excess VFAs. The system pH is controlled by CO_2 concentration in the gas phase, and the alkalinity and HCO_3 of the liquid phase. The alkalinity requirement varies with waste and process types. A constant pH leads to stability of the system (Droste. 1997). The molar ratio of (1.4/1) of bicarbonate/VFA or buffering capacity of 70 meq $CaCO_3$/L should be maintained to have a stable digestion process (Apples et al., 2008).

2.5.3 Ammonia

Free ammonia (NH_3) can inhibit the anaerobic digestion process and is considered toxic to methanogenic bacteria. Ammonia is a weak base and dissociates in water to form ammonium (NH_4^+) and hydroxyl ion. The amount of free ammonia is a function of temperature and pH (Tchobanoglous, 2003). Free ammonia is more toxic than ammonium ion and is more common at high pH ranges. The toxicity threshold for free ammonia has been reported to be 100 mg/L but with acclimatization time, the threshold may increase to 500 mg/L (Tchobanoglous, 2003). Ammonium toxicity is reported in the range of 1,500-3,000 mg/L at pH>7.4 and 3,000 mg/L is reported to be toxic at any pH (Tchobanoglous, 2003). Waste with high protein can produce more ammonia. Usually the protein level in the municipal waste sludge is not high enough to cause ammonia toxicity. Elevated ammonia level increases the alkalinity. Most often, a portion of the effluent from digester is recycled to add alkalinity to the influent and maintain the buffering capacity of the digester (Droste, 1997).

2.5.4 Sludge retention time (SRT)

The sludge retention time (SRT) is the average time that a solid particle stays in the reactor. In a suspended growth reactor without recycle, the hydraulic retention time (HRT) and SRT are the same. An increase in the SRT increases the extent of reactions. In order to maintain the steady state condition and avoid the process failure, cell growth must compensate the bacterial fraction that was withdrawn from the anaerobic digesters. Laboratory studies showed that SRT less than 5 days resulted in washout of methanogenic bacteria (Droste, 1997). Accumulation and unsteady digestion of VFAs were observed for SRT of 5-8 days. An SRT of 10 days was suggested as the shortest duration for anaerobic digestion at mesophilic conditions to prevent washout of bacterial populations (Apples et al., 2008). The peak hydraulic load should be taken into account for selecting design SRT. All biological systems require a safety factor of 3-20 times the minimum SRT for successful operation (Droste, 1997).

2.6 Pretreatments for advanced anaerobic digestion

The main goal of sludge pretreatment is to change the physical or chemical properties of sludge to accelerate the subsequent anaerobic digestion and enhance dewatering steps. Pretreatment units can be located at various places in a treatment plant to meet different needs. When a pretreatment is combined with the aeration tank in a recirculation loop or after thickening, the objective is either the volume minimisation or production of more degradable material (Pérez- Elvira et al., 2006). Faster kinetics allows for the same performance in a smaller digester and decrease the retention time requirement. The PS of municipal WWTP is usually easily biodegradable and therefore pretreatment is less effective (Ge et al, 2010). During hydrolysis, cell walls are fractured and EPS are degraded to more soluble organics and they are consumed by acidogenic microorganisms. This step has a significant role in digestion of secondary sludge or WAS, because most of the organic constituent of WAS are cells. Cell walls contain peptide chains and glycan, which are resistant to anaerobic biodegradation (Weemaes and Verstreate, 1998). Therefore, hydrolysis has been identified as the rate limiting step in anaerobic digestion (Tiehm et al, 2001).

Pretreatment methods disintegrate floc structures by disrupting the polymeric and cationic network and disrupt cell walls which results in cell lysis or disintegration or sludge cells. Various thermal, mechanical and chemical pretreatment methods are being used to enhance the performance of anaerobic digestion, biogas production and subsequent dewatering stage. In the following sections, thermal pretreatment methods including conventional heating and microwave irradiation are being reviewed along with their working mechanisms and potentials to be used for full-scale applications.

2.7 Thermal pretreatment

Thermal pretreatment of sludge is one of the most common pretreatment methods used for advanced anaerobic digestion. Thermal energy allows for degradation of gel structure of sludge and releases the linked water and improves the anaerobic digester performance. This method was first used to enhance the dewaterability of sludge (Skidas et al., 2005).

Many studies reported that optimal operating conditions for the process are heating at 160-180^{o}C for 30-60 min (Bougrier et al, 2008; Tanaka et al., 1997). The pressures associated with these temperatures are in the range of 600-2500 kPa (Pinnekamp et al, 1989). In general, increase of solubilization of sludge COD has a linear correlation with methane production yield (Carrere et al., 2008). The effect on methane production depends on sludge type (Carrere et al., 2008); better improvement was observed in with thermal hydrolysis of WAS (Eskicioglu et al., 2008a). Although pretreatment increased solubilization at temperatures above 150^{o}C, it did not result in more methane production (Dwyer et al., 2008). Maillard reactions occur at excessively high temperature (170-190^{o}C). During these reactions, carbohydrates and amino acids transform to melanoidins which are difficult to degrade (Bougrier et al., 2008). They increase the color from the anaerobic digesters and the final effluent which reduces the efficiency of UV disinfection before final discharge (Dwyer et al., 2008). The pretreatment time has a little effect on biodegradation at high temperature range (Neyens and Baeyens, 2003). A fast thermal pretreatment was studied by Dohanyos et al. (2004) at 170^{o}C only for 60 seconds and observed 49% increase in biogas production of batch anaerobic digesters after 20 days. However at temperatures less than the boiling point (70^{o}C) led to less increase in biogas production (Bougrier et al, 2008). Also, non-methanogenic biological activity was observed during the low temperature pretreatment step due to increased hydrogen percentage (Gavala et al., 2003).

In addition to the increased methane yield, thermal pretreatments sanitize the sludge and remove the pathogenic vectors. They also reduce the sludge viscosity and enhance the handling as it is easier to pump the waste sludge. Another advantage is that the energy requirement of the process can be covered by excess biogas production. The disadvantages of the thermal pretreatment are increased ammonia inhibition, final effluent color and poorer centrifuge or press solid capture due to the increase in fine particles (Batstone et al., 2010).

Two common methods for thermal pretreatment are conventional heating and microwave irradiation. The thermal treatments can utilize electrical and heat energy produced from biogas. The amounts of produced energy via biogas are usually in excess of the treatment plant energy requirements (Carrere et al., 2010).

2.7.1 Conventional heating

Conventional heating treatments involve heating of sludge at high temperature under pressure for a short period of time. Thermal treatments are capable of changing the physical, chemical and biological characteristics of sludge. These alterations are independent of reaction time and heavily depend on the treatment temperature (Valo et al., 2004). Heat can disrupt the gel like structure of the flocs, but the solids which have lower affinity to water coagulate (Tchobanoglous et al., 2003).

Numerous studies were conducted with conventional heating pretreatments for enhanced anaerobic digestion. Some of the findings are summarized in Table 2.3. Bougrier et al. (2006) reported that the average particle size of sludge increased from 36.3 µm to 76.8 µm and 77.1 µm after heating at 170^{o}C and 190^{o}C, respectively. At these temperatures, the viscosity of sludge decreased and it behaved more like a Newtonian fluid. Valo et al. (2004) showed that thermal treatment of WAS at 130^{o}C, 150^{o}C and 170^{o}C led to high solubilization of organic matters, but it did not affect the mineral content of sludge. In another study, thermal treatment of thickened WAS (TWAS) at 96^{o}C caused considerable increase of proteins, sugars, VFAs and COD in the soluble phase (Eskicioglu et al., 2006). Formation of acidic compounds at high temperatures (170^{o}C and 190^{o}C) reduced the pH value of sludge to 5.8 (Bougrier et al., 2006b). Eskicioglu et al. (2006) reported that heating at 96^{o}C increased the acetic acid content of TWAS from 0 to 778 mg/L. At high temperatures, pressure difference causes the cell destruction. This leads to sludge sterilization and potential agricultural use and land application of sludge (Bougrier et al., 2006b).

2.7.1.1 Full scale conventional heating for waste sludge treatment

One of the first full-scale thermal pretreatment plants was implemented in UK in 1939. The process heated the raw sludge cake to 185^{o}C for 30 minutes (Neyens and Baeyens, 2003). However, thermal treatments have been widely used only since 1970 (Brook, 1970). In some full-scale operations, thermal pretreatment is combined with chemical or mechanical disintegration methods to accelerate the hydrolysis further.

Cambi^{TM} (Kepp et al., 2000) and BioTHELYS® (Chauzy et al., 2000) are two commercial, more recent processes based on thermal hydrolysis. Both processes consist of vapor injection at 150-180^{o}C for 30-60 min. The first Cambi process was implemented in a WWTP in Norway in 1995. The energy balance showed that thermal hydrolysis could increase the electricity production by 20% (Kepp et al., 2000). BioTHELYS is a similar thermal treatment sold by Kruger Inc. which is a subsidiary of Veolia Water (Chauzy et al., 2000).

Table 2.3 Thermal pretreatment studies

Reference	Treatment condition	Sludge type	Comments
Tanaka et al. (1997)	180°C for 1 hr in an autoclave	Mixture of domestic and industrial WAS (8,400 mg/L SS).	• 90% increase of methane production • VSS solubilization of 30%
Pinnekamp (1989)	120 - 220°C in an autoclave	Excess sludge/PS (sludge loading rate: 0.03 – 2.00 (kg BOD_5/kg MLSS.d)	• Maximum biogas production at 170°C • Positive correlation between the gas yield and pretreatment temperature
Bougrier et al. (2007)	135 - 190°C in a Zipperclave (autoclave with a PID temperature controller)	Thickened WAS (secondary sludge) collected from the municipal WWTP with 14.5 ± 0.7 gr/L total solid concentration	• 25% increase in methane production at 190°C
Valo et al. (2004)	170°C, samples were heated in a Zipperclave	WAS from WWTP with 90% urban and 10% wine wastewater loading and 17.1 gr/L total solid concentration	• 95% increase of TS reduction • 92% higher gas production
Bougrier et al. (2006a)	170 and 190°C, samples were heated in a Zipperclave	Municipal thickened WAS diluted to total solid concentration (TS) of 20 g/L.	• 40-45% COD solubilization • 51% decreased in biogas yield at 190°C • CST decreased from 151 s to 39 s and 29 s • Average particle size of sludge increased from 36.3 µm to 76.8 and 77.1 µm for 170 and 190°C • 51% decrease in organic solids

2.7.2 Microwave irradiation

Microwave (MW) treatment has been used widely in industrial, domestic and medical applications such as food pasteurisation, organic decomposition, sterilization of medical tools, polymerisation, dehydration, analyses and extraction (Pino-Jelcic et al., 2006; Wu, 2008). However, MW irradiation of sludge is a relatively new thermal pretreatment process and the applications of MW as remediation tool for treatment of soils, sludge and wastewater have been steadily growing (Nuchter et al., 2004). Several limitations such as the absence of sufficient data to quantify the dielectric properties of the treated sludge and technical difficulties in upgrading laboratory or pilot-scale processes to the industrial scale prevent MW technology from being widely employed in biosolids treatment (Nuchter et al., 2004; Wu, 2008).

2.7.2.1 Mechanism

In order to understand the reaction mechanisms and waste degradation pathways, it is necessary to be aware of the fundamentals of chemistry in MW. Microwaves (frequencies of 0.3–300 GHz and wave lengths of 1 m to 1 mm) lie between radio wave frequencies and infrared frequencies in the electromagnetic spectrum. Almost all of the MW ovens operate at 2.45 GHz due to the right penetration depth to interact laboratory scale samples.

The properties of substances being heated by MW can be quantified by two parameters:

- The dielectric constant: it shows the polarisation ability of polar molecules in the electromagnetic field.

- The dielectric loss factor: it shows the efficiency of substances in converting the electromagnetic energy into heat (Pino-Jelcic et al., 2006).

When a piece of material is exposed to MW irradiation, MWs can be absorbed, transmitted or reflected. If a material exhibits dielectric losses, the absorbed MW energy converts to heat in the oscillating electromagnetic field and increases the temperature. Solids, liquid and gases can interact with MW and be heated. MW is reflected from the surface of an electrical conductor (e.g. metals and graphite). It can penetrate good insulators (e.g. ceramics, quartz glass and porcelain) without absorption or heat losses (Bogdal and Prociak, 2007). The heating rate of the material under MW irradiation depends on the shape and size of the sample (Bogdal and Prociak, 2007).

2.7.2.1 Microwave pretreatment of sludge

Microwave treatment provides uniform and rapid heating to the sludge and alters many sludge properties. MW irradiation leads to a more treatable sludge in terms of degradability and dewatering. Several studies have been done on application of MW in sewage sludge treatment and stabilization (Wojciechowska, 2005; Kennedy et al., 2007; Eskicioglu at al. 2009; Toreci et al., 2010; Coelho et al, 2011; Saha et al.,2011; Mehdizadeh et al., 2012).

Some benefits and challenges of MW application in sludge processing are listed in Table 2.4. The most attractive results of MW treatment are COD solubilization and pathogen removal (Wong et al., 2006). Water is the primary component of sludge affected by MW. For sludge treatment application, the minimum temperature of 70^{o}C for 30 minutes or more reaches the near-pasteurization condition (Wong et al., 2006).

Microwave irradiation destructs the polymeric network of sludge and release intracellular and extra cellular materials into soluble phase (Eskicioglu et al. 2006). In the study by Wong et al. (2006), it was demonstrated that at temperatures above 120^{o}C, complete cell lysis occurred and heavy metals and nutrients are released into supernatant along with COD solubilization. Kennedy et al. (2007) found that pretreatment temperature in the range of 45-85^{o}C increased the COD solubility; however the sludge concentration (1-5% w/v) and MW intensity did not have a significant effect on particulate COD solubilization quantified by SCOD/TCOD ratios. Similarly, MW treatment of WAS at 37-60^{o}C significantly increased the COD solubilization (Pino-Jelcic et al., 2006). Level of improvement in solubilization and biodegradation depends on sludge type. Sludge characteristics influence the final pretreatment outcome and a general statement cannot be made about the effects of pretreatment.

In addition to improved solubilization, MW irradiation can improve the dewaterability of the sludge after anaerobic digestion process (Pino-Jelcic et al., 2006; Eskicioglu et al., 2007a). Significant COD solubilization after MW pretreatment reduces the TS of sludge. In general, the less TS value means the less CST which indicates faster dewaterability rate. However, Pino-Jelcic et al. (2006) observed that even specific or normalized CST (the CST divided by the TS value) improved after MW treatment. It was observed that quantitative improvement of dewaterability depended on the sludge type with a more significant effect noticed for MW irradiation of PS compared to mixed or digested sludges (Wojciechowska, 2005).

Table 2.4 Benefits and challenges of MW application in sludge processing (Mudhoo and Sharma, 2011)

Benefits	Challenges
• Volumetric and uniform heating (due to energy penetration) • Cost savings (time and energy, reduced floor spacing) • Increased biogas yield and solubilization • Short processing time	• Better understanding of MW fundamentals and modeling of MW – material interactions • Availability of affordable equipment and supporting technologies • Efficient transfer of MW energy to material or sample • Compatibility of MW process with the rest of process line.

Biogas production from anaerobic digesters fed by MW pretreated sludge was higher than conventionally heated sludge to the same pretreatment temperature of 63 ± 2^{o}C (Pino-Jelcic et al., 2006). Microwave acclimated inocula in an anaerobic process digesting pretreated WAS produced 16% more biogas compared to control at a pretreatment temperature of 96^{o}C (Eskicioglu et al., 2007b). Eskicioglu et al. (2007a) studied the cumulative biogas production of 54 batch anaerobic digesters in a multi-level factorial experimental design and concluded that biogas production was significantly affected by percentage of pretreated sludge, MW temperature and WAS concentration.

2.7.2.3 Full scale microwave irradiation for waste sludge treatment

Microwave irradiation is still very costly and difficult to implement at the full-scale for environmental engineering applications. MW heating technology includes difficulties associated with the scaling up of laboratory units to industrial capacities and a lack of fundamental data on material dielectric properties (Jones et al., 2002). Although full scale MWs have been developed by companies like ANSA technology and Thermathron for drying and disinfection purposes, MW technology will become commercialized for sludge pretreatment when it offers more advantage as compared with conventional heating. Nevertheless, the results obtained from continuous-flow digesters implied that MW at temperatures under the boiling point (100^{o}C at 1 atm) has a major potential to improve the biodegradability of WAS in full-scale continuous flow sludge digesters (Eskicioglu et al., 2007c).

2.7.4 Comparison of microwave and conventional pretreatment

Microwave heating methods are volumetric heating that gives rapid energy transfer to the material (Bogdal and Prociak, 2007). In conventional heating (CH), heat flow initiates from the surface of the material and the rate of heating depends on the material thermal properties and temperature differential. Eskicioglu et al. (2007c) pretreated WAS to 96^{o}C by MW and conventional heating to study the athermal effect of microwave. In a pretreatment range of 50–96^{o}C, both MW and CH WAS samples resulted in similar particulate chemical oxygen demand (COD) and biopolymer (protein and polysaccharide) solubilization and there was no noticeable MW athermal effect on the COD solubilization of WAS. However, in improved biogas production for MW samples over CH samples was observed in the same study. It was concluded that the MW athermal effect had a positive impact on the mesophilic anaerobic biodegradability of WAS (Eskicioglu et al., 2007c). It is due to polarization of macromolecules, and their alignment with the electromagnetic field poles that may cause the possible breakage of hydrogen bonds (Loupy, 2002; Eskicioglu et al., 2008b).

Despite of extensive development in thermal pretreatment of biosolids, a comprehensive comparison between MW and CH at wide range of temperatures (below and above boiling points) has not been done at the lab-scale due to lack of instrument. The intent of this research is to systemically compare CH and MW pretreatment with the aid of programmable pressure sealed vessel able to simulate a heating profile of a programmable MW unit.

Chapter 3 Materials and methods

3.1 Waste sludge and landfill leachate samples

Waste sludge samples were collected biweekly from the municipal WWTP in Kelowna (BC, Canada). At the WWTP, gravity thickened primary sludge (PS) and thickened waste activated sludge (WAS) by a dissolved air flotation (DAF) unit are mixed (40/60 percent by volume) before these streams are sent to a centrifuge as displayed in Figure 3.1. The sludge mixture has approximately 4.2 ± 0.5% and 17.5 ± 1% TS before and after centrifugation, respectively. In this study, dewatered sludge mixture called dewatered sludge cake (DWSC) was used during thermal pretreatments in order to make the heating more energy efficient. Previous studies indicated that heating concentrated sludge samples minimizes the input energy requirement per dry weight to achieve desired temperatures due to minimized loss to heat the water (Tang et al, 2010; Saha et al., 2011). Upon thermal pretreatments, DWSC samples with 17.5% TS were diluted to 3.5% TS with landfill leachate and tap water (3:5 ratio in the liquid mixture) to lower the solids loading to a level of a typical anaerobic digester. City of Kelowna has excess landfill leachate which is currently being pumped to the Kelowna WWTP. The purpose of using landfill leachate in this study was to evaluate whether a potential digester located near the Glenmore landfill can utilize this waste stream along with dewatered biosolids (as previously displayed in Figure 1.2) without any inhibitory effect on the acid and methane formers in the digester.

3.2 Inocula sample and acclimation

Lab-scale anaerobic digesters were set-up with both thermophilic and mesophilic inocula in the Environmental Engineering Laboratory at the UBC Okanagan. Thermophilic inoculum was taken from the effluent line of the full-scale digesters at Annacis Island WWTP in Vancouver (BC, Canada). These full-scale digesters utilize a mixture of WAS and PS. The mesophilic inoculum was taken from Penticton WWTP (BC, Canada). The digester at this plant was being fed only PS.

For acclimation, four semi-continuously (SC) fed digesters (2, 2.0 L of mesophilic and 2, 2.0 L of thermophilic) were run for more than 7 months at a sludge retention time (SRT) of 20 days. The configuration of SC digesters is explained in section 3.6. Acclimation digesters were fed with MW irradiated DWSC. From previous studies, MW acute toxicity on methanogenic microorganisms increases with MW temperature (Eskicioglu et al., 2007a; Hong et al., 2002). Therefore, an elevated MW temperature of 175^{o}C was used to avoid severe acute inhibition at pretreatment temperatures above boiling points. Organic loading rates (OLR) of the acclimation digesters was started from 1.58 ± 0.27 g COD/L/d and gradually doubled during 7 months under feed concentrations ranged from 1.71 ± 0.15% to 3.65 ± 0.30% TS by weight.

Although the mesophilic culture was fed with PS only at Penticton WWTP, it had a good performance, similar to thermophilic inoculum, during acclimation with MW irradiated DWSC. All four digesters were acclimatized to thermally pretreated sludge without any indication of acute or chronic toxicity. When inocula were being acclimatized to the pretreated DWSC, daily biogas productions, biogas composition and VFA readings reached steady state (< ± 10% variation in measurements). The actual (fourteen SC) digesters were set-up with the acclimatized mesophilic and thermophilic inocula to identify an optimum digester scenario for Kelowna municipal biosolids.

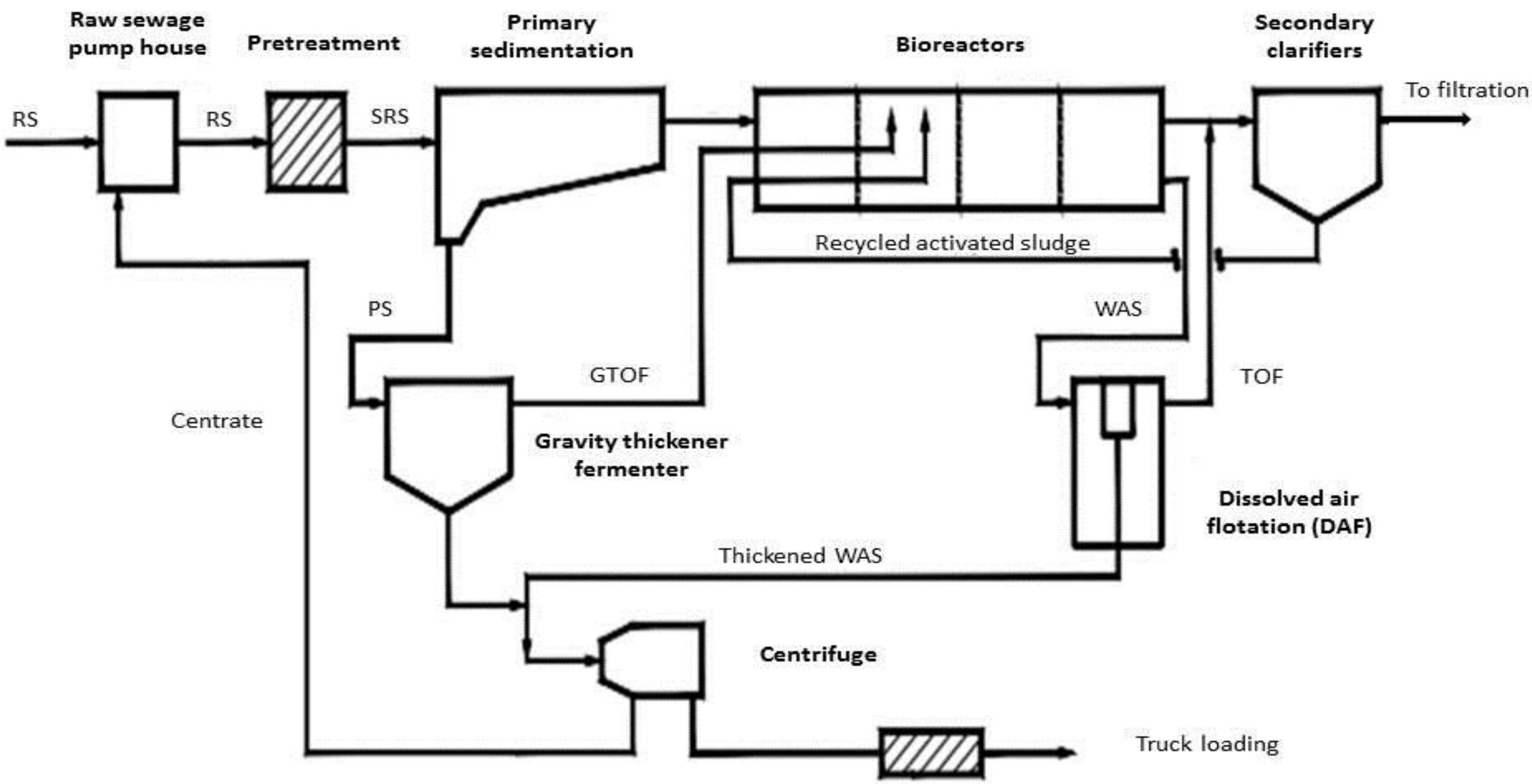

Figure 3.1 City of Kelowna treatment plant existing process flow diagrams (PS: primary sludge WAS: waste activated sludge, RS: raw sewage, SRS: screened raw sewage, GTOF: gravity thickener overflow, TOF: thickener overflow)

3.3 Experimental plan

Upon acclimation, fourteen lab-scale anaerobic digesters (total and wet volumes of 1 and 0.5 L, respectively), were set-up to optimize the SRT and biogas potential. Both mesophilic (35 ± 2°C) and thermophilic (55 ± 2°C) temperatures were investigated on waste disintegration and methane production. Microwave (MW) and conventional heating (CH) pretreatments were applied to enhance the hydrolysis step. Three pretreatment temperature levels (80, 120 and 160°C) were tested to investigate the effect of temperature and possible athermal effects of MW pretreatment below and above boiling point. Furthermore, three SRT of 20, 10 and 5 days were applied to anaerobic digesters. Figure 3.2 shows the schematic flow diagram of the experimental plan for the project. The experimental design resulted in a total of seven solubilization responses and fourteen SC anaerobic digesters at each SRT.

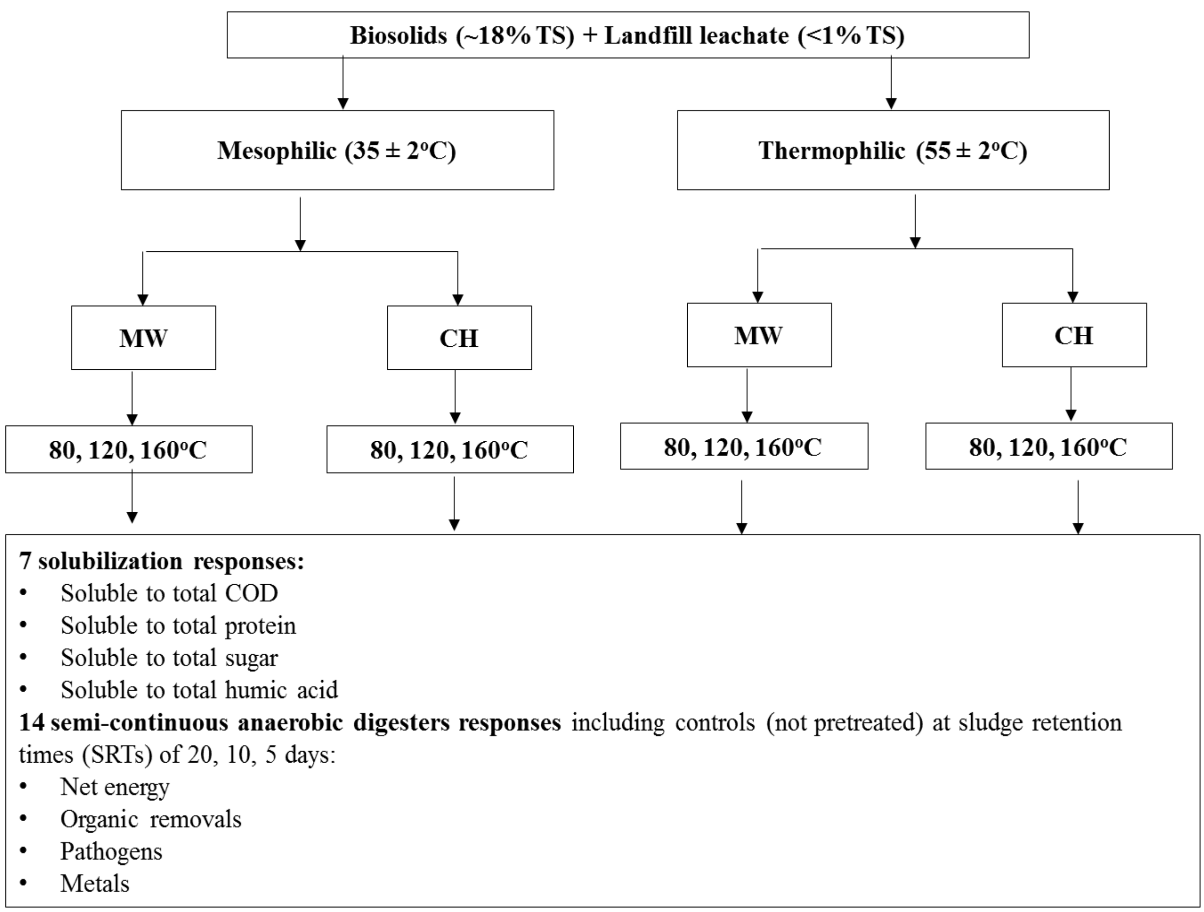

Figure 3.2 Full factorial experimental plan for different pretreatments and sludge retention times (SRT)

3.4 Pretreatment of sludge

In this study, two thermal pretreatment methods (MW and CH) were applied to accelerate the hydrolysis step and enhance the biogas production in anaerobic digestion process. The objective was to systematically compare the effect of these two methods on pretreatment of Kelowna's municipal sludge. Therefore, the challenge was to build a CH system which was able to heat samples with identical to MW heating as well as cooling profiles.

3.4.1 Microwave pretreatment

A Milestone Microwave Lab station [Ethos EZ, 2450 MHz, 0-1200 W and maximum temperature and pressure of 300^{o}C and 35 bars] with ATC-400-CE temperature probe (thermocouple) within pressure sealed vessels was used. Ethos EZ is equipped with temperature and pressure probes within the cavity and a turning carousel with a maximum of 12 pressure sealed vessels of 100 mL capacity each. This unit can be programmed to heat samples at different ramping rates and holding times, therefore allows for optimizing solubilization and subsequent methane potential from waste sludge samples. Kelowna sludge samples (540 g) were irradiated to 80, 120 and 160^{o}C at 7.5^{o}C/min ramp rate in 12 Teflon vessels (45 g of DWSC per vessel) rotating on the carousel. Pictures of the MW unit and pressure vessels are shown in Figure 3.3. Upon reaching the target pretreatment temperature, samples were hold at the target temperature for one minute. Active cooling is done in the MW system for 25 minutes to reduce the time vessel components are exposed to temperature and pressure extremes. Cooling was done in closed vessels to avoid evaporation of organics and pretreated samples were stored at in a fridge 4^{o}C until they are fed to the lab-scale digesters.

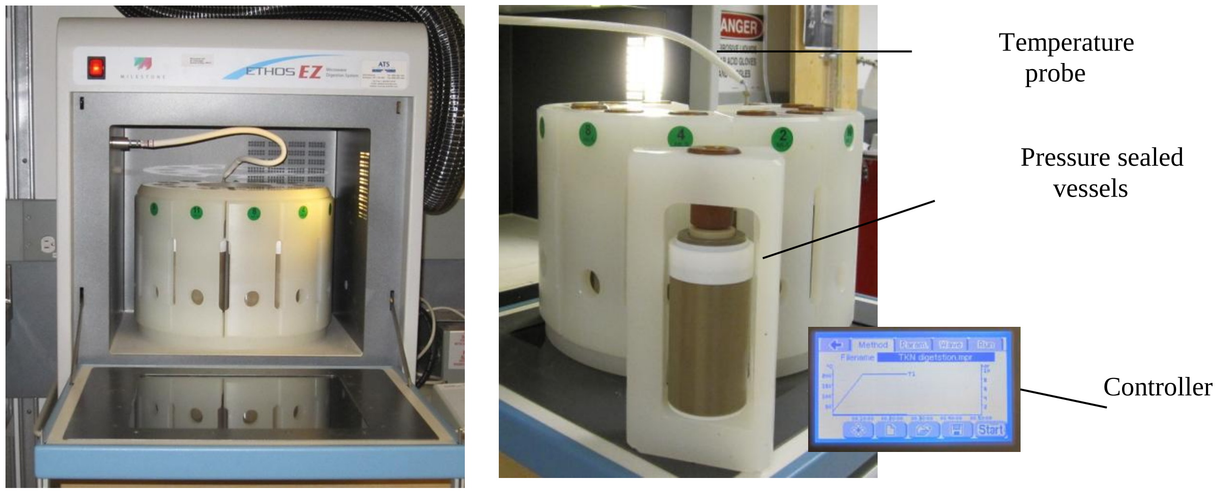

Figure 3.3 Ethos microwave station (2.45 GHz, 0-1200 Watt, 25-300^{o}C, 0-35 bars)

3.4.2 Conventional heating pretreatment

A pressure sealed vessel was designed and built at the machine shop of School of Engineering, UBC Okanagan. The vessel was made from copper and wrapped with a 500 Ω heater made from nichrome wire. The heater wire is secured to the vessel using high-temperature epoxy. A thermocouple measures the temperature of the material inside of the pressure cell. Using this system and programmable power supply, the waste sludge can be heated from room temperature up to 200^{o}C following any arbitrary temperature profile. This pressure vessel (Figure 3.4) was able to achieve identical pretreatment temperatures (80, 120 and 160^{o}C) at identical heating rates (7.5^{o}C/min) in the reference vessel of the MW unit, and therefore, for the first time, allowed us to systematically compare the thermal and athermal effects of the electromagnetic pretreatments at both under and above boiling temperatures. Figure 3.5 displays the heating and cooling profiles achieved by the Ethos MW unit and the pressure sealed vessel at three pretreatment temperatures.

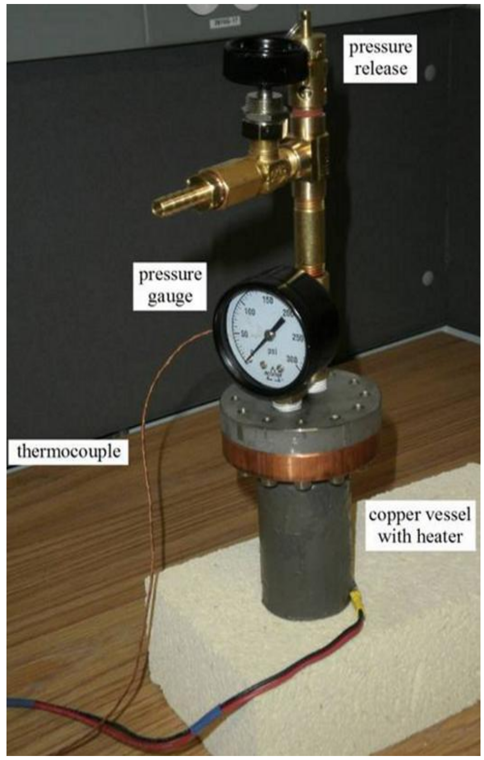

Figure 3.4 Custom built pressure vessel controlled by a PC

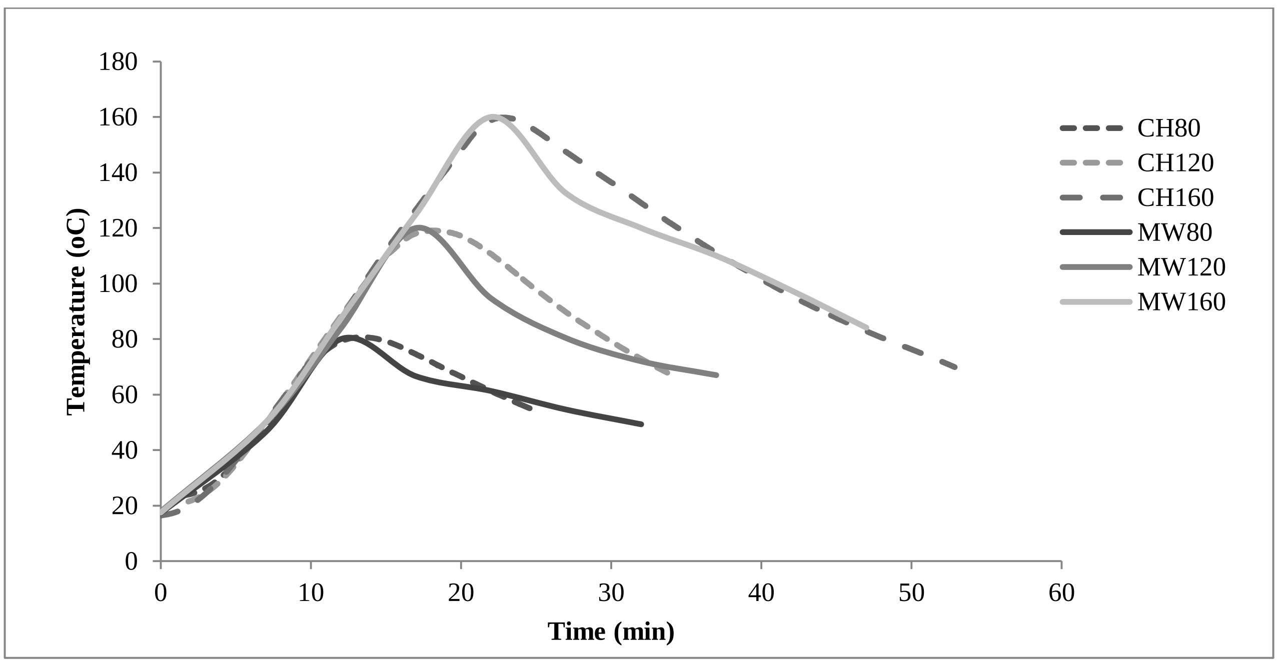

Figure 3.5 Heating and cooling profiles of MW unit and the pressure sealed vessel (MW: microwave; CH: conventional heating; 80, 120 and 160: ultimate pretreatment temperature (^{o}C)).

3.5 Characterization of sludge samples

3.5.1 Total solids and volatile solids

Standard Methods procedures 2540 B and 2540 E (APHA, 2005) were used for TS and volatile solids (VS) determination. A well-mixed sample was evaporated in a weighed dish and dried to constant weight in the oven at 104 ± 1^{o}C. The increase in weight over that of the empty dish represents the TS. The residue of the TS was ignited to constant weight at 550^{o}C. The remaining solids represent the fixed solids and the weight lost on ignition was the VS fraction.

3.5.2 Chemical oxygen demand (COD)

The closed reflux colorimetric COD measurements were performed based on Standard Methods procedure 5250D (APHA, 1995) with a Spectronic 20D+ (Thermo-Electron Corporation) spectrophotometer and 600 nm wavelength absorbencies. Before SCOD determination, sludge samples were centrifuged (for 15 minutes at 8,000 rpm) and filtered through membrane discs with 0.45 µm pore sizes.

In this method, samples were digested for 3 hours at 150^{o}C. The dichromate ion oxidizes the COD materials in the sample. This results in the change of chromium ion from hexavalent to trivalent state. The applied wavelength is for COD values between 100-900 mg/L. Therefore samples were diluted before addition of reagents and digestion. A standard curve (refer to Appendix A, Figures A.1) corresponding to 100-700 mg COD/L was generated using potassium hydrogen phthalate (KHP) solution as standard. KHP has a theoretical COD of 1.176 mg COD/mg.

3.5.3 Sugar

Soluble and total sugar concentrations of the samples were determined based on the procedure developed by Dubois et al. (1956). Samples were transferred to 10 mm test tubes with Teflon-lined screw-caps, 1 mL of sample, 1 mL of 5% phenol and 5 mL of sulphuric acid (98%) solutions were added to each tube. Resulting solutions were vortexed, kept 10 minutes and then heated at 30^oC in a water bath for 20 minutes and then brought to room temperature. Light absorbencies were measured at 490 nm with a Spectronic 20D+ spectrophotometer (Thermo-Electron Corporation). A standard curve (refer to Appendix A, Figures A.2) was generated using 2.5 – 40 mg/L of glucose as standard.

3.5.4 Proteins and humic acids

Total and soluble proteins and humic acids were measured using modified Lowry protein assay (Frolund et al., 1995). Calibration curves for proteins and humic acids (refer to Appendix A, Figures A.3 and A.4) were generated using 6.7 – 33.2 mg/L of bovine serum albumin (Fisher Sci., Ottawa, ON) and humic acid (H16752, Sigma-Aldrich, Canada, Ltd) as standards, respectively. The compositions of reagents are presented in (Appendix A, A.2). 0.5 mL of samples were transferred to 16 mm test tubes with Teflon-lined screw-caps and mixed with 2.5 mL of C_1 solution for determination of proteins or C_2 solution for humic acids. Samples were incubated at room temperature for 10 min, and then mixed with 0.25 mL Folin Reagent. Reactions were incubated at room temperature for an additional 30 min in dark, and then measured at 750 nm using a GENESYS 10 series spectrophotometer.

3.5.5 Ammonia

Dissolved ammonia concentration measurements were done on supernatant of sludge. Samples were centrifuged with Sorval LEGEND XT centrifuge machine for 15 minutes at 8,000 rpm. An ammonia selective electrode connected to the accumet excell XL25 dual channel pH/ ion meter was used for analyses. Measurements were done according to Standard Methods 4500D procedures (APHA, 2005). In this method, dissolved ammonia (NH_3 (aq) and NH_4^+) is converted to $NH_{3\ (aq)}$ at pH > 11. Ammonia-N calibration curve is presented in Figure A.5 (Appendix A).

3.5.6 Alkalinity

Alkalinity of samples was determined according to Standard Method 2320B (APHA, 1995). In this method, 25 mL of supernatant of sludge sample (centrifuged for 15 minutes at 8,000 rpm) were titrated with 0.1 N sulfuric acid to reach the pH value of 4.6.

3.5.7 Gas Chromatography for volatile fatty acids (VFAs) and biogas composition

Total VFAs, summation of acetic, propionic and butyric acids, were measured by injecting supernatants (filtered through membrane with discs with 0.2 μm pore size) into the Agilent 7890A Gas Chromatograph (GC) with a capillary column (Agilent 19091F-112, HP-FFAP polyethylene glycol TPA column length x ID: 25 m × 320 μm) and a flame ionization detector (oven, inlet and outlet temperatures: 200, 220 and 300^{o}C, respectively, carrier gas flow rate: 25 mL helium/min) equipped with an autosampler. The method developed by Ackman (1972) used iso-butyric acid as an internal standard.

Biogas composition in the headspace of lab-scale digesters was determined with an Agilent 7820A GC with a packed column (Agilent G3591-8003/80002) and thermal conductivity detector (oven, inlet and outlet temperatures: 70, 100 and 150^{o}C, respectively) using helium as the carrier gas (flow rate: 25 mL/min). The method was developed by Van Huyssteen (1967).

3.5.8 Others

Coliform, metals and total Kjeldahl nitrogen (TKN) analyses were done by a commercial laboratory (CARO Analytical Services, Kelowna, BC). According to their reports, CARO Analytical Services employs methods which are based on those found in "Standard Methods for the Examination of Water and Wastewater", 21st Edition, 2005, published by the American Public Health Association (APHA); US EPA protocols found in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846", 3rd Edition; protocols published by the British Columbia Ministry of Environment (BCMOE); and/or CCME Canada-wide Standard Reference methods.

3.6 Semi continuous anaerobic digestion

Side-armed erlenmeyer flasks which were sealed with two-hole rubber stoppers were used as lab-scale anaerobic digesters. The configuration digesters are shown as in Figure 3.6. The volume of the flasks used for anaerobic digesters were 1 L with 500 mL of anaerobic culture. Ports in the rubber stopper were used to collect biogas and to withdraw sludge. Digesters were being fed semi-continuously (i.e., one feeding per day) through the side arm of the flask. 2 L tedlar bags were used for biogas collection and biogas production was measured daily by using a manometer. Figure A.6 (refer to Appendix A) shows the calibration curve for the manometer.

Figure 3.6 Configuration of semi-continuous anaerobic digesters

Chapter 4 Results and discussion

4.1 Characterization of raw dewatered sludge cake (DWSC) and landfill leachate

The results of characterization of the DWSC and landfill leachate samples are summarized in Table 4.1. The DWSC was acidic and the pH was less than 6.0 and it had low alkalinity. However the landfill leachate had a pH value of 7.2 and an approximate alkalinity of 3,600 mg/L. As part of the anaerobic digester feed, alkalinity of the landfill leachate is advantageous, as the first step of the anaerobic digestion is acid fermentation and there is alkalinity consumption during this stage. Volatile solids (VS) to TS ratios are given in Table 4.1. According to these ratios, approximately 14% of DWSC and 82% of landfill leachate were likely non-biodegradable.

Table 4.1 Characterization of Kelowna's dewatered sludge cake and Glenmore Landfill leachate*

Parameters	Kelowna-DWSC	Glenmore- Landfill Leachate
pH (-)	5.72 (0.21;5)†	7.24 (0.15;5)
TS (% w/w)	17.28 (1.5;10)	0.48 (0.09;4)
VS (% w/w)	14.83 (1.5;10)	0.088 (0.03;4)
VS/TS*100 (%)	85.8	18.4
Alkalinity (mg $CaCO_3$/L)	850 (200;2)	3,622 (185;5)
Ammonia (mg/L)	1,182 (120;2)	109 (31;4)
TCOD (mg/L)	202,768 (8650:6)	330 (25;4)
SCOD (mg/L)	15,872 (672;6)	297 (17;4)
Volatile fatty acids (VFA) in the supernatant phase		
Acetic acid (mg/L)	1,005 (107;2)	10 (3;6)
Propionic acid (mg/L)	762 (47;2)	18 (1;6)
Butyric acid (mg/L)	29 (11;2)	3 (1;6)

***DWSC: dewatered sludge cake, TS: total solids, VS: volatile solids, TCOD : total chemical oxygen demand, SCOD: soluble chemical oxygen demand

†Data represent arithmetic mean of replicates (standard deviation; number of data points)

Soluble to total chemical oxygen demand ratio (SCOD/TCOD) of DWSC was approximately 8% before thermal pretreatments. The average TCOD of the landfill leachate was 330 ± 25 mg/L. As expected from the low VS/TS ratio in Table 4.1, the leachate had low concentrations of VFAs. Throughout the duration of the laboratory experiments (~8 months), both DWSC and landfill leachate have been characterized after each biweekly sampling. The sample characterization results deviated less than 10% from the values reported in Table 4.1.

4.2 Inoculum acclimation to high temperature microwave pretreatment

In this study, both thermophilic and mesophilic inocula were acclimated (for 7 months in semi-continuously fed digesters) to MW pretreated DWSC at 175^{o}C to minimize the methanogenic inhibition and to improve the rate and extent of biodegradation in actual digesters. To be on the safe side, a temperature of 175^{o}C, which is higher than the maximum pretreatment temperature of interest (160^{o}C), was selected for acclimation. Furthermore, Toreci et al. (2011) reported the greatest improvement in sludge solubilization and biogas production from biochemical methane potential (BMP) assays utilizing municipal WAS pretreated at 175^{o}C. Acclimation digesters were fed with pretreated and diluted DWSC to 2.0 ± 0.3 TS% at a safe SRT and corresponding organic loading rate (OLR) of 20 days and 1.58 ± 0.27 g TCOD/L/d, respectively. Thermophilic and mesophilic inocula characteristics before and after acclimation are given in Table 4.2. After acclimation period, thermophilic [1.18 ± 0.08% TS (w/w)] and mesophilic [1.17 ± 0.04% TS (w/w)] inocula had similar TS% and 14 semi-continuous digesters were started with 500 ml acclimated inocula volume in each digester.

4.3 Effect of pretreatment on hydrolysis of biosolids

The effects of thermal pretreatment method and pretreatment temperature were investigated on solubilization of DWSC. Dewatered sludge was heated at temperatures below and above boiling points (80, 120 and 160^{o}C) with MW and CH methods. In order to avoid bias among control and pretreated samples due to evaporation of water following pretreatments, both MW and CH pretreatments were applied in pressure sealed vessel and COD and biopolymer results were reported as SCOD/TCOD, soluble to total protein, sugar and humic acid.

Table 4.2 Inocula characteristics for semi-continuous digesters*

Inocula characteristics	Thermophilic before acc.	Thermophilic after acc.	Mesophilic before acc.	Mesophilic after acc.
pH (-)	7.67	7.51	7.09	7.11
TS (%, w/w)	1.68 ± 0.04†	1.18% ± 0.08	1.57 ± 0.03	1.17% ± 0.04
VS (%, w/w)	1.08% ± 0.03	0.78% ± 0.03	0.88% ± 0.01	0.76% ± 0.05
TCOD (mg/L)	14,270 ± 250	12,596 ± 230	11,711 ± 820	12,333 ± 367
SCOD (mg/L)	963 ± 72	986 ± 106	329 ± 78	483 ± 58
Alkalinity (mg $CaCO_3$/L)	4425 ± 352	2,324 ± 12	1712 ± 52	2,094 ± 16
NH_3-N (mg/L)	660 ± 62	1,071 ± 32	319.2 ± 24	930 ± 21
TVFA (mg/L)	1,008 ± 18	0	131 ± 2	0

*TVFA: total fatty acids (summation of acetic, propionic and butyric acids), acc.: acclimation, TCOD: total chemical oxygen demand, SCOD: soluble chemical oxygen demand, TS: total solids, VS: volatile solids.
†Data represent arithmetic mean of duplicates ± absolute difference between mean and duplicates.

4.3.1 Effect of pretreatment on particulate COD solubilization of waste sludge

Previous studies indicated both ultimate pretreatment temperature and heating rate are significant factors in enhancing thermal hydrolysis and subsequent methane production (Eskicioglu et al., 2007b; 2009). Toreci et al. (2010) applied two MW heating rates of 3.78°C/min and 7.5°C/min on municipal TWAS with 6% TS and 11.85% TS. It was observed that for the concentrated sludge, the effect of intensity on solubility was not significant for treatment temperatures of 110°C and 150°C in terms of soluble to total ratios of COD, protein and sugar. Therefore in this study, between the two heating rates previously studied, faster rate (7.5°C/min) was applied for pretreating municipal DWSC at ~17.5% TS.

In the temperature range of 80-160°C, as pretreatment temperature increased, particulate COD solubilization increased as shown in Figure 4.1. Among three pretreatment temperatures, 160°C was found to be the most effective for converting particulate COD to soluble COD. SCOD/TCOD ratios in samples pretreated with MW and CH at 160°C increased by a factor of 2.8 ± 0.1 and 3.2 ± 0.3 respectively, compared to the controls (untreated or raw DWSC samples).

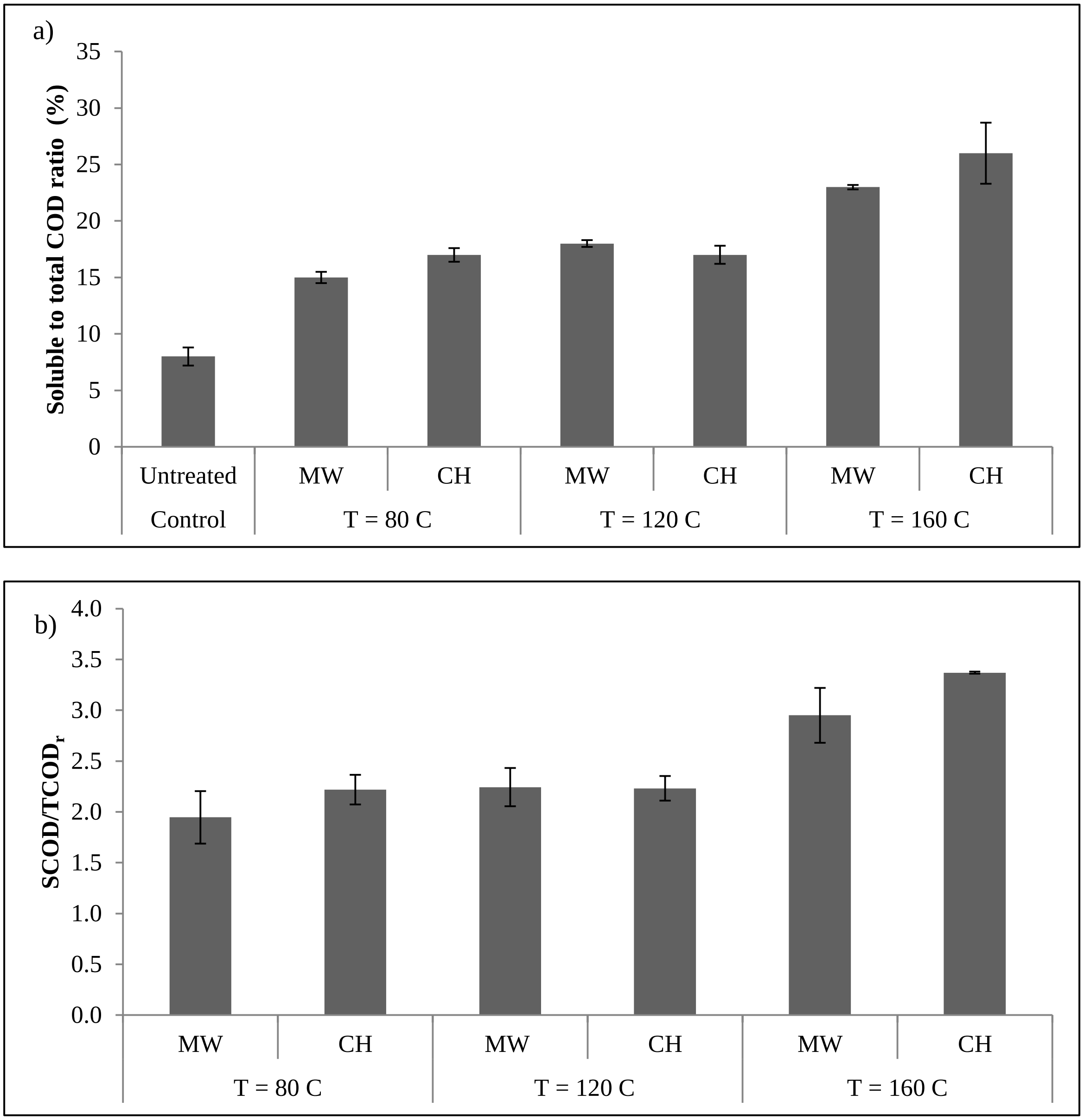

Figure 4.1 Solubilization effect of microwave (MW) and conventional heating (CH): a) Soluble to total COD, b) relative to control soluble to total COD. ($SCOD/TCOD_r = SCOD/TCOD_{pretreated}/ SCOD/TCOD_{control}$); (T = 80, T = 120, T = 160: pretreatment temperatures at 80, 120 and 160°C respectively; data represent arithmetic mean of duplicates and error bars represent variability between mean and duplicate measurements)

Two-way analysis of variance (ANOVA) was used to detect the significant factors in DWSC solubilization prior to anaerobic digestion. In this ANOVA test, the response was relative SCOD/TCOD ratio ($SCOD/TCOD_r = SCOD/TCOD_{pretreated}/ SCOD/TCOD_{control}$) in order to eliminate the effect of solubilization from control DWSC sample. p-values test the statistical significance of each factor in the ANOVA method. Table 4.3 indicates that the p-value of pretreatment temperature (T) is less than 0.05 and therefore has statistically significant effect on DWSC solubilization at the confidence level of 95%. Furthermore, interestingly, the type of pretreatment method (M), i.e. CH versus MW, and the interaction of method and pretreatment temperature had no statistically significant effect (p-value > 0.05) on DWSC solubilization. The normal probability plot of residues is shown in Appendix B (Figure B.1). This figure displays that the error distribution is normal for $SCOD/TCOD_r$. At similar temperatures, both CH and MW heating achieved similar COD solubilization ratios which were also confirmed by biopolymer (protein, sugar and humic acids) solubilization experiments reported in the following section. These results are important, as it was observed for the first time, that MW irradiation did not have a statistically significant athermal effects on solubilization of sludge both under and above boiling temperatures when compared to CH under identical heating profiles (7.5^oC/min) and cooling profiles (2.2 ± 0.3^oC/min).

Table 4.3 Results of ANOVA for relative to control SCOD/TCOD ratio[a]

Source	Degree of freedom	Sum of squares	Mean square	F-ratio	p-value
M	1	0.153	0.153	4.35	0.082
T	2	2.715	1.357	38.54	0.000
Interaction	2	0.095	0.047	1.36	0.326
Error	6	0.211	0.035		
Total	11	3.175			

[a]TCOD: total chemical oxygen demand, SCOD: soluble chemical oxygen demand, M: pretreatment method (conventional heating or microwave irradiation), T: pretreatment temperature.

4.3.2 Effect of pretreatment on mineralization of waste sludge

Disintegration of DWSC was evaluated with VS, TS and fixed solids (FS = TS -VS) and results are presented in Figure 4.2. Mineralization may occur after intense pretreatment. It is not desirable due to decrease in the VS concentration and therefore methane potential of waste sludge (Saha et al., 2011). In this study, the mineralization was not statistically significant ($p > 0.05$) and VS/TS ratios remained in 85 ± 1% range for all pretreatment conditions. The results indicate that organic matter in DWSC was mainly solubilized rather than being mineralized by both thermal pretreatments.

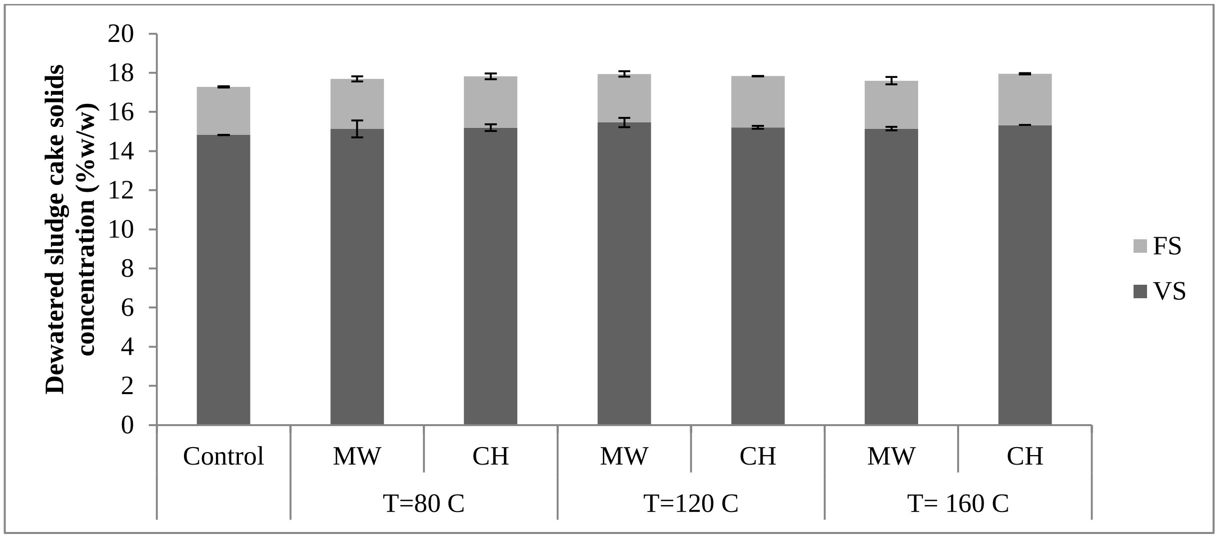

Figure 4.2 Mineralization of microwave (MW) and conventional heating (CH) pretreated dewatered sludge cake (T = 80, T = 120, T = 160: pretreatment temperatures at 80, 120 and 160^{o}C respectively; data represent arithmetic mean of duplicates and error bars represent absolute difference between mean and duplicates).

4.3.3 Effect of pretreatment on soluble biopolymer of waste sludge

Organic fraction of biosolids contains intra-cellular (within the bacterial cell) and extra-cellular (within the polymeric matrix) biopolymers, such as proteins, sugars, lipids and nucleic acids. Soluble biopolymers have been found to be a good measure of the solubilization of organic matter in biological sludge. After pretreatment, biopolymers are released into the supernatant to the extent which depends on the intensity of pretreatment. In this study, solubilization of biopolymers was monitored by protein, sugar and humic acid analyses. Soluble to total sugar, protein and humic acid results displayed in Figures 4.3, 4.4 and 4.5, respectively. As pretreatment temperature increased, concentration of soluble sugar, protein and humic acids increased. Soluble to total sugar ratios significantly increased at a pretreatment temperature of 160^{o}C and the ratio reached to 31.0 ± 0.5%. Similarly, maximum soluble to total protein ratios were 28.6 ± 2.2% and 30.7 ± 1.4% at 160^{o}C after MW and CH pretreatments, respectively (Figure 4.4).

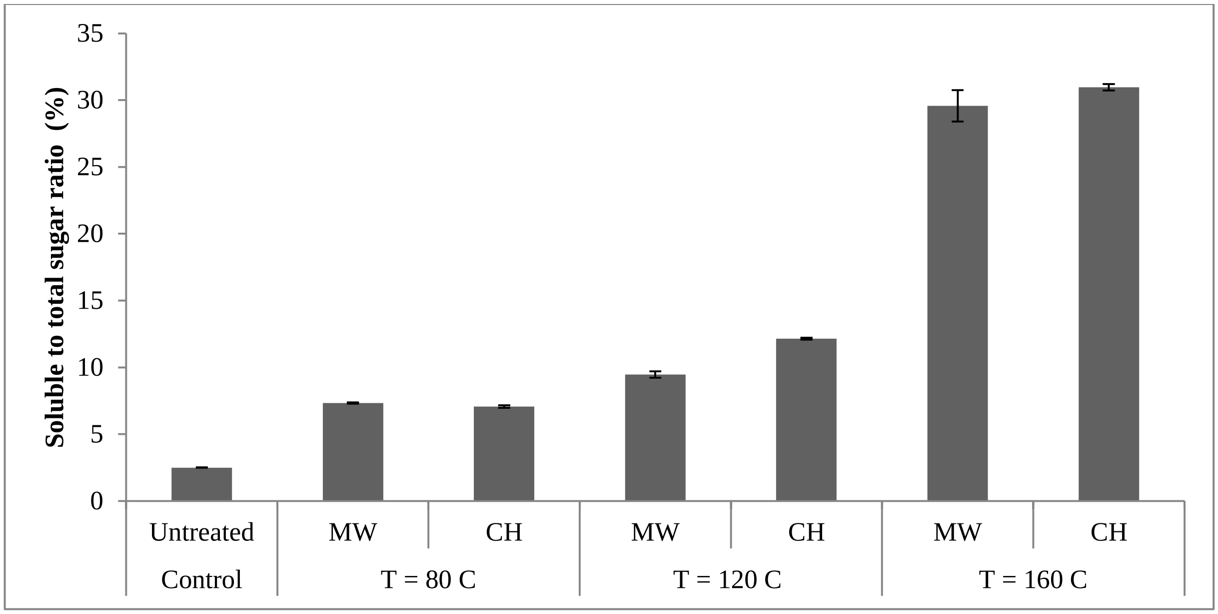

Figure 4.3 Solubilization of sugars in microwave (MW) and conventional heating (CH) pretreated dewatered sludge cake (T = 80, T = 120, T = 160: pretreatment temperatures at 80, 120 and 160°C respectively; data represent arithmetic mean of duplicates and error bars represent absolute difference between mean and duplicates)

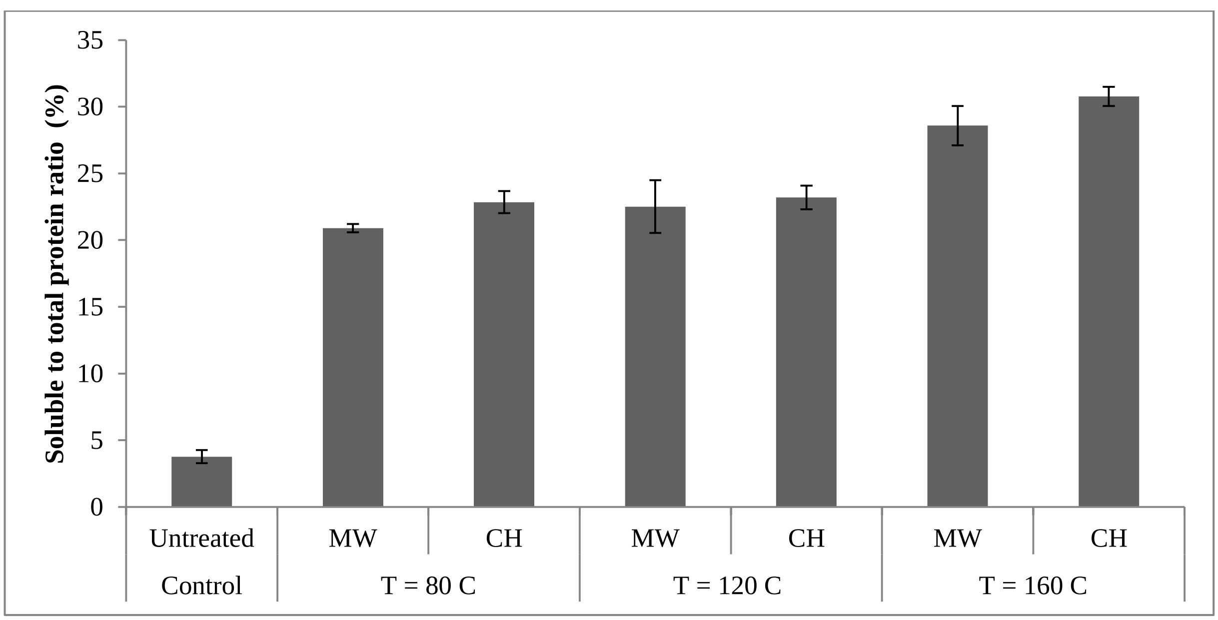

Figure 4.4 Solubilization of proteins in microwave (MW) and conventional heating (CH) pretreated dewatered sludge cake (T = 80, T = 120, T = 160: pretreatment temperatures at 80, 120 and 160°C respectively; data represent arithmetic mean of duplicates and error bars represent absolute difference between mean and duplicates).

Humic acids are the main components of humic substances and are produced by biodegradation of dead organic matter. Humic acids are difficult to degrade during subsequent treatment of the wastewater, but it can be extracted and used as fertilizer. Sludge humic acids contain a wider variety of organic substances, more lipids and nitrogen compared to commercial humic acids (Li et al., 2009).

Figure 4.5 shows the effect of thermal hydrolysis on solubilization of particulate humic acids. Similar to other biopolymers, the solubilization of humic acids increased as the pretreatment temperature increased. Maximum soluble to total humic acid ratios of 23.9 ± 1.2% and 23.5 ± 1.4% were achieved by MW and CH pretreatments, respectively, at 160^{o}C.

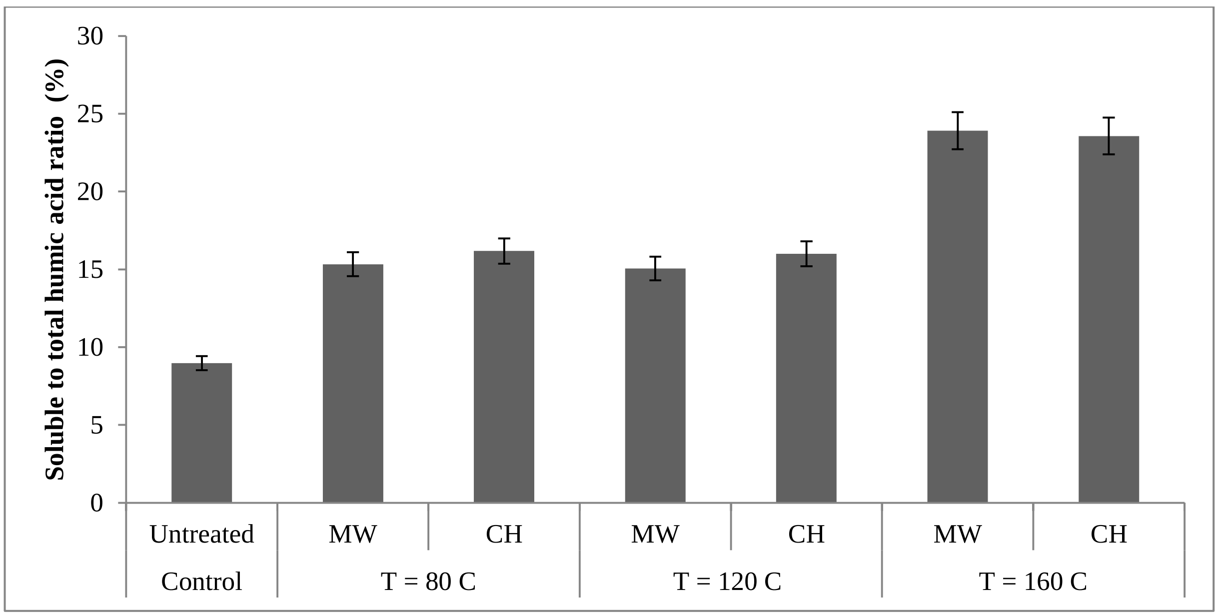

Figure 4.5 Solubilization of humic acids in microwave (MW) and conventional heating (CH) pretreated dewatered sludge cake (T = 80, T = 120, T = 160: pretreatment temperatures at 80, 120 and 160^{o}C respectively; data represent arithmetic mean of duplicates and error bars represent absolute difference between mean and duplicates)

Similar conclusions were obtained from ANOVA tests for sugar, protein and humic acid solubilization. Analysis showed that p-value of pretreatment temperature (T) is less than 0.05 and it has statistically significant effect on solubilization at the confidence level of 95%. However, the pretreatment method (CH versus MW) had no statistically significant effect ($p > 0.05$) on DWSC biopolymer solubilization. ANOVA results for solubilization of sugar, protein and humic acids are presented in Tables B.2, B.3 and B.4 in Appendix B, respectively.

4.4 Effect of pretreatment on semi-continuous flow digestion of biosolids

Upon achieving acclimation, 14 lab-scale digesters (total and wet volumes of 1 and 0.5 L, respectively), set-up with acclimatized inocula, were operated for additional 5 months to optimize energy (methane) output and SRT requirements of untreated (control) and thermally pretreated digesters. In terms of digester feed characterization, two different thermal pretreatments (MW and CH) and three pretreatment temperatures (80, 120 and 160^{o}C) were tested.

Table 4.4 Mixture of sludge cake and landfill leachate fed to semi-continuous anaerobic digesters*

	Control	MW-80	MW-120	MW-160	CH-80	CH-120	CH-160
pH	6.66	6.71	6.75	6.56	6.72	6.70	6.62
(-)	(0.38,12)†	(0.31,12)	(0.02,12)	(0.25,12)	(0.06,12)	(0.26,12)	(0.40,12)
TS	3.48	3.38	3.37	3.42	3.60	3.28	3.46
(% w/w)	(0.31,24)	(0.23,24)	(0.28,24)	(0.19,24)	(0.28,24)	(0.14,24)	(0.19,24)
VS	2.74	2.84	2.78	2.85	2.84	2.63	2.73
(% w/w)	(0.22,24)	(0.01,24)	(0.2,24)	(0.21,24)	(0.19,24)	(0.12,24)	(0.18,24)
TCOD	34,743	33,149	37,611	33,786	39,753	30,280	38,248
(mg/L)	(1677,24)	(3495,24)	(1589,24)	(3327,24)	(2604,24)	(2828,24)	(497,24)
SCOD	3,222	5,342	6,324	7,084	5,918	6,254	9,220
(mg/L)	(67,4)	(62,4)	(17,4)	(125,4)	(53,4)	(38,4)	(81,4)
Alkalinity	1636	1199	953	968	1398	1277	1258
(mg $CaCO_3$/L)	(150,3)	(86,3)	(46,3)	(58,3)	(87,3)	(89,3)	(139,3)
NH_3-N	668	640	305	430	302	400	627
(mg/L)	(21,2)	(15,2)	(46,2)	(26,2)	(11,2)	(32,2)	(54,2)
Volatile fatty acids							
Acetic acid	795	552	426	241	534	419	192
(mg/L)	(343,3)	(316,3)	(17,3)	(80,3)	(151,3)	(132,3)	(106,3)
Propionic acid	390	187	98	69	232	164	70
(mg/L)	(301,3)	(75,3)	(45,3)	(39,3)	(128,3)	(39,3)	(17,3)
Butyric acid	38	21	10	8	9	13	19
(mg/L)	(22,3)	(0,3)	(1,3)	(4,3)	(0,3)	(4,3)	(4,3)

*TS: total solids, VS: volatile solids, TCOD: total chemical oxygen demand, SCOD: soluble chemical oxygen demand
†(standard deviation, number of data points)

Although small, DWSC samples showed variation in terms of solid concentration due to minor operational changes at the WWTP and seasonal properties of wastewater. In order to eliminate this variation, TS concentration was measured after each sampling and the solid percentage of the digester feed bottles were adjusted to 3.5% TS by weight. For feed preparation, the DWSC samples pretreated with CH and MW at three different temperatures of (80, 120 and 160^{o}C) were diluted with the mixture of landfill leachate and tap water (3:5) to reach 3.5% TS. Table 4.4 summarized the characteristic of the digester feeds.

Digestion operation was first started at a typical (safe) SRT of 20 d (OLR of 1.37 ± 0.04 g VS/L/d and 1.76 ± 0.16 g TCOD/L/d) used in anaerobic digestion to avoid instability due to high organic loading. The reactors were operated, in a semi-continuously fed mode, until they reached steady-state conditions and then maintained in this state over a period of three SRTs (Ekama et al., 1986). Upon completion of this run, the SRT was reduced to 10 d. Again steady operation over almost three SRTs was maintained. The lowest SRT tested was 5 days (OLR of 5.40 ± 0.28 g VS/L/d). As an example of digester operational pattern, daily biogas productions at standard temperature and pressure (STP; 0^{o}C, 1 atm) from digesters fed with untreated DWSC and MW pretreated sludge at 120^{o}C is shown in Figure 4.6. Steady state was defined as the period of time in which less that 10% variation was observed in biogas production. The steady state properties of the digesters at SRTs of 20, 10 and 5 days are summarized in Table 4.5, Table 4.6 and Table 4.7, respectively. Tabulated values are the arithmetic means of measurements taken during steady state of each SRT.

Control or pretreated digesters did not show any stability problems at SRTs of 20 and 10 days. Except for the control digesters at a 5 day SRT, all control and pretreated digesters achieved steady state after ~ 7 days of operation at all three SRTs, corresponding to volumetric OLRs of 1.76 ± 0.16 to 6.68 ± 0.26 g TCOD/L/d. At the SRT of 5 days, both mesophilic and thermophilic controls stopped producing biogas after 20 days of operation (Figure 4.6) with total VFA concentrations exceeding 1,818 mg/L at pH < 5.64 for mesophilic and 2,853 mg/L at pH <7.02 for thermophilic controls while the pretreated digesters continued producing biogas.

The digester results indicate that both thermal pretreatments have potential to reduce SRT, therefore digester volume requirement at the full-scale. The effect is more apparent when the loading rate is increased to a point where control digesters are challenged to achieve both hydrolysis as well as methane conversion within the short SRT. In addition, digesters fed with pretreated sludge produced more biogas compared to the controls and the differences were statistically significant [t-test, $\alpha = 0.05$, $p < 0.05$ for $\mu_1 = \mu_2$ (Montgomery, 2005)]. Although the t-test indicated that methane productions from control and pretreated digesters were significantly different ($p<0.05$), the increase in the pretreatment temperature above $80^{o}C$ did not yield a statistically significant effect (further increase or decrease) on the methane production. This implies that from a simple methane recovery point of view, the lowest pretreatment temperature tested ($80^{o}C$) was sufficient.

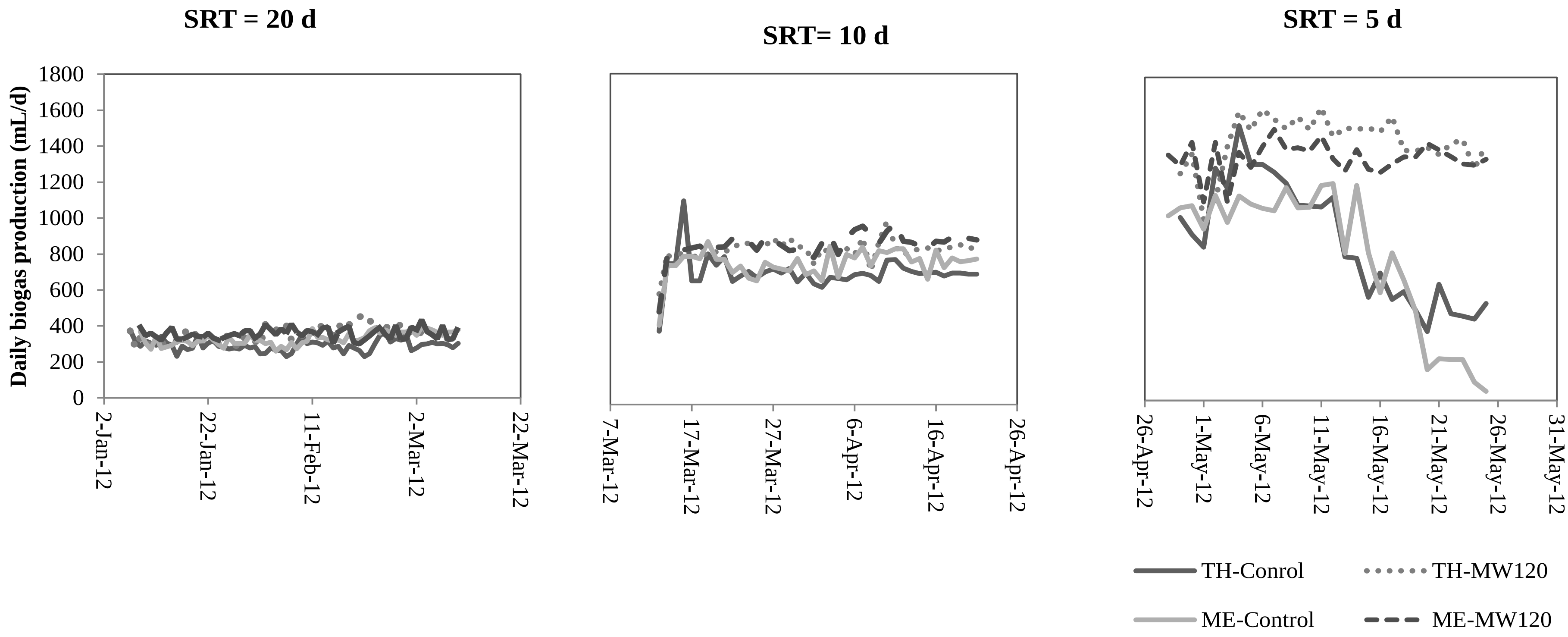

Figure 4.6 Daily biogas production (at STP) of anaerobic digesters fed with untreated sludge (control) and sludge microwaved at 120^{o}C (SRT: sludge retention time, MW: microwave, ME: mesophilic digester, TH: thermophilic digester)

Table 4.5 Steady state results for semi-continuous digesters at 20 d SRT[a]

	SRT = 20 d													
	Thermophilics							Mesophilics						
Parameters	Control	MW-80	MW-120	MW-160	CH-80	CH-120	CH-160	Control	MW-80	MW-120	MW-160	CH-80	CH-120	CH-160
Loading conditions for reactors														
OLR	1.37	1.42	1.39	1.42	1.42	1.31	1.37	1.37	1.42	1.39	1.42	1.42	1.31	1.37
[g VS/L*/d]	(0.11,4)†	(0.05,4)	(0.1,4)	(0.11,4)	(0.10,4)	(0.11,4)	(0.09,4)	(0.11,4)	(0.05,4)	(0.1,4)	(0.11,4)	(0.10,4)	(0.11,4)	(0.09,4)
OLR	1.74	1.66	1.88	1.69	1.99	1.51	1.91	1.74	1.66	1.88	1.69	1.99	1.51	1.91
[g TCOD/L*/d]	(0.08,4)	(0.17,4)	(0.07,4)	(0.16,4)	(0.13,4)	(0.14,4)	(0.02,4)	(0.08,4)	(0.17,4)	(0.07,4)	(0.16,4)	(0.13,4)	(0.14,4)	(0.02,4)
Removal efficiency														
VS	56.7	55.9	53.4	56.4	55.0	50.9	55.8	53.9	52.9	49.6	53.1	53.3	48.6	51.2
[%]	(3.3,14)	(3.4,14)	(4.8,14)	(2.2,14)	(3.2,14)	(3.5,14)	(3.2,14)	(3.3,14)	(2.1,14)	(2.0,14)	(1.5,14)	(2.1,14)	(1.4,14)	(1.5,14)
TS	37.4	37.7	32.7	37.7	35.0	30.9	35.4	46.0	43.8	44.0	45.2	45.8	44.7	46.3
[%]	(3.3,14)	(4.9,14)	(5.4,14)	(3.1,14)	(4.1,14)	(5.1,14)	(3.4,14)	(1.7,14)	(3.6,14)	(1.8,14)	(1.4,14)	(2.0,14)	(1.6,14)	(1.4,14)
TCOD	49.9	46.6	43.9	57.6	37.7	36.4	47.2	38.8	46.6	43.4	43.2	38.2	37.7	41.2
[%]	(3.9,14)	(3.1,14)	(2.8,14)	(3.7,14)	(3.4,14)	(2.6,14)	(4.6,14)	(1.1,14)	(1.0,14)	(1.8,14)	(1.3,14)	(1.7,14)	(1.5,14)	(1.2,14)
Biogas at STP	0.58	0.68	0.70	0.68	0.64	0.64	0.64	0.66	0.70	0.72	0.80	0.68	0.72	0.70
[L/L*/d]	(0.03,60)	(0.04,60)	(0.05,60)	(0.04,60)	(0.04,60)	(0.03,60)	(0.03,60)	(0.04,60)	(0.03,60)	(0.03,60)	(0.05,60)	(0.04,60)	(0.04,60)	(0.05,60)
CH_4	66	65	66	65	65	67	61	66	65	65	66	65	65	62
[%]	(2,4)	(0,4)	(1,4)	(2,4)	(2,4)	(3,4)	(0,4)	(2,4)	(0,4)	(1,4)	(2,4)	(2,4)	(3,4)	(0,4)
pH in reactors	7.76	7.77	7.76	7.78	7.80	7.76	7.75	7.35	7.40	7.43	7.41	7.42	7.42	7.43
	(0.08,9)	(0.11,9)	(0.1,9)	(0.13,9)	(0.09,9)	(0.09,9)	(0.09,9)	(0.06,9)	(0.07,9)	(0.07,9)	(0.09,9)	(0.09,9)	(0.04,9)	(0.07,9)
Effluent supernatant characteristics														
SCOD	2482	2189	2041	2211	2096	1829	2194	638.4	901	838	1,235	818	849	1,219
[mg/L]	(218,10)	(294,10)	(232,10)	(253,10)	(154,10)	(103,10)	(49,10)	(42.3,10)	(106,10)	(60,10)	(92,10)	(113,10)	(96,10)	(130,10)
NH_3-N	1360	1690	1665	1545	1794	1666	1555	1277	1421	1491	1616	1538	1584	1486
[mg/L]	(84,6)	(170,6)	(136,6)	(170,6)	(229,6)	(133,6)	(134,6)	(99,6)	(146,6)	(118,6)	(64,6)	(142,6)	(139,6)	(67,6)
Alkalinity	4,321	4,458	4,703	4,580	4,621	4,454	4,697	3,982	4,346	4,469	4,673	4,371	4,595	4,445
[mg $CaCO_3$/L]	(155,6)	(284,6)	(173,6)	(275,6)	(266,6)	(198,6)	(302,6)	(197,6)	(81,6)	(212,6)	(131,6)	(226,6)	(235,6)	(213,6)
TVFA	30	44	26	47	5	15	19	29	6	2	2	1	0	0
[mg/L]	(14,3)	(35,3)	(1,3)	(24,3)	(4,3)	(25,3)	(33,3)	(12,3)	(6,3)	(2,3)	(1,3)	(1,3)	(0,3)	(0,3)

[a]MW: microwave, CH: conventional heating, OLR: organic loading rate, STP: standard temperature and pressure (0°C, 1 atm), TVFA: total volatile fatty acids (summation of acetic, propionic and butyric acids), TS: total solids, VS: volatile solids, STP: 0°C, 1 atm, *liter of reactor. †Data represent arithmetic mean of measurements (standard deviation, number of data points).

Table 4.6 Steady state results for semi-continuous digesters at 10 d SRT[a]

	SRT = 10 d													
	Thermophilics							Mesophilics						
Parameters	Control	MW-80	MW-120	MW-160	CH-80	CH-120	CH-160	Control	MW-80	MW-120	MW-160	CH-80	CH-120	CH-160
	Loading conditions for reactors													
OLR	2.59	2.88	2.72	2.89	2.66	2.53	2.27	2.59	2.88	2.72	2.89	2.66	2.53	2.27
[g VS/L*/d]	(0.08,4)†	(0.08,4)	(0.02,4)	(0.03,4)	(0.05,4)	(0.09,4)	(0.07,4)	(0.08,4)	(0.08,4)	(0.02,4)	(0.03,4)	(0.05,4)	(0.09,4)	(0.07,4)
OLR	3.19	3.31	3.76	3.35	3.44	3.03	3.82	3.19	3.31	3.76	3.35	3.44	3.03	3.82
[g TCOD/L*/d]	(0.06,4)	(0.10,4)	(0.07,4)	(0.05,4)	(0.07,4)	(0.09,4)	(0.06,4)	(0.06,4)	(0.10,4)	(0.07,4)	(0.05,4)	(0.07,4)	(0.09,4)	(0.06,4)
	Removal efficiency													
VS	44.4	52.3	54.1	56.4	45.2	45.7	53.9	38.7	50.7	51.9	53.7	40.7	43.5	51.7
[%]	(2.7,14)	(2.8,14)	(1.9,14)	(1.1,14)	(2.9,14)	(2.5,14)	(2.0,14)	(2.4,14)	(2.1,14)	(2.5,14)	(2.2,14)	(3.6,14)	(2.5,14)	(1.4,14)
TS	34.3	45.3	43.0	41.3	37.9	42.3	43.9	29.1	42.1	41.2	37.2	34.7	41.1	41.8
[%]	(3.1,14)	(3.7,14)	(2.4,14)	(1.5,14)	(4.1,14)	(3.7,14)	(2.9,14)	(3.0,14)	(2.2,14)	(2.7,14)	(2.2,14)	(4.1,14)	(3.7,14)	(1.4,14)
TCOD	40.5	53.3	53.2	38.9	38.9	47.2	46.5	46.8	53.1	55.1	54.2	43.4	47.8	55.6
[%]	(2.5,14)	(2.2,14)	(2.0,14)	(4.4,14)	(1.8,14)	(2.7,14)	(1.2,14)	(2.9,14)	(2.4,14)	(1.9,14)	(3.9,14)	(2.7,14)	(2.2,14)	(0.6,14)
Biogas at STP	1.42	1.56	1.70	1.60	1.56	1.54	1.66	1.56	1.66	1.76	1.74	1.64	1.64	1.66
[L/L*/d]	(0.09,36)	(0.08,36)	(0.05,36)	(0.07,36)	(0.07,36)	(0.06,36)	(0.09,36)	(0.06,36)	(0.06,36)	(0.05,36)	(0.05,36)	(0.05,36)	(0.05,36)	(0.04,36)
CH_4	66	64	65	67	66	64	65	64	65	66	67	65	65	64
[%]	(1,4)	(3,4)	(1,4)	(2,4)	(2,4)	(3,4)	(1,4)	(1,4)	(2,4)	(2,4)	(2,4)	(2,4)	(1,4)	(3,4)
pH in reactors	7.76	7.81	7.80	7.83	7.85	7.85	7.85	7.47	7.54	7.54	7.55	7.55	7.56	7.59
	(0.05,8)	(0.04,8)	(0.04,8)	(0.02,8)	(0.06,8)	(0.08,8)	(0.03,8)	(0.05,8)	(0.04,8)	(0.04,8)	(0.02,8)	(0.06,8)	(0.08,8)	(0.03,8)
	Effluent supernatant characteristics													
SCOD	2,163	2.659	2,386	3,169	2,148	2,628	3,007	944	889	922	1,613	1,015	924	1,809
[mg/L]	(205,12)	(283,12)	(264,12)	(296,12)	(106,12)	(170,12)	(260,12)	(118,12)	(77,12)	(94,12)	(162,12)	(101,12)	(54,12)	(127,12)
NH_3-N	1,127	1,116	1,186	1,191	1,111	1,113	1,129	997	1,011	1,144	1,171	1,026	1,177	1118
[mg/L]	(90,6)	(109,6)	(73,6)	(106,6)	(54,6)	(104,6)	(98,6)	(35,6)	(29,6)	(105,6)	(82,6)	(54,6)	(70,6)	(71,6)
Alkalinity	4,545	4,983	4,963	4,963	5,156	5,039	5,318	3,980	4,604	4,991	4,852	4,840	4,841	4,828
[mg $CaCO_3$/L]	(186,6)	(228,6)	(134,6)	(121,6)	(72,6)	(107,6)	(422,6)	(233,6)	(91,6)	(311,6)	(414,6)	(398,6)	(290,6)	(378,6)
TVFA	215	102	51	35	45	17	34	6	7	13	11	13	12	11
[mg/L]	(164,8)	(75,8)	(24,8)	(39,8)	(36,8)	(22,8)	(32,8)	(7,8)	(8,8)	(6,8)	(4,8)	(9,8)	(4,8)	(4,8)

[a]MW: microwave, CH: conventional heating, OLR: organic loading rate,*liter of reactor, TVFA: total volatile fatty acids (summation of acetic, propionic and butyric acids), TS: total solids, VS: volatile solids, STP: 0°C, 1 atm. †Data represent arithmetic mean of measurements (standard deviation, number of data points).

Table 4.7 Steady state results for semi-continuous digesters at 5 d SRT[a]

SRT = 5 d														
	Thermophilics							**Mesophilics**						
Parameters	Control	MW-80	MW-120	MW-160	CH-80	CH-120	CH-160	Control	MW-80	MW-120	MW-160	CH-80	CH-120	CH-160
Loading conditions for reactors														
OLR	5.15	5.79	5.61	5.66	5.44	5.11	5.07	5.15	5.79	5.61	5.66	5.44	5.11	5.07
[g VS/L*/d]	(0.10,4)†	(0.08,4)	(0.09,4)	(0.11,4)	(0.10,4)	(0.08,4)	(0.09,4)	(0.1,4)	(0.08,4)	(0.09,4)	(0.11,4)	(0.10,4)	(0.08,4)	(0.09,4)
OLR	6.96	6.63	6.95	6.69	6.88	6.26	6.39	6.96	6.63	6.95	6.69	6.88	6.26	6.39
[g TCOD/L*/d]	(0.11,4)	(0.17,4)	(0.07,4)	(0.10,4)	(0.11,4)	(0.13,4)	(0.16,4)	(0.11,4)	(0.17,4)	(0.07,4)	(0.10,4)	(0.11,4)	(0.13,4)	(0.16,4)
Removal efficiency														
VS	21.7	45.8	43.1	47.3	34.3	36.9	44.1	16.2	37.0	36.3	42.7	29.0	29.9	42.6
[%]	(8.7,14)	(1.0,14)	(1.8,14)	(1.9,14)	(2.5,14)	(2.3,14)	(1.9,14)	(8.9,14)	(2.4,14)	(6.0,14)	(2.3,14)	(2.8,14)	(1.7,14)	(1.4,14)
TS	15.2	37.8	33.1	34.3	28.8	36.9	34.0	10.6	32.0	27.5	35.2	24.2	28.2	34.0
[%]	(5.8,14)	(1.0,14)	(2.0,14)	(2.0,14)	(2.2,14)	(1.7,14)	(2.4,14)	(5.1,14)	(3.2,14)	(5.3,14)	(2.4,14)	(2.4,14)	(2.3,14)	(2.5,14)
TCOD	16.7	34.4	31.4	36.8	26.6	36.4	35.7	17.9	27.6	34.0	35.4	30.4	32.7	29.3
[%]	(7.3,14)	(2.7,14)	(5.5,14)	(7.1,14)	(9.6,14)	(6.8,14)	(10.1,14)	(6.3,14)	(5.4,14)	(6.3,14)	(4.4,14)	(6.7,14)	(5.5,14)	(3.3,14)
Biogas at STP	1.76	2.64	2.94	2.68	2.84	2.82	2.60	1.58	2.48	2.72	2.50	2.68	2.46	2.48
[L/L*/d]	(0.35,26)	(0.12,26)	(0.12,26)	(0.14,26)	(0.15,26)	(0.13,26)	(0.15,26)	(0.40,26)	(0.08,26)	(0.08,26)	(0.14,26)	(0.10,26)	(0.12,26)	(0.14,26)
CH_4	57	63	62	59	63	63	63	49	63	63	64	64	64	58
[%]	(4,9)	(1,9)	(1,9)	(1,9)	(1,9)	(0,9)	(1,9)	(11,9)	(1,9)	(1,9)	(1,9)	(1,9)	(1,9)	(4,9)
pH in reactors	7.19 (0.11,8)	7.45 (0.06,8)	7.55 (0.08,8)	7.42 (0.08,8)	7.53 (0.1,8)	7.57 (0.1,8)	7.5 (0.12,8)	6.34 (0.6,8)	7.07 (0.18,8)	7.07 (0.15,8)	7.04 (0.10,8)	7.07 (0.16,8)	7.2 (0.18,8)	7.02 (0.09,8)
Effluent supernatant characteristics														
SCOD	4,965	3,599	3,374	4,087	3,340	2,704	4,109	3,243	3,148	2,661	3,516	2,210	2,462	3,738
[mg/L]	(281,12)	(389,12)	(151,12)	(571,12)	(197,12)	(332,12)	(246,12)	(245,12)	(138,12)	(146,12)	(274,12)	(201,12)	(185,12)	(166,12)
NH_3-N	1,131	1,299	1,269	1,356	1,199	1,235	1,179	971	1,171	1,267	1,434	1,401	1,387	1,266
[mg/L]	(159,6)	(47,6)	(98,6)	(119,6)	(100,6)	(126,6)	(54,6)	(242,6)	(110,6)	(122,6)	(118,6)	(157,6)	(146,6)	(81,6)
Alkalinity	3,570	4,215	4,427	4,230	4,302	4,503	4,269	2,751	3,321	3,842	3,667	3,760	3,953	3,689
[mg $CaCO_3$/L]	(598,8)	(157,6)	(152,6)	(209,6)	(303,6)	(133,6)	(242,6)	(525,6)	(110,6)	(408,6)	(2934,6)	(174,6)	(216,6)	(297,6)
TVFA	1,949	1,626	1,391	1,539	1,385	992	1,330	1,824	1,414	1,412	1,292	1,115	1,284	1,911
[mg/L]	(729,12)	(735,8)	(451,8)	(478,8)	(630,8)	(557,8)	(499,8)	(362,12)	(193,8)	(386,8)	(568,8)	(191,8)	(468,8)	(588,8)

[a]MW: microwave, CH: conventional heating, OLR: organic loading rate,*liter of reactor, TVFA: total volatile fatty acids (summation of acetic, propionic and butyric acids), TS: total solids, VS: volatile solids, STP: 0^{o}C, 1 atm. †Data represent arithmetic mean of measurements (standard deviation, number of data points).

Figure 4.7 shows average daily methane production of reactors at standard temperature and pressure (STP; $0^{o}C$, 1 atm) for different SRTs. As it was expected, the daily methane production from digesters increased as the SRT was reduced due to increased organic loadings. The large standard deviation (error bars) for the control samples at the SRT of 5 days was due to the instable operation of controls. Furthermore, similar to solubilization and methane production results, ANOVA test showed that the heating method (conventional versus microwave) did not have statistically significant effect on biogas production (p-values > 0.05 for three different SRTs). Thus there was not any apparent athermal effect on biogas production for digesters being fed with MW pretreated sludge.

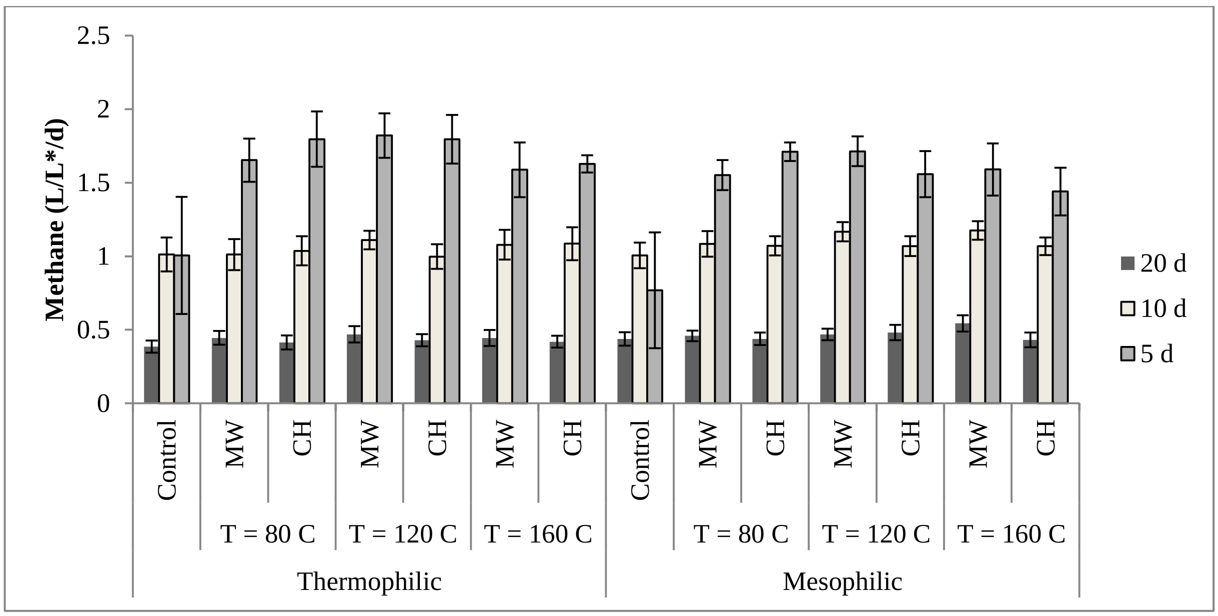

Figure 4.7 Average daily methane productions at STP ($0^{o}C$, 1 atm) for sludge retention time (SRTs) of 20, 10 and 5 days (L*: liter of reactor).

Mesophilic microorganisms are more tolerant to changes in environmental conditions than thermophilic microorganisms (Droste, 1997). Therefore, thermophilic digesters are less often applied in full-scale systems (Gavala et al., 2003). Although the increased temperatures facilitate faster hydrolysis and biodegradation rates in thermophilic systems, they are known to be less stable. Furthermore, the energy input is higher for thermophilic than mesophilic systems. In this study, digester temperature (mesophilic or thermophilic conditions) did not have a statistically significant effect on biogas production (p-value > 0.05) at three SRTs of

5, 10 and 20 days. This could be due to adequate acclimation (for 7 months) provided for both mesophilic and thermophilic inocula to the thermally pretreated DWSC prior to setting up SC digesters. Furthermore, as the thermal pretreatment accelerates the hydrolysis step and enhances the biodegradability of sludge, it may eliminate the need for thermophilic anaerobic digestion. However, this point needs to be re-evaluated after measuring coliform concentrations in the digestate samples as thermophilic digesters are often needed for digested biosolids to qualify as Class A under the BC Organic Matter Recycling Regulations (OMRR) if the final product is used as soil amendment without any restrictions (OMRR, 2008).

Figure 4.8 shows relative to control improvements in methane production. As the digester SRT was shortened, the improvements in methane production over controls increased. Although control digesters were challenged at the SRT of 5 days, all other digesters fed with pretreated sludge were capable of converting organics into biogas and they had > 50% increase in methane production over controls. Mesophilic digesters fed with MW pretreated sludge at 120^{o}C achieved the maximum improvement in methane production with 122% and 16% more methane compared to controls for SRTs of 5 and 10 days, respectively.

Table 4.8 shows the average methane yields from 14 anaerobic digesters operated at different SRTs. The maximum theoretical yield of methane is 0.35 m^3 CH_4/ kg COD removed at STP (Droste, 1997). It was observed that digesters operated at the SRT of 10 days had the highest methane yields under both mesophilic and thermophilic conditions.

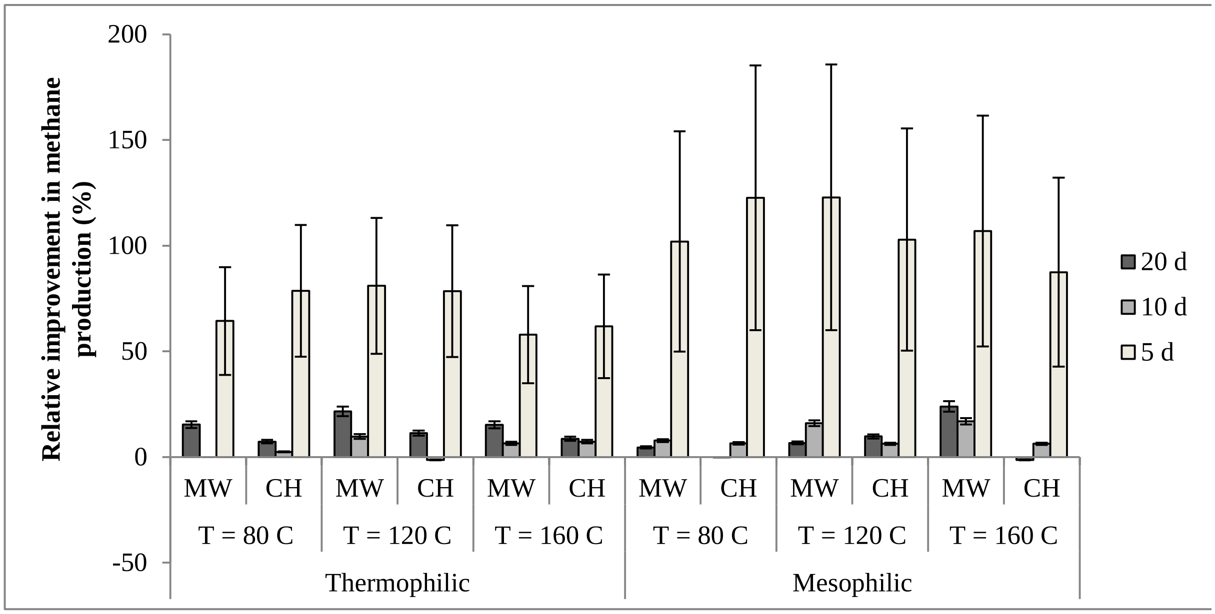

Figure 4.8 Relative (to control) improvement in methane productions at sludge retention time (SRTs) of 20, 10 and 5 days (MW: microwave, CH: conventional heating).

Organic removal efficiency of digestion is generally evaluated by VS or TCOD removals. As it can be seen from Tables 4.5, 4.6 and 4.7, although TS and VS removal performances of digesters decreased when the SRT was decreased, the relative to control removal values increased. Control digesters performed less efficiently at shorter SRTs and they could not tolerate the high organic loading rate at the SRT of 5 days.

Table 4.8 Methane yields (m^3/kg $COD_{removed}$ at STP) from control and pretreated digesters at sludge retention times (SRTs) of 20, 10 and 5 days (MW: microwave, CH: conventional heating).

	Thermophilics							**Mesophilics**						
SRT (d)	**Control**	**MW-80**	**MW-120**	**MW-160**	**CH-80**	**CH-120**	**CH-160**	**Control**	**MW-80**	**MW-120**	**MW-160**	**CH-80**	**CH-120**	**CH-160**
20	0.22†	0.26	0.25	0.26	0.21	0.28	0.22	0.25	0.27	0.25	0.31	0.22	0.31	0.23
10	0.29	0.30	0.29	0.32	0.30	0.33	0.28	0.31	0.33	0.31	0.35	0.31	0.35	0.28
5	0.14	0.25	0.26	0.24	0.26	0.28	0.26	0.11	0.24	0.25	0.24	0.25	0.25	0.23

†Data represent arithmetic mean of yields calculated from data collected during steady states. The standard deviations were less than 10% except for the controls at an SRT of 5 days due to unstable performance.

Figures 4.9 and 4.10 show improvements (relative to control) in TS and VS removal efficiencies for digesters fed with CH and MW irradiated sludge. As it is clear from the figures, the relative improvements in TS and VS removal efficiencies significantly increased as the SRT shortened. The relative improvement in TS removal efficiencies was respectively in the range of 128-232% and 89-149% for mesophilic and thermophilic digesters, fed with pretreated DWSC, at SRT of 5 days. Eskicioglu et al. (2007c) reported maximum of 32% relative improvement in TS removal at SRT of 5 days in a mesophilic digester fed with CH pretreated sludge sample at 96^{o}C under the OLR of 4.4 gr VS/L/d. The relative improvement values obtained in this study were much higher due to the failure of the control digesters at the shortest SRT of 5 days as well as higher pretreatment temperatures tested. However, the relative improvements in TS and VS removals at SRTs of 20 and 10 days were comparable with the results obtained by Eskicioglu et al. (2007c) and Toreci et al. (2009). Toreci et al. (2009) reported maximum of 10% relative improvement in VS removal for a single-stage mesophilic digester fed with MW irradiated sample at 175^{o}C and a cooking rate of 3.75^{o}C/min at SRT of 20 days. Similarly, the maximum relative improvement in VS removal was only 12% for mesophilic digesters fed with MW and CH pretreated sludge at 96^{o}C reported by Eskicioglu et al. (2007c) at an SRT of 20 days. All of these studies once again confirm that biodegradation rate improvements by thermal pretreatments become more pronounced at shorter SRTs.

Relative to control improvements for TCOD removal are plotted in Figure 4.11. Relative improvements in TCOD removal efficiencies were 54-132% in digesters fed with pretreated sludge at 5 days SRT. Similarly, there were only 2-31% improvement in TCOD removal efficiencies at an SRT of 10 days and the controls were performing as well as the other digesters at an SRT of 20 days. Toreci et al. (2009) reported about 70% improvement in TCOD removal for a mesophilic single-stage digester with 10 days SRT at pretreatment temperature of 175^{o}C at cooking rates of 1.25^{o}C/min. It was mentioned that reducing the SRT from 20 days to 10 days and then to 5 days improved VS, TS and TCOD relative removal efficiencies, but opposite results obtained for 5 days SRT at the low microwave intensity of 1.25^{o}C/min (Toreci et al., 2009).

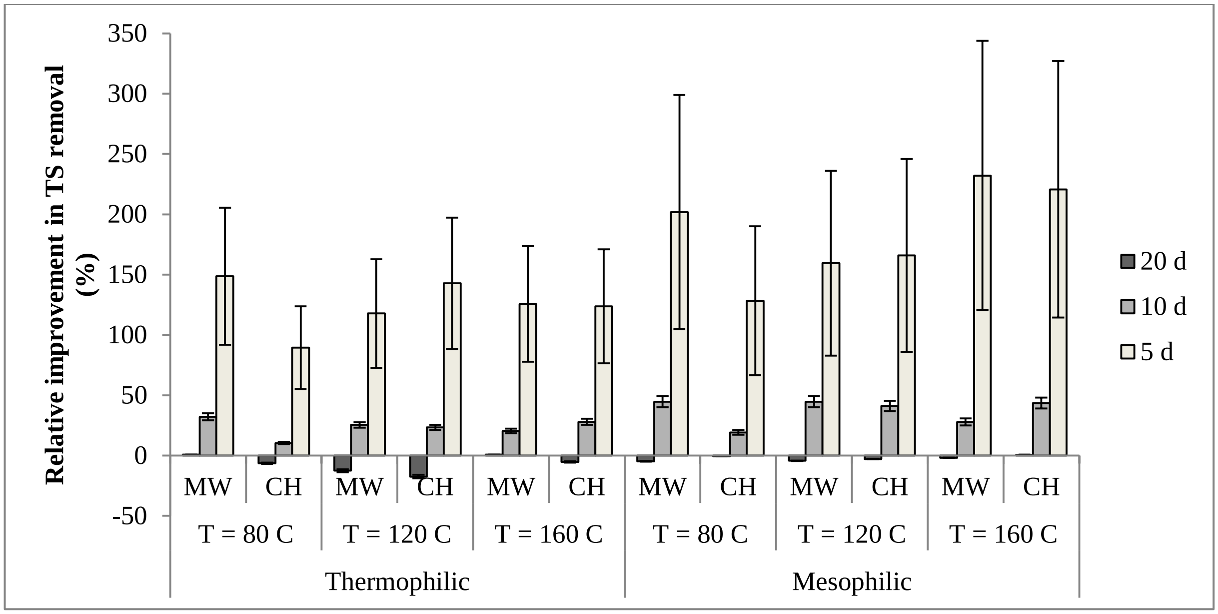

Figure 4.9 Relative (to control) improvement in total solids (TS) removal efficiencies at sludge retention times (SRTs) of 20, 10 and 5 days (MW: microwave, CH: conventional heating)

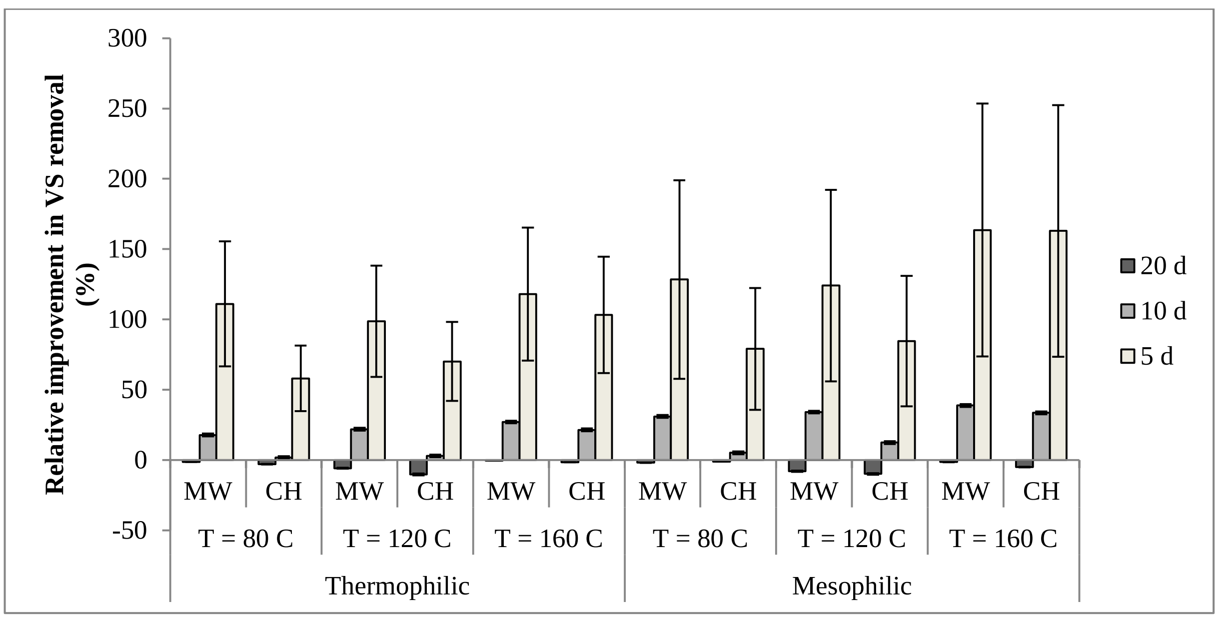

Figure 4.10 Relative (to control) improvement in volatile solids (VS) removal efficiencies at sludge retention times (SRTs) of 20, 10 and 5 days (MW: microwave, CH: conventional heating).

The results obtained in this study were logical, since pretreatments are known to increase the solubilization of sludge and accelerate the hydrolysis step of anaerobic digestion without changing the total organic material in the sample. Microorganisms have enough time for hydrolysis as well as methane conversion at longer SRTs, thus the effect of pretreatment on organic removal was not discernible, and for some scenarios yielded negative improvements relative to controls at SRT of 20 days. It is worth to mention that VS removal values are more reliable for judging the digesters performance, because of the high dilution ratios (1:200) used for TCOD analysis of dewatered sludge cake in the laboratory.

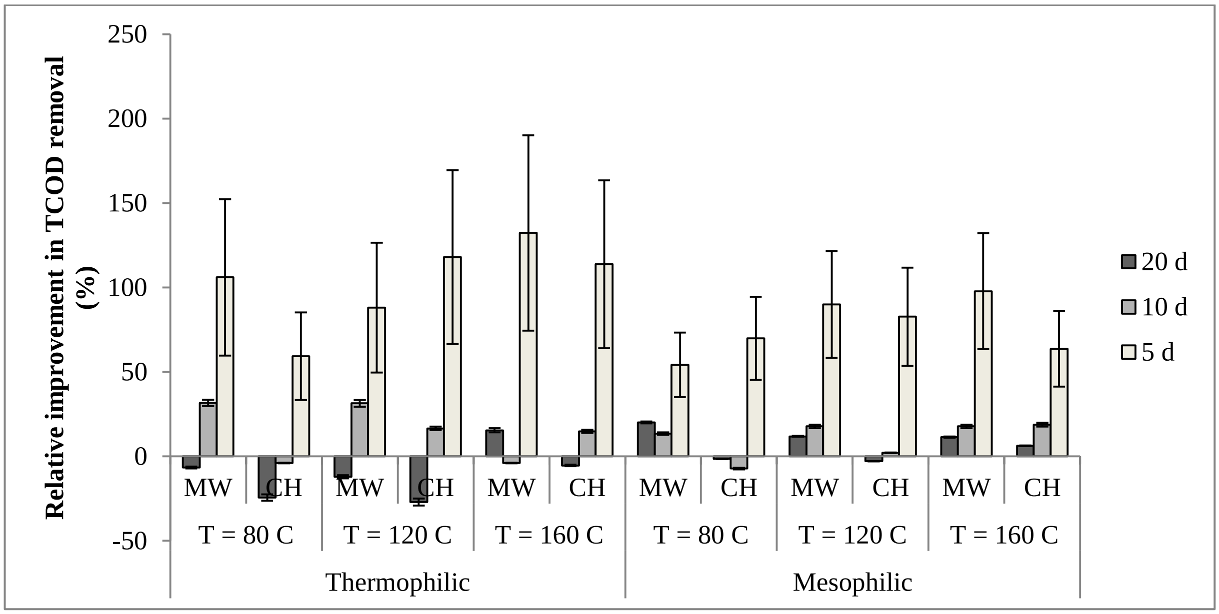

Figure 4.11 Relative (to control) improvement in total chemical oxygen demand (TCOD) removal efficiencies at sludge retention times (SRTs) of 20, 10 and 5 days (MW: microwave, CH: conventional heating).

4.4.1 Effect of pretreatment on digester effluent (digestate) supernatant characteristics

While VFA concentrations were negligible at SRTs of 20 and 10 days, the VFA content of digesters were much higher than the safe range of < 250 mg/L (Tchobanoglous et al., 1991) at an SRT of 5 days. As a consequence of the elevated levels of VFAs (~2,000 mg/L in Table 4.7), both mesophilic and thermophilic control digesters lost their activities after 12 days of operation under OLRs of 5.15 g VS/L/d and 6.96 g TCOD/L/d.

In this study, the alkalinity concentration of effluents (which is also representative of alkalinity of digester content) was also measured (Tables 4.5 - 4.7). Alkalinity is the most common chemical agent needed for pH control and in anaerobic digestion, the VFAs: alkalinity ratio should be less than the range of 0.3-0.4 (Droste, 1997). Alkalinity values were in the safe range for the digesters at SRT of 20 and 10 days. However, as expected from the instable operation, the VFAs: alkalinity ratios were 0.54 and 0.66 for thermophilic and mesophilic control digesters, respectively, at SRT of 5 days. It was interesting to note that, although the pretreated digesters were under the similar (highest) organic loading rates as the control digesters at the 5-d SRT, the VFA/alkalinity ratios were much lower (0.22-0.38 for thermophilic and 0.25-0.48 for mesophilic) in the pretreated digesters confirming higher VFA to methane conversion, therefore more stable operation.

The pH values were higher for thermophilic digesters compared to mesophilic ones. This was most likely related to the higher Henry's Law constants for CO_2 and lower liquid concentration of CO_2 with increasing temperature (Moen et al., 2003). In addition, higher pH values of thermophilic digesters may be due to their higher alkalinity values present compared to the mesophilic conditions in all SRTs (Tables 4.5 – 4.7).

Upon dewatering the anaerobically digested material, the centrate from the dewatering process have the potential to be a significant nitrogenous nutrient load to the mainstream wastewater treatment process as it is generally recycled back to the beginning of the treatment plant. Removal or reduction of nitrogen from wastewater is essential prior to discharge in order to control the growth of algae in the receiving water. Thus, the level of nitrogenous components in the supernatant of anaerobic digester is important. Total nitrogen is comprised of organic and inorganic nitrogen. Ammonia is the main component of inorganic nitrogen. Organic fraction consists of complex mixture of compounds including proteins, amino acids and amino sugars (Tchobanoglous et al., 1991). Organic nitrogen is determined analytically using Kjeldahl method. Total Kjeldahl nitrogen (TKN) is summation of total organic nitrogen and ammonia.

In this study, the ammonia concentration was measured in anaerobic digesters (Table 4.5-4.7). More ammonia was generated in digesters fed with pretreated sludge compared to controls due to higher solubilization and degradation efficiency of nitrogenous organic matter in pretreated digesters. Figure 4.12 shows the relative (to control) increase of ammonia concentrations in the digester supernatants. The maximum relative increase in ammonia concentration in digesters was 47 ± 1% for the mesophilic MW pretreated digester at 160°C and the SRT of 5 days.

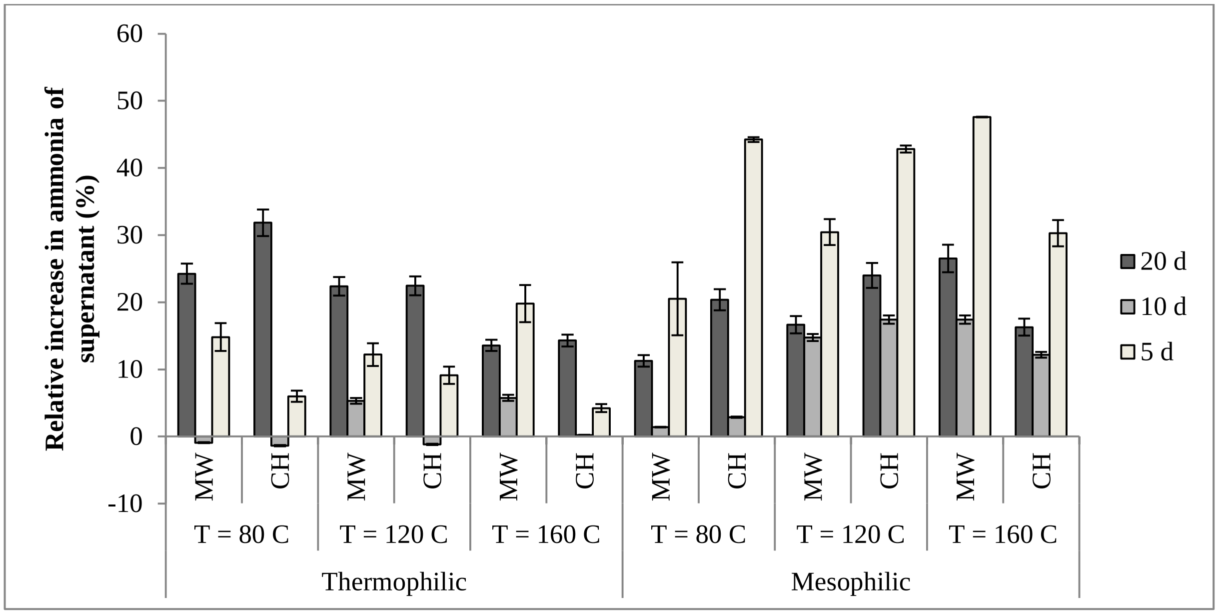

Figure 4.12 Relative (to control) increase in ammonia of digester supernatant at sludge retention times (SRTs) of 20, 10 and 5 days (MW: microwave, CH: conventional heating).

Ammonia toxicity generally occurs in anaerobic treatment of sludge with high concentration of proteins and/or amino acids. Moen et al. (2000) reported no inhibitory effects for mesophilic and thermophilic anaerobic digestion of municipal sludge up to the concentrations of 1,900-2,400 mg/L ammonium. In this study, the ammonium concentration in digesters were less than 1,900 mg/L for SRTs of 5, 10 and 20 days, and all digesters were able to tolerate ammonia concentrations without noticeable effect on methane production.

4.5 Energy assessment of pretreatment techniques for full-scale digester scenarios

An energy analysis was performed for digestion scenarios in terms of net energy production, i.e., electrical energy consumption minus recovery associated with methane production. Table 4.9 shows the electrical energy consumed by the sludge samples for thermal hydrolysis of sludge by both MW and CH units at identical cooking rate of 7.5°C/min. Although no energy was used for pretreating the sludge feed for the control digesters, the amount of input energy used to increase the temperature of the feed sludge from room temperature (21°C) to the digestion temperatures (35°C for mesophilic and 55°C for thermophilic) was considered in net energy calculation. Heat capacity of feed of digesters assumed to be similar to heat capacity of water (4.18 J $K^{-1}g^{-1}$).The amount of energy was calculated according to equation (4-1) below:

$$Q = m\,C\,(T_2-T_1) \tag{4-1}$$

Where Q is the amount of energy used to increase the temperature of the feed (J/d), m is mass flow rate of the feed (g/d), C is heat capacity of the feed J $K^{-1}g^{-1}$, T_1 : room temperature (21°C) and T_2: digestion temperature (°C). Furthermore, it was assumed that pretreated digesters did not need additional energy for heating the digesters themselves. Details of calculations for total and actual energy delivered to the sample during bench-scale heating by both MW and CH unit can be found in Appendix C.

Table 4.9 Daily actual energy delivered to the feed of anaerobic digesters during pretreatment

Digester	Input energy (GJ/d/Tonne TS $_{added}$)
Control (mesophilic)*	1.87
Control (thermophilic)*	4.53
MW-80	3.48
MW-120	5.18
MW-160	9.32
CH-80	2.60
CH-120	4.47
CH-160	6.95

*Energy for increasing the feed temperature from room temperature (T1 = 21°C) to digestion temperature (T2 = 35°C) for mesophilic and (T2 = 55°C) for thermophilic control digesters. Control feeds were assumed to be heated at 3.5% total solids concentrations. However, the rest of the digesters utilized pretreated sludge at 18% total solids and then diluted to 3.5% concentrations.

As mentioned before, methane content of biogas produced by the digesters varied in 60-67% range except for the control digesters at the SRT of 5 days. Energy of biogas is entirely associated with methane which has 37 MJ/m^3 energy content (Droste, 1997). The characteristics of the full scale digester designed for digestion of the City of Kelowna's biosolids are presented in Table 4.10. Average historical data (1/1/2007-1/31/2011) of WWTP showed that daily production of DWSC is 52,423 kg/d with 18.8% total solids content. Therefore 9,856 kg of dry solids are added to digester each day. As it can be seen from Table 4.10, if thermal pretreatments are applied, digesters have the potential to be stable at the SRT of 5 days. Therefore, the total volume required for digestion of biosolids can be decreased from 4,380 m^3 (at SRT of 20 days) to 1,095 m^3 (at SRT of 5 days). Figure 4.13 shows the daily amount of the energy produced by digesters at different SRTs. The maximum energy efficiency was obtained by the digesters at SRT of 10 days.

Table 4.10 Specification of Kelowna's full scale digester case study

Input biosolids							
Kelowna dewatered sludge cake production (kg/d)			52,423				
Average sludge cake TS%			18.8				
Digester feed TS% (after dilution with leachate/water)			4.5				
Average total solids fed to the digester (kg/d)			9,856				
		Control			†CH - 80		
Sludge retention time (SRT)		**20 d**	**10 d**	[1]**5 d**	**20 d**	**10 d**	**5 d**
OLR (g TS/L*/d)		2.25	4.50	9.0	2.25	4.50	9.0
OLR (g VS/L*/d)		1.73	3.46	6.93	1.73	3.46	6.93
Digester VS removal (%)	Thermophilic	56.7	44.4	21.7	55.0	45.2	34.3
	Mesophilic	53.9	38.7	16.2	53.3	40.7	29.0
Biogas Volume (m^3/d)[a]	Thermophilic	3,251 ± 131	3,979 ± 197	2,466 ± 383	3,587 ± 175	4,372 ± 153	3,979 ±154
	Mesophilic	3,699 ± 175	4372 ± 131	2,214 ± 438	3,811 ± 175	4,596 ± 109	3,755 ±109
Methane (m^3/d)[a]	Thermophilic	2,145 ± 87	2626 ± 130	1,405 ± 218	2,332 ± 114	2,885 ± 101	2,507 ± 103
	Mesophilic	2,440 ± 116	2,798 ± 84	1,085 ± 214	2,476 ± 114	2,987 ± 71	2,403 ± 70
Net energy (GJ/d)	Thermophilic	42.3 ± 4.5	60.8 ± 5.6	11.9 ± 4.7	61.8 ± 6.9	83.8 ± 8.0	69.2 ± 7.2
	Mesophilic	80.5 ± 8.3	94.9 ± 8.8	24.9 ± 12.7	67.1 ± 6.4	87.4 ± 5.4	64.7 ± 4.7
Digester volume (m^3)		4,380	2,190	1,095	4,380	2,190	1,095

[a]at STP (0°C, 1atm), *liter of reactor, CH: conventional heating, TS: total solids, [1]control digesters were not stable at SRT of 5 days, †maximum net energy scenario

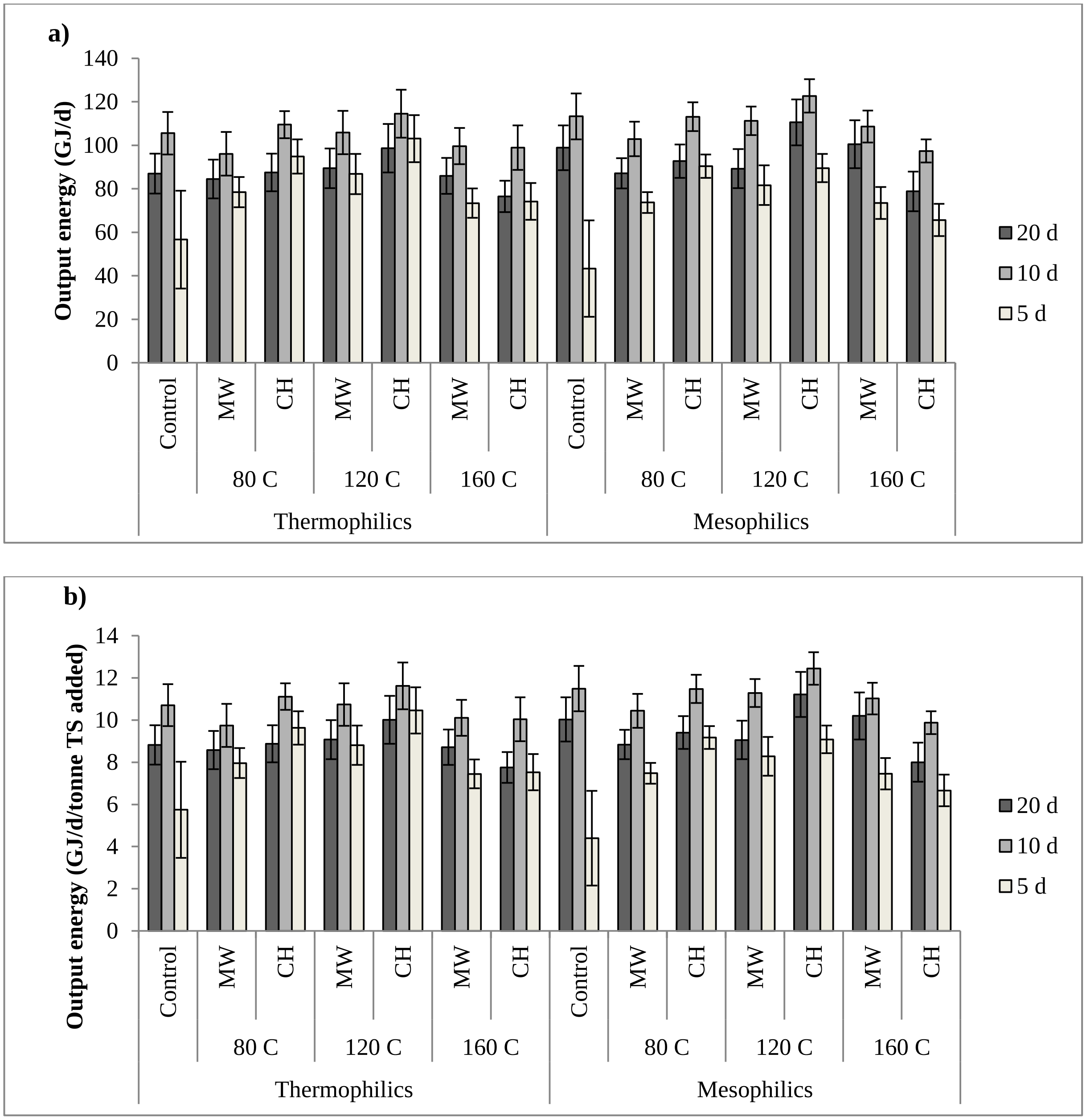

Figure 4.13 Daily output energy via methane from semi-continuous anaerobic digesters. (Control: untreated sludge, MW: microwave, CH: conventional heating, 80, 120, 160^{o}C represent pretreatment temperatures).

Figure 4.14 displays the results of net energy calculation. As it can be seen from the figure, at elevated pretreatment temperature of 160^{o}C, the amount of methane recovered at the highest organic loading of 5.66 ± 0.11 g VS/L/d (corresponding SRT of 5 d) was not enough to compensate for the energy input yielding negative energy productions. Among the digesters with positive net energy productions, digesters operated at SRT of 10 were more favorable and maximum net energy was achieved by mesophilic control (94.8 GJ/d) and conventionally pretreated digester at 80^{o}C (87.4 GJ/d) respectively. In addition to maximum net energy production, all the digesters operated at 10 days SRT were more stable during the operation (less variation from the average performance data) and did not show VFA accumulation compared to digesters at a 5-d SRT. Furthermore, although the pretreated digesters achieved near stable operation at an SRT of 5 days, this may not provide enough safety factor for a full-scale digester, therefore may not be chosen as the design SRT.

It is necessary to emphasize that at the full-scale, extra heat from the pretreated scenarios at elevated temperatures can be recovered and contribute positively to the energy balance. Furthermore, the energy input of the samples for a larger scale implementation need to be examined to verify the efficiencies of the heating systems before the full-scale application.

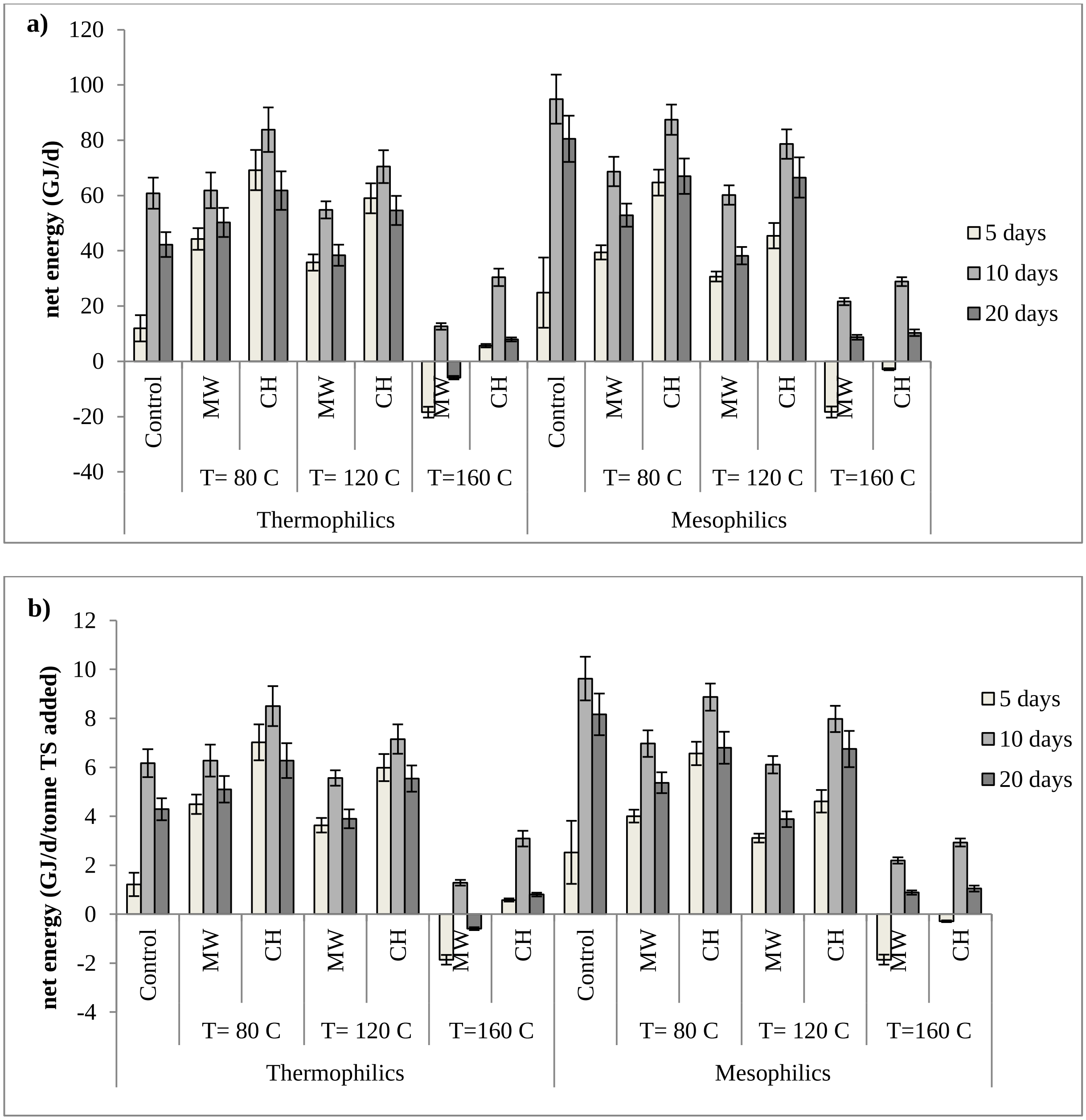

Figure 4.14 Net energy (output-input) analyses of full scale digesters. (Control: untreated sludge, MW: microwave, CH: conventional heating, 80, 120, 160^{o}C represent pretreatment temperatures).

4.6 Land application of digested biosolids

Addition of digested biosolids to soil improves the condition of soil for germination and growth. For instance, application of 450 tonne/ha of sewage sludge on a Sandy loam increased the potato yield from 18,500 kg/ha to 66,600 kg/ha (Larson et al., 1974; Sanin et al., 2011). However, stringent regulations have been established by governments for land application of waste sludge to protect the society. These regulations must be considered in selecting appropriate methods for processing, reuse and disposal of biosolids produced in anaerobic digestion. In British Columbia, the biosolids should meet the guidelines and numerical limits established by BC Ministry of Environment (OMRR, 2008) for the reuse and disposal of solids generated from processing of municipal wastewater.

4.6.1 Pathogens

OMRR (2008) regulations provide maximum allowable values for both fecal coliform as well as trace elements in the digested biosolids to qualify as Class A or Class B biosolids. Class A biosolids are the highest quality biosolids achievable under the OMRR. They contain lower fecal coliform densities (<1,000 most probable number or MPN per g dry biosolids) and lower trace element concentrations than Class B biosolids. Class B biosolids are allowed to contain higher fecal coliform densities (<2,000,000 most probable number or MPN per g dry biosolids) and less stringent trace elements. However, there are more restrictions on land application and distribution of Class B compared to Class A biosolids.

Previous digester studies showed that thermal pretreatment methods are capable of destructing coliforms to generate Class A biosolids, and fecal coliforms were not detected after MW irradiation of primary sludge at 65^{o}C and 85^{o}C for waste activated sludge (Hong et al., 2006). In this study, total coliforms and E.coli were measured in effluents of digesters at an SRT of 10 days to assess the adequacy of the process to produce Class A or B biosolids according to OMRR requirements. Coelho et al. (2011) suggest that the minimum of 10 days SRT is necessary for complete removal of pathogenic bacteria in mesophilic (35 ± 2^{o}C) or thermophilic (55 ± 2^{o}C) temperatures. Total coliforms are a broader class of coliforms and they are usually more numerous than the fecal coliforms. Results are presented in Table 4.11. As it can be seen from the table, all mesophilic digesters have very high coliform densities (> 5×10^{6} MPN per g dry weight) and therefore could not be classified as Class B or Class A. Among the thermophilic digestates, CH digesters at 80 and 160^{o}C as well as MW 120 had coliform densities lower than the Class A limits. The rest of the thermophilic digestates classified as Class B biosolids in terms of coliform concentrations.

Although results presented in Table 4.11 indicated lower coliform concentrations for thermophilic compared to mesophilic digesters as expected, the fact that samples from digesters pretreated at similar temperatures by MW and CH indicated different coliform concentrations needs further testing to explain.

Table 4.11 Coliform content of effluents from anaerobic digesters at SRT of 10 days.

		Class A Biosolids*	Class B Biosolids *	Control	MW80	CH80	MW120	CH120	MW160	CH160	RDL*
				Coliforms (MPN/gr dw)							
Thermophilics	**Coliforms, Total (MPN)**	**<1,000**	**<2,000,000**	1,934	2,547	515	502	3,298	1,971	515	6
	E. coli (MPN)			1,934	2,547	515	199	3,298	1,971	197	6
Mesophilics	**Coliforms, Total (MPN)**			24,665,880	10,328,425	25,781,736	10,351,035	24,585,696	24,923,507	5,402,448	6
	E.coli (MPN)			24,665,880	10,328,425	25,781,736	10,351,035	24,585,696	24,923,507	5,402,448	6

RDL: reported detection limit, **MPN:** most probable number

The values reported are for 10 days SRT, *obtained from: (OMRR, 2008)

4.6.2 Total Kjeldahl nitrogen (TKN)

Annual loading of biosolids are typically limited by plant uptake rate and other losses of nutrients. Most often, the limiting nutrient is nitrogen (Sanin et al., 2011). Application of ammonia and mineralization of organic nitrogen produces nitrate in aerobic environment. Nitrate is highly soluble and it is a direct health concern in groundwater that may be used as a source of drinking water (Sanin et al., 2011). Under the OMRR, class A or class B biosolids that meet class A pathogen and vector attraction reduction requirements can be used as a component of biosolids growing medium (BGM). Table 4.12 shows the TKN values measured for the effluents of digesters at SRT of 10 days. The TKN measurements were more than 7% in both mesophilic and thermophilic digester. However, according to the OMRR guidelines the TKN <0.6% is required in BGM. Thus the class A and class B biosolids produced in the digester can be mixed with other organic and inorganic feedstock materials to produce the BGM (OMRR, 2008). Although the C/N ratio was not regulated for digested biosolids, the C/N ratio of (>15:1) is required for BGM (OMRR, 2008).

Table 4.12 Total Kjeldahl nitrogen of the supernatant at SRT = 10 d. (MW: microwave, CH: conventional heating, w_d: dry weight, RDL: reported detection limit, pretreatment temperature: 80, 120 and 160^{o}C)

		Control	MW-80	CH-80	MW-120	CH-120	MW-160	CH-160	RDL
Thermophilics	(mg/L)	2150	2040	2050	1730	2190	2150	1930	50
	(w/w_d %)	10.34	9.61	9.15	7.93	9.96	10.15	8.89	
	*C/N [g TCOD/ g organic N]	16.5	18.8	17.4	27.8	13.6	17.5	21.0	
Mesophilics	(mg/L)	2280	2160	2520	2090	2280	2270	2090	50
	(w/w_d %)	10.17	9.62	10.75	9.29	10.20	9.29	9.28	
	C/N [g TCOD/ g organic N]	11.8	13.6	10.1	15.4	13.1	11.4	14.4	

*organic N = TKN-ammonia

4.6.3 Heavy metals

Heavy metals retained in the biosolids from the influent wastewater during biological treatment process are major restrictive agricultural use of sludge (Wang et al., 2006). Heavy metals are non-biodegradable; they accumulate in environment and pose eco-toxicity (Lester et al., 1983). The amount of trace metals including regulated heavy metals under OMRR (2008) from the digester effluents were measured at SRT of 5 days (at the highest loading to determine maximum concentration) and reported in Table 4.13 and Table 4.14 for thermophilic and mesophilic digesters, respectively. This information can be used to assess the potential mobility or bioavailability of these metals, and provide evidence on the suitability and feasibility of the sewage disposal for land application. Experimental data revealed that chromium and copper were present in both thermophilics and mesophilic effluents. Thus neither of the digestates could be classified as Class A biosolids according to the heavy metal concentration ceiling limits given in OMRR (2008). However, digestates can be classified as Class B biosolids.

Table 4.13 Metal content of effluents from thermophilic anaerobic digesters at SRT = 5 days[a]

	Class A Biosolids*	**Class B Biosolids**	Control	MW80	CH80	MW120	CH120	MW160	CH160	**RDL**
			Results (mg/kg dw)							
Aluminum	n/r	n/r	4500	4900	5300	4000	5900	5300	6600	20
Antimony	n/r	n/r	2	2	2.1	2	2.2	2.1	2.1	0.1
Arsenic	n/r	n/r	2.3	1.9	2	2.1	2	2.2	2.1	0.4
Barium	n/r	n/r	180	190	190	180	190	200	200	1
Beryllium	n/r	n/r	<0.1			<0.1	<0.1	<0.1	<0.1	0.1
Bismuth	n/r	n/r	27	25	25	24	25	27	27	0.1
Boron	n/r	n/r	41	43	40	43	49	40	47	2
Cadmium	**20**	**20**	1.2	1.2	1.1	1.1	1.1	1.4	1.2	0.04
Calcium	n/r	n/r	18000	19000	18000	18000	19000	20000	19000	100
Chromium	**0**	**1,060**	18	18	18	17	19	19	19	1
Cobalt	**150**	**150**	1.9	2	2	1.9	2	2.1	2	0.1
Copper	**0**	**2,200**	920	920	1100	920	1400	980	1500	0.2
Iron	n/r	n/r	4300	4300	4200	4000	4200	4500	4400	20
Lead	**500**	**500**	22	21	20	20	19	23	21	0.2
Lithium	n/r	n/r	2	1.9	1.8	1.6	1.8	1.8	1.8	0.1

	Class A Biosolids*	Class B Biosolids	Control	MW80	CH80	MW120	CH120	MW160	CH160	RDL
			Results (mg/kg dw)							
Magnesium	n/r	n/r	10000	11000	12000	13000	12000	11000	10000	10
Manganese	n/r	n/r	140	140	130	130	130	150	140	0.4
Mercury	**5**	**15**	1.2	1.5	1.3	1.1	1.2	1.3	1.2	0.05
Molybdenum	**20**	**20**	11	11	10	11	11	11	11	0.1
Nickel	**180**	**180**	15	15	14	15	16	15	15	0.4
Phosphorus	n/r	n/r	33000	36000	35000	38000	38000	35000	35000	10
Potassium	n/r	n/r	11000	11000	10000	12000	13000	12000	12000	10
Selenium	**14**	**14**	5.9	5.8	5.5	5.7	5.5	6	5.6	0.5
Silicon	n/r	n/r	<3000			<3000	<3000	<3000	<3000	3000
Silver	n/r	n/r	4.8	5.1	5.4	4.6	4.5	4.7	5.1	0.2
Sodium	n/r	n/r	14000	11000	10000	15000	14000	14000	13000	40
Strontium	n/r	n/r	170	150	150	160	160	170	180	0.2
Sulfur	n/r	n/r	5800	6700	6500	6000	6800	7000	6800	1000
Tellurium	n/r	n/r	<0.1			<0.1	<0.1	<0.1	<0.1	0.1
Thallium	n/r	n/r	<0.1			<0.1	<0.1	<0.1	<0.1	0.1
Thorium	n/r	n/r	<0.5	0.7		<0.5	<0.5	<0.5	<0.5	0.5

	Class A Biosolids*	**Class B Biosolids**	Control	MW80	CH80	MW120	CH120	MW160	CH160	
			Results (mg/kg dw)							**RDL**
Tin	n/r	n/r	25	25	25	25	26	27	27	0.2
Titanium	n/r	n/r	54	60	60	49	59	55	57	2
Uranium	n/r	n/r	13	13	12	13	12	13	12	0.1
Vanadium	n/r	n/r	6.1	6.4	5.8	5.6	6	6.5	6.3	0.4
Zinc	**1,850**	**1,850**	450	450	440	450	470	470	520	2
Zirconium	n/r	n/r	20	22	23	17	24	19	29	2

[a]MW: microwave; CH: conventional heating; dw: dry weight; RDL: reported detection limit, n/r: not regulated; 80, 120, 160 indicate pretreatment temperatures at 80, 120, 160^{o}C

Table 4.14 Metal content of effluents from mesophilic anaerobic digesters at SRT = 5 days[a]

	Class A Biosolids	Class B Biosolids	Control	MW80	CH80	MW120	CH120	MW160	CH160	RDL
			Results (mg/kg dw)							
Aluminum	n/r	n/r	2700	4800	5200	3800	5600	4700	7300	20
Antimony	n/r	n/r	1.2	2	2.1	2	2.1	2.2	2.2	0.1
Arsenic	n/r	n/r	1.2	2	1.9	2.1	1.9	2.1	2.1	0.4
Barium	n/r	n/r	110	190	180	180	180	180	220	1
Beryllium	n/r	n/r	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
Bismuth	n/r	n/r	18	26	24	25	25	26	27	0.1
Boron	n/r	n/r	24	37	40	37	42	35	42	2
Cadmium	**20**	**20**	0.83	1.2	1.1	1.1	1.1	1.2	1.3	0.04
Calcium	n/r	n/r	11000	17000	17000	17000	18000	19000	19000	100
Chromium	**0**	**1060**	12	18	17	18	18	18	19	1
Cobalt	**150**	**150**	1.3	2	1.8	1.9	2	2	1.8	0.1
Copper	**0**	**2200**	510	900	1000	890	1300	890	1600	0.2
Iron	n/r	n/r	2700	4200	4000	4100	4200	4400	4400	20
Lead	**500**	**500**	13	20	19	21	19	22	21	0.2
Lithium	n/r	n/r	1.2	1.7	1.9	1.7	1.7	1.9	1.9	0.1

	Class A Biosolids	Class B Biosolids	Control	MW80	CH80	MW120	CH120	MW160	CH160	RDL
			Results (mg/kg dw)							
Magnesium	n/r	n/r	7200	11000	12000	11000	12000	11000	13000	10
Manganese	n/r	n/r	87	130	130	130	130	140	130	0.4
Mercury	**5**	**15**	0.63	1.9	1.3	1.3	1.1	1.1	1.4	0.05
Molybdenum	**20**	**20**	6.5	11	10	11	11	11	11	0.1
Nickel	**180**	**180**	8.9	14	14	15	15	15	15	0.4
Phosphorus	n/r	n/r	22000	35000	37000	35000	36000	33000	38000	10
Potassium	n/r	n/r	8100	11000	11000	12000	10000	11000	12000	10
Selenium	**14**	**14**	3.3	5.3	5.1	5.6	5.5	5.3	5.3	0.5
Silicon	n/r	n/r	<3000	<3000	<3000	<3000	<3000	<3000	<3000	3000
Silver	n/r	n/r	2.7	5	5.6	4.6	4.5	4.5	5.2	0.2
Sodium	n/r	n/r	9100	11000	11000	14000	12000	12000	13000	40
Strontium	n/r	n/r	98	150	150	150	170	160	170	0.2
Sulfur	n/r	n/r	3700	6800	6700	6500	7100	6700	6900	1000
Tellurium	n/r	n/r	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
Thallium	n/r	n/r	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
Thorium	n/r	n/r	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5

	Class A Biosolids	Class B Biosolids	Control	MW80	CH80	MW120	CH120	MW160	CH160	RDL
			Results (mg/kg dw)							
Tin	n/r	n/r	14	24	24	24	25	26	27	0.2
Titanium	n/r	n/r	46	68	62	44	56	48	86	2
Uranium	n/r	n/r	7.9	13	12	13	12	12	12	0.1
Vanadium	n/r	n/r	3.4	5.9	5.4	5.5	5.7	6.1	6.3	0.4
Zinc	**1850**	**1850**	280	450	430	430	470	450	540	2
Zirconium	n/r	n/r	12	18	23	19	23	18	35	2

[a]MW: microwave; CH: conventional heating; dw: dry weight; RDL: reported detection limit, n/r: not regulated; 80, 120, 160 indicate pretreatment temperatures at 80, 120, 160^{o}C

Chapter 5 Conclusions

5.1 Summary

This research was completed in two stages. First the effects of MW and CH were investigated on hydrolysis of particulate COD and biopolymers. Thermal pretreatment was done at temperatures below and above boiling points (80, 120 and 160^{o}C) and heating rate of 7.5^{o}C/min. A programmable custom built pressure sealed vessel was used to systematically compare MW and CH methods for the first time. Then the anaerobic digester studies started with acclimation of mesophilic and thermophilic anaerobic inocula to thermally pretreated (at 175^{o}C) biosolids at 18% total solids (TS) concentration. Pretreated biosolids were diluted and fed to the digesters. Upon achieving acclimation, fourteen lab-scale digesters (total and wet volumes of 1 and 0.5 L, respectively), set-up with acclimatized inocula, were operated for 5 months to optimize energy (methane) output and SRT requirements of untreated (control) and thermally pretreated digesters. Digestion operation was first started at a typical SRT of 20 d used in anaerobic digestion. The reactors were operated until reactors reached steady-state conditions and then maintained in this state over a period of three SRTs. Then the SRT was reduced to 10 and 5 days.

Based on the experimental data and analysis the following conclusions are drawn:

1. Heating method (conventional versus microwave) had no statistically significant effect ($p>0.05$) on biosolids solubilization. At similar temperatures, both conventional and microwave heating achieved similar COD solubilization ratios which were also confirmed by biopolymer (protein, sugar and humic acids) solubilization experiments.

2. Both conventional heating and microwave pretreatments indicated that in a pretreatment range of 80-160^{o}C, temperature was a statistically significant factor ($p<0.05$). Also, there was a linear relation between pretreatment temperature and level of hydrolysis. SCOD/TCOD ratios (%) increased from 8% (control; un- pretreated) to 16%, 18% and 26% at MW pretreatment temperatures of 80, 120 and 160^{o}C, respectively. In this study mineralization was not statistically significant and VS/TS ratios remained constant (85 ± 1%) for all pretreatment temperatures.

3. Digesters daily methane production increased as the SRT was reduced. Both mesophilic and thermophilic control (untreated) digesters showed instable operation at SRT of 5 days, while pretreated digesters were stable and continued producing biogas. Control digesters stopped producing biogas after 20 days of operation with total VFA concentrations exceeding 1,818.4 mg/L at pH < 5.64 for mesophilic and 2,853 mg/L at pH < 7.02 for thermophilic controls.

4. Relative (to control) organic removal efficiencies, in terms of TS, VS and COD concentrations, dramatically increased as SRT was shortened from 20 to 10 and 5 days, indicating that the control digesters were challenged as the organic loading rate was increased.

5. Similar to solubilization results, the heating method (conventional versus microwave) had no statistically significant effect ($p > 0.05$) on methane production at all three SRTs. There was no pattern of MW digesters showing better performances due to *athermal* effects. Therefore, any possible MW *athermal* effects were smaller than *thermal* effects at the applied pretreatment temperatures.

6. Although statistical analysis showed that two populations (methane productions from control and pretreated digesters) were significantly different ($p < 0.05$), but the increase in the pretreatment temperature above $80^{o}C$ did not significantly increase the methane production. Therefore the lowest pretreatment temperature tested ($80^{o}C$) was sufficient for enhancing methane recovery.

7. Net energy analysis showed that maximum energy recovery (55 – 95 GJ/d) was achieved at SRT of 10 days and pretreatment temperatures less than $160^{o}C$ for a full scale digester with the volume of 2190 m^3, 4.5 %TS and dry solid input of 9.9 Tonne TS/d.

8. All thermophilic digestates classified as Class B biosolids in terms of both coliform concentrations and heavy metal concentration. Although few digesters had coliform concentrations less than OMRR (2008) ceiling limits for Class A biosolids, they were classified as Class B due to presence of chromium and copper. Mesophilic digestates had high amount of coliforms and further treatment is needed before land application.

5.2 Recommendations for future work

This work presented the effect of thermal hydrolysis on anaerobic digestion of municipal biosolids in lab scale semi-continuous digesters. Microwave and conventional heating methods were compared systematically to optimize the SRT, methane recovery and organic removal efficiency. The followings are some suggested future research areas:

1. Application of other pretreatment methods such as ultrasound, alkaline and etc. before anaerobic digestion of biosolids to compare them with thermal pretreatment.
2. Microscopic analysis pretreated biosolids in order to see the effect of pretreatment on flocs structure and biological activity.
3. Dewaterability of digestate should be investigated. Improvements in dewaterability could be a benefit for the anaerobic digestion process.
4. Comprehensive cost and benefit analysis including the capital cost of equipment needed for pretreatment should be done in addition to energy assessment. The result would be beneficial for making the final decision about the pretreatment method to be used for the full scale digester.

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Appendices

Appendix A

A.1 Calibration curves

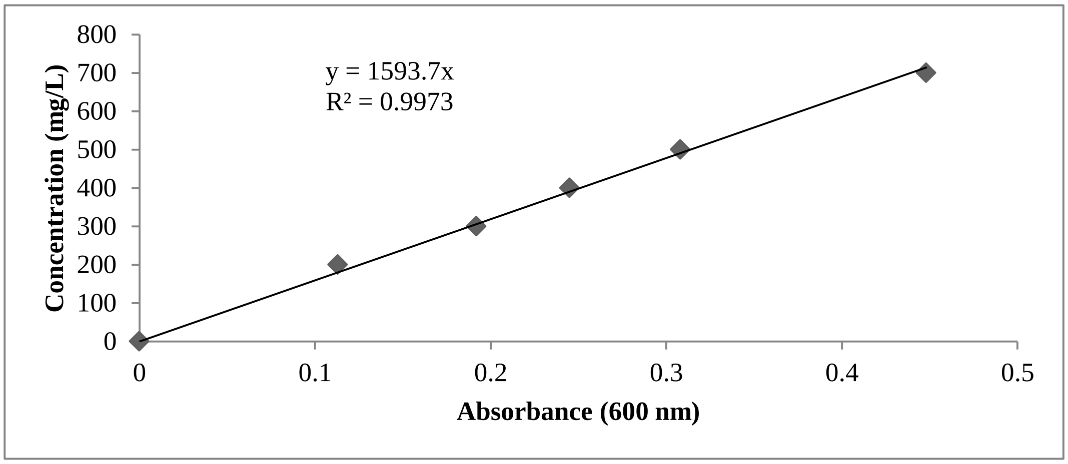

Figure A.1 Calibration curve for COD determination

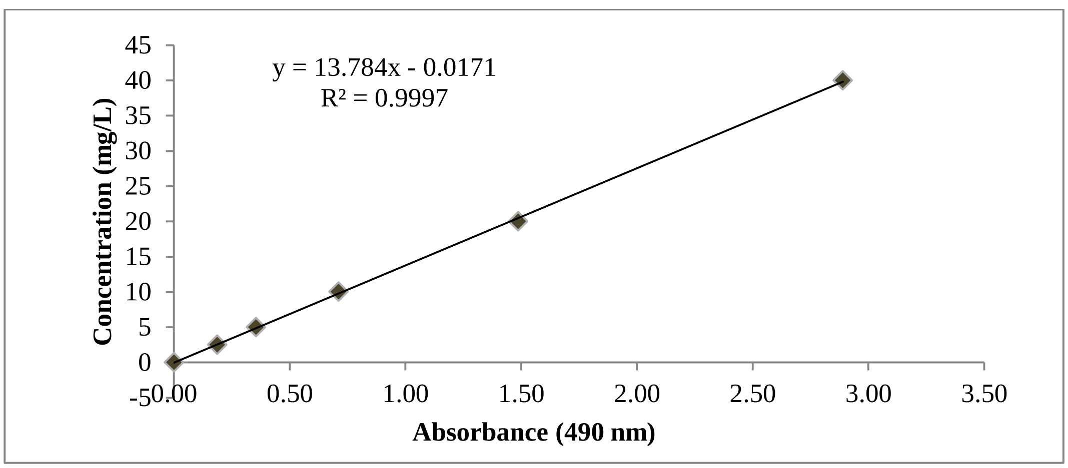

Figure A.2 Calibration curve for sugar determination

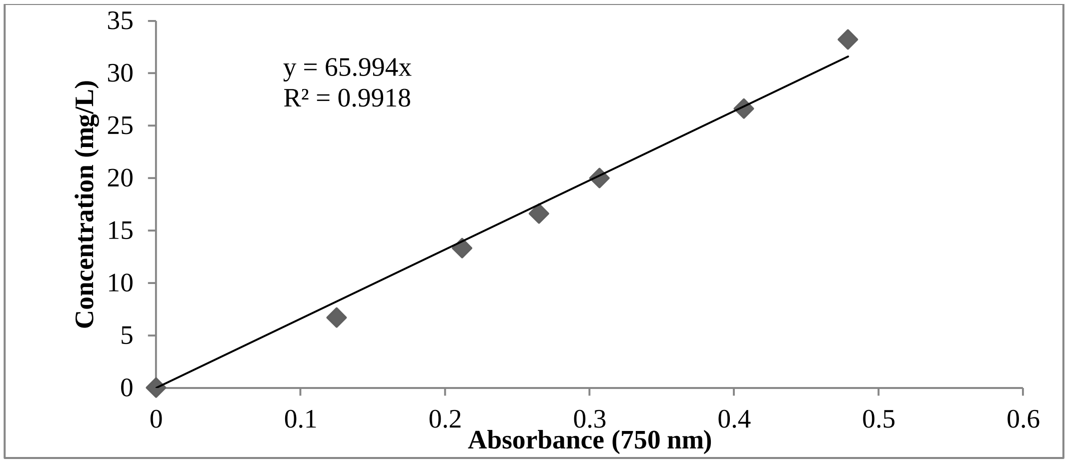

Figure A.3 Calibration curve for protein determination

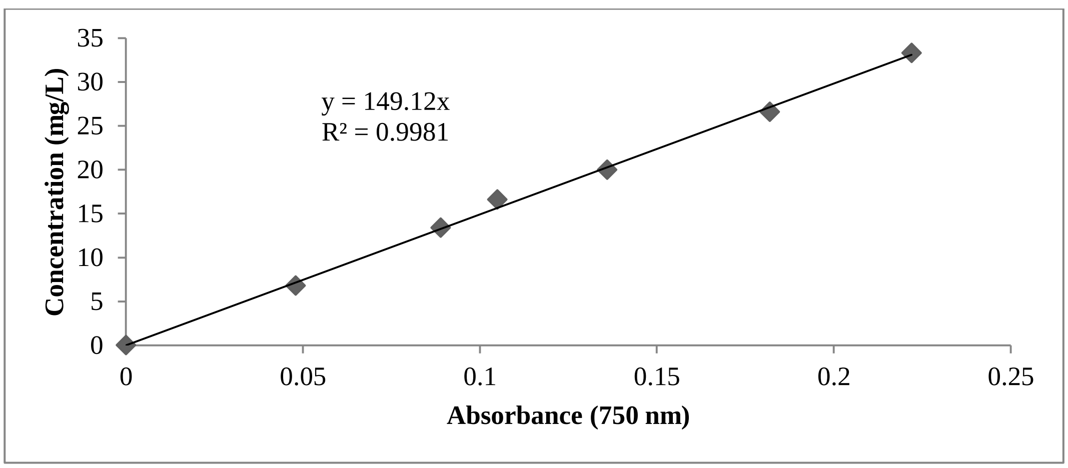

Figure A.4 Calibration curve for humic acid determination

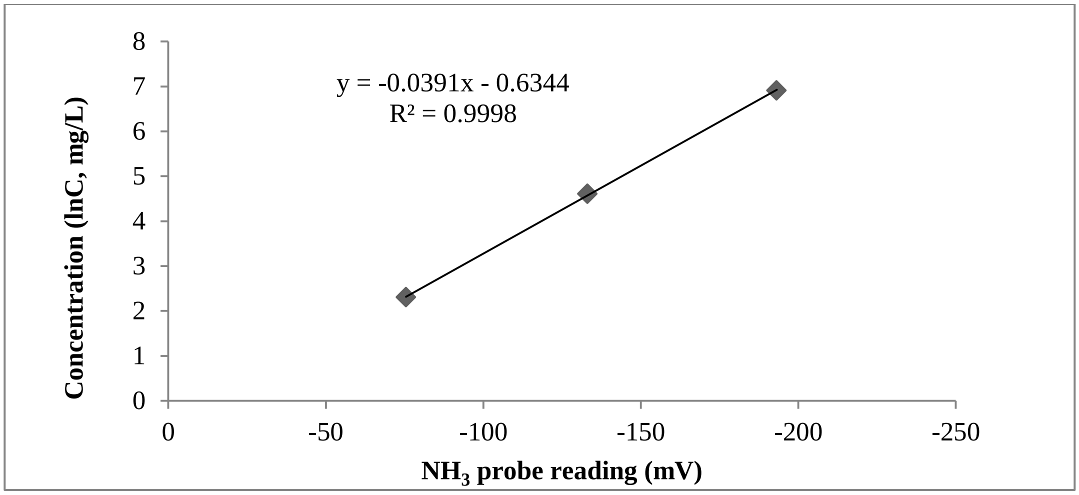

Figure A.5 Calibration curve for NH_3-N determination

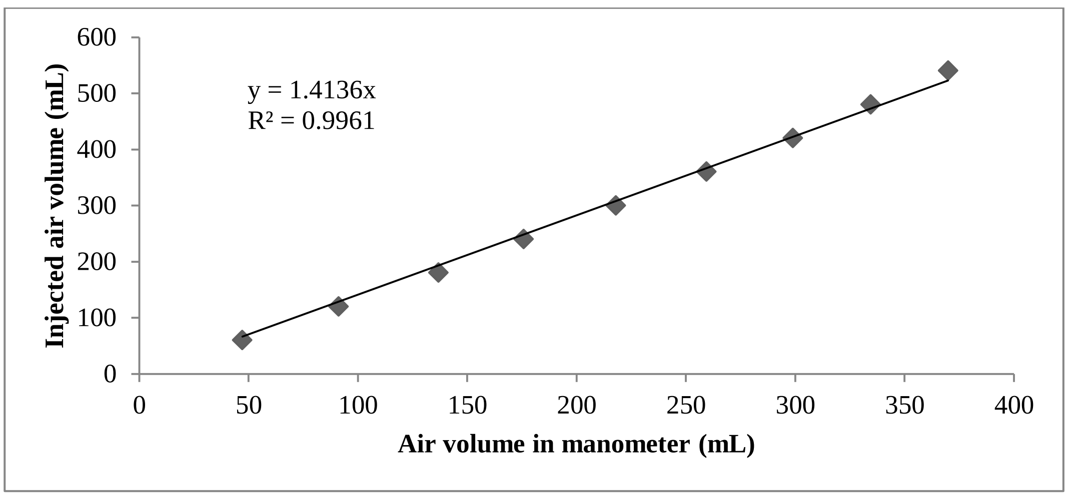

Figure A.6 Calibration curve for biogas measurement via manometer at STP (0^oC and 1atm)

A.2 Reagents for proteins and humic acids determination

- A : 20g Na_2CO_3 in 1000 ml of NaOH 0.1 N
- B_1 : 0.25 g $CuSO_4$ in 50 ml distilled water
- B_2 : 0.5 g Tartrate K, Na in 50 ml distilled water
- C_1 : 48 ml of A+1 ml B_1 + 1 ml B_2
- C_2 : 48 ml of A+1 ml DW + 1 ml B_2
- Stock solution : 20 mg BSA in 100 ml DW (final conc.= 0.2 g/l)
- Stock solution : 20 mg humic acids in 100 ml DW (final conc. = 0.2 g/)

Appendix B

Table B.1 General characteristics of Kelowna's pretreated DWSC

Properties	Control	MW-80	CH-80	MW-120	CH-120	MW-160	CH-160
pH [-]	5.72	5.84	5.64	5.72	5.83	5.63	5.53
TS%	17.29	17.69	17.82	17.94	17.83	17.60	17.95
	(0.04)	(0.25)	(0.1)	(0.09)	(0.07)	(0.28)	(0.04)
VS%	14.82	15.13	15.19	15.46	15.21	15.15	15.33
	(0.02)	(0.04)	(0.2)	(0.2)	(0.07)	(0.08)	(0.01)
Alkalinity	8,53	1,286	1,357	929	1,214	1,000	1,357
[mg $CaCO_3$/L]	(44)	(107)	(108)	(78)	(105)	(82)	(42)
NH_3-N [mg/L]	1,182	1,449	1,514	1,133	1,476	1,198	2,032
	(92.0)	(126.0)	(114.6)	(74.2)	(151.2)	(76.6)	(117.3)
Total fraction							
Protein [mg/L]	6282	66389	6671	6405	5424	6124	7087
	(373)	(18)	(28)	(21)	(317)	(224)	(168)
Sugar [mg/L]	153	434	452	557	724	1905	1939
	(2)	(1)	(13)	(30)	(10)	(82)	(10)
Humic acid [mg/L]	607	1118	1211	1435	1431	2069	2181
	(36)	(32)	(5)	(16)	(16)	(42)	(37)
Soluble fraction							
Protein [mg/L]	473	1387	1374	1442	1259	1750	2168
	(2)	(16)	(21)	(79)	(26)	(25)	(112)
Sugar [mg/L]	6151	5932	6398	5877	5968	6447	6263
	(29)	(52)	(58)	(110)	(129)	(83)	(102)
Humic acid [mg/L]	6770	6113	6859	7306	7351	6963	7411
	(548)	(84)	(117)	(337)	(253)	(569)	(443)

(Absolute difference between mean and duplicate)

Table B.2 Results of ANOVA for soluble to total sugar (M: pretreatment method, T: pretreatment temperature)

Source	Degree of freedom	Sum of squares	Mean square	F-ratio	p-value
M	1	0.787	0.787	6.60	0.052
T	2	198.073	99.036	829.78	0.000
Interaction	2	0.697	0.348	2.92	0.130
Error	6	0.716	0.119		
Total	11	200.274			

Table B.3 Results of ANOVA for soluble to total protein (M: pretreatment method, T: pretreatment temperature)

Source	Degree of freedom	Sum of squares	Mean square	F-ratio	p-value
M	1	0.106	0.105	0.94	0.370
T	2	9.372	4.686	41.69	0.000
Interaction	2	0.144	0.072	0.64	0.559
Error	6	0.674	0.112		
Total	11	10.297			

Table B.4 Results of ANOVA for soluble to total humic acid (M: pretreatment method, T: pretreatment temperature)

Source	Degree of freedom	Sum of squares	Mean square	F-ratio	p-value
M	1	0.003	0.003	0.01	0.907
T	2	3.899	1.949	9.73	0.013
Interaction	2	0.004	0.002	0.01	0.990
Error	6	1.201	0.200		
Total	11	5.107			

The ANOVA tables are only useful if their assumptions are met: residuals are independently and identically distributed in a normal distribution with a mean zero and variance sigma squared (σ^2). Figures B.1 displays the normal probability plots of residuals from ANOVA for $SCOD/TCOD_r$. Residues of relative to control soluble to total biopolymers (sugar, protein and humic acid) had normal distribution and the ANOVA assumptions were valid. Normal probability plots of residues for solubilization of sugar, protein and humic acids are presented in Figure B.2, B.3 and B.4, respectively.

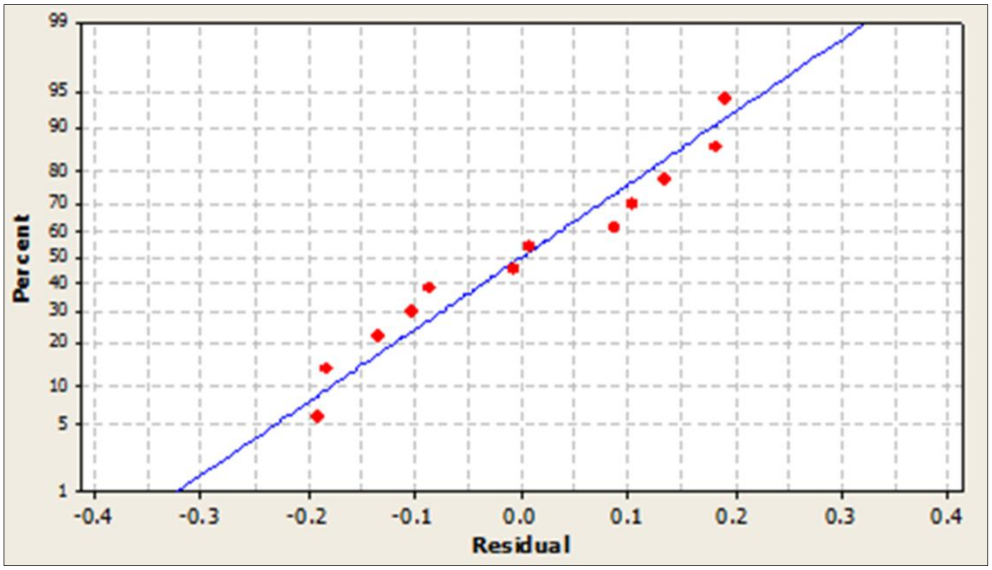

Figure B.1 Normal probability plot of residuals for relative to control SCOD/TCOD

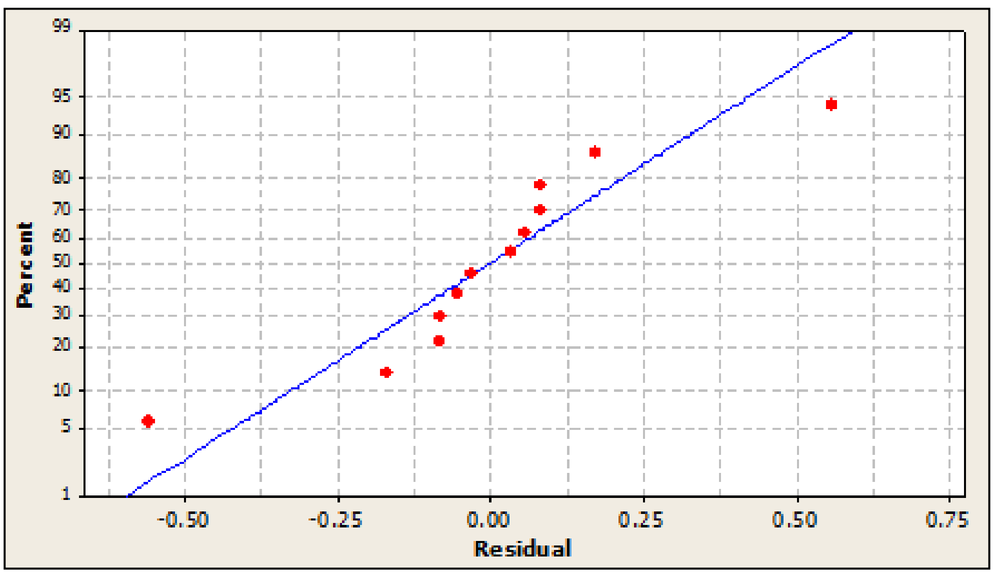

Figure B.2 Normal probability plot of residuals for relative to control soluble to total sugar

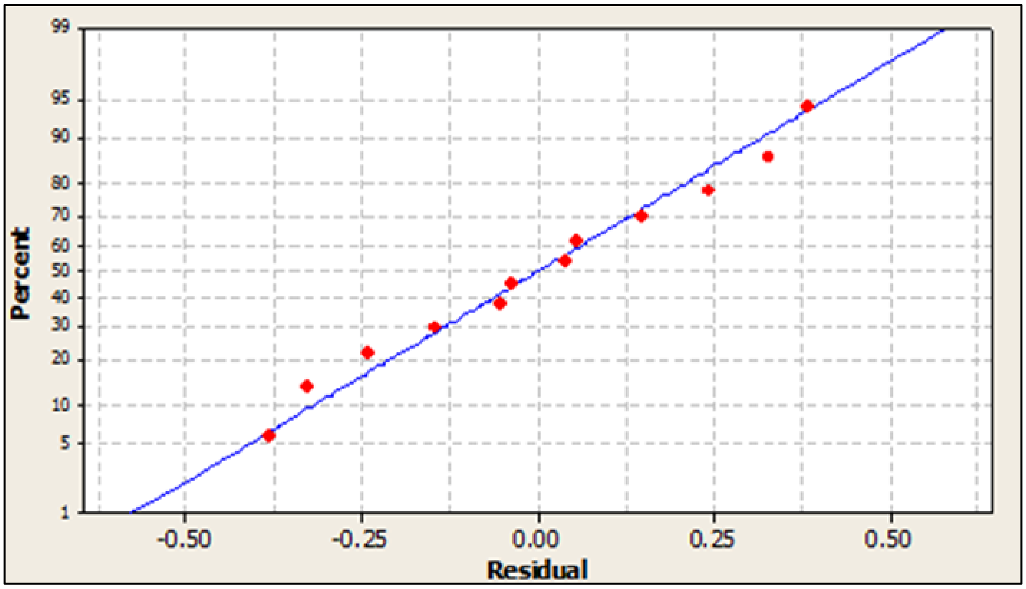

Figure B.3 Normal probability plot of residuals for relative to control soluble to total protein

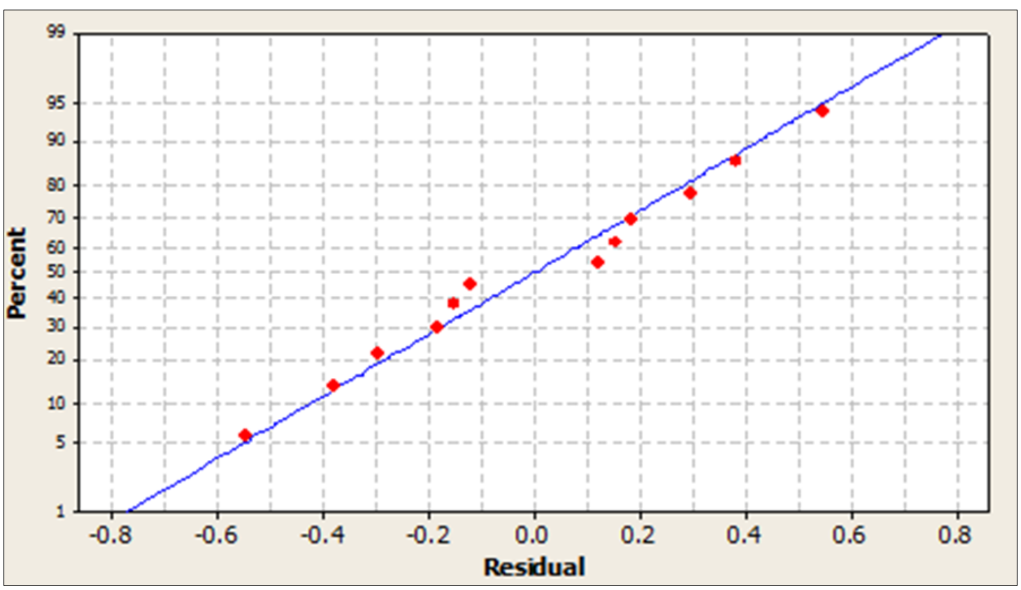

Figure B.4 Normal probability plot of residuals for relative to control soluble to total humic acid

Appendix C

C.1 Energy assessment of conventional heating in the pressure sealed vessel

Dewatered sludge cake (DWSC) was heated from room temperature (21^{o}C) to a fixed maximum temperature at a rate of 7.5^{o}C/min inside of a copper pressure cell. The outside of the pressure cell was wrapped with a heater made from nichrome wire. By measuring the voltage (V) across the heater and current (I) in the heater, the power dissipated by the heater (P = V I) was recorded as a function of time. The power versus time is shown in the figures below for 50 gr DWSC heated to 80, 120, and 160^{o}C. The power is defined as the time rate of change of the energy $P = dE/dt$ such that:

$$\boldsymbol{E = \int_{0}^{t} P\, dt} \qquad (1)$$

Therefore, the energy required to heat the sludge is equal to the area beneath the plot of power as a function of time. The energy results are given in figures below (Figures C.1, Figure C.2 and Figure C.3) for ultimate pretreatment temperature of 80, 120 and 160^{o}C. Note that the energy is used to heat both the sludge and the pressure cell. In a larger system in which the heat capacity of the sludge is much more than the heat capacity of the pressure cell, the E/m value will improve (decrease).

Estimating the fraction of energy used to heat the copper pressure cell and the fraction used to heat the 50 g of waste water requires knowledge of the heat capacity of both the copper and water. At room temperature the heat capacity of copper per unit volume is 3.45 J K^{-1} cm^{-3} and heat capacity per unit mass of water is 4.18 J $K^{-1}g^{-1}$. Therefore, the heat capacity of the 50 g of water loaded into the pressure cell is approximately <u>209 J/K</u>. Figure C.4 shows the dimensions of the copper pressure vessel in inches.

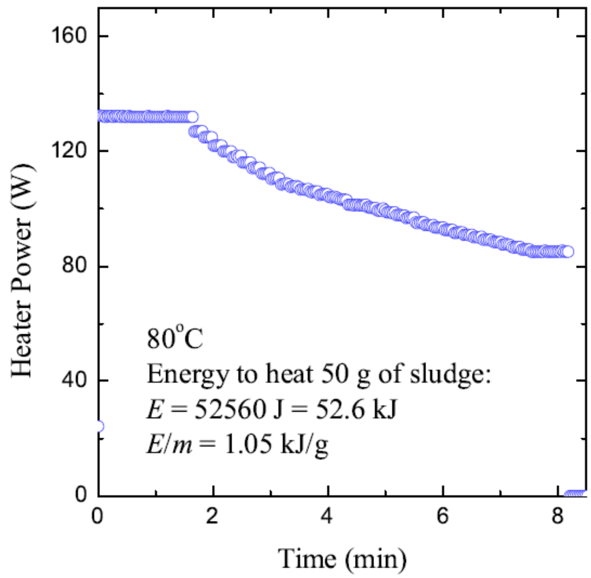

Figure C.1 Total energy for conventional heating of 50 gr of dewatered sludge cake (17.5% TS) to 80^{o}C.

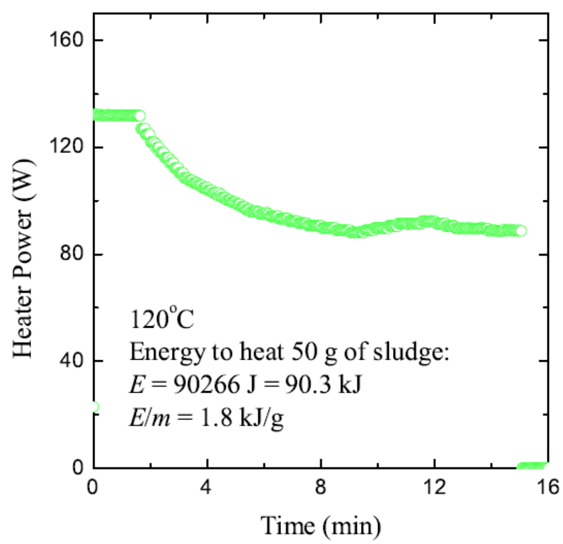

Figure C.2 Total energy for conventional heating of 50 gr of dewatered sludge cake (17.5% TS) to 120^{o}C.

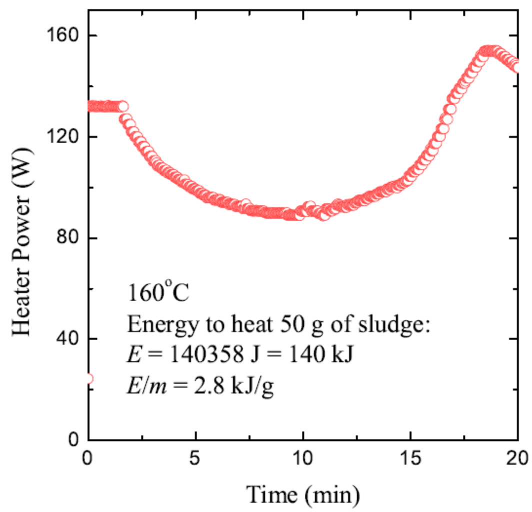

Figure C.3 Total energy for conventional heating of 50 gr of dewatered sludge cake (17.5% TS) to 160°C.

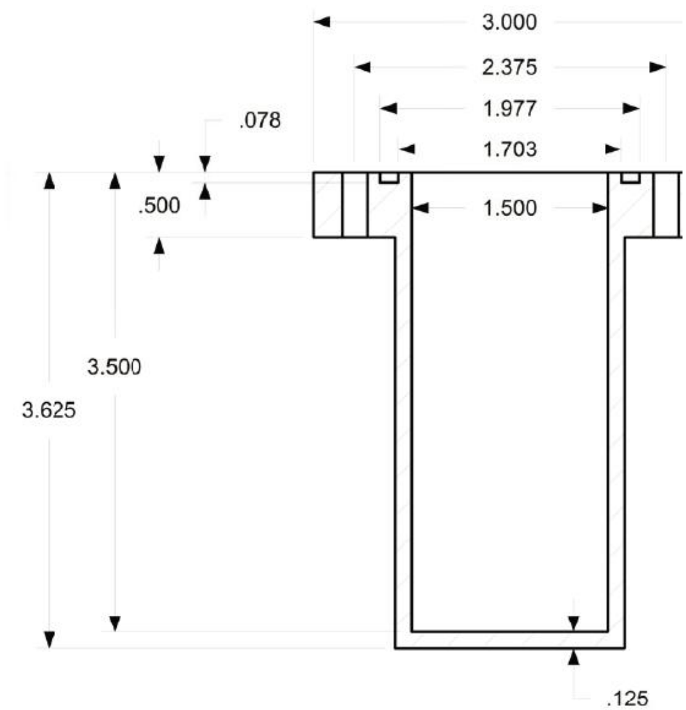

Figure C.4 Dimensioned drawing of a cross-section of the copper pressure vessel. All dimensions are in inches. The thicknesses of vertical walls of the vessel are 0.125 inches.

The volume of copper used to make the pressure cell is approximately 4.8 cubic inches or 78 cm^3. Therefore the heat capacity of the copper is approximately 270 J/K. Since the heat capacity of the copper and water is comparable, approximately 56% of the energy dissipated in the heater is used to heat the copper. In other words, less than half of the energy (43%) is used to heat the water. The heat loss is due to convection and radiation. Insulation and reflective aluminium foil were used to limit, but could not eliminate these effects.

C.2 Energy assessment of microwave pretreatment

Similar method was applied to evaluate the energy efficiency of the MW unit. An ampere meter was installed between the MW unit and electricity source to measure the total energy. Current values were recorded every 30 seconds and the power was calculated according to equation (2) in which I is the current (A) and V is the voltage (V). Equation (1) was used for energy calculations.

$$\boldsymbol{P} = \mathbf{V.I} \tag{2}$$

The amounts of energy delivered to the samples to increase the temperature were recorded by the MW. The approximate conversion efficiency of the Ethos EZ unit is 42% at pretreatment of 80^{o}C. Total and actual input powers delivered to the sample are presented in Figure C.5, Figure C.6 and Figure C.7 for the pretreatment of DWS at 80, 120 and 160^{o}C, respectively. Integration of the areas under these figures will yield energy in units of joules. The efficiency increased to 54% and 57%at pretreatment temperatures of 120 and 160^{o}, respectively (Table C.1).

Table C.1 Energy efficiency of MW unit (Ethos EZ)

	MW pretreatment temperature (^{o}C)		
	80	120	160
Total energy used (kJ/gr wet sludge)	1.41	1.67	2.75
Actual energy delivered to sample (kJ/gr wet sludge)	0.59	0.91	1.57
Efficiency (%)	42	54	57

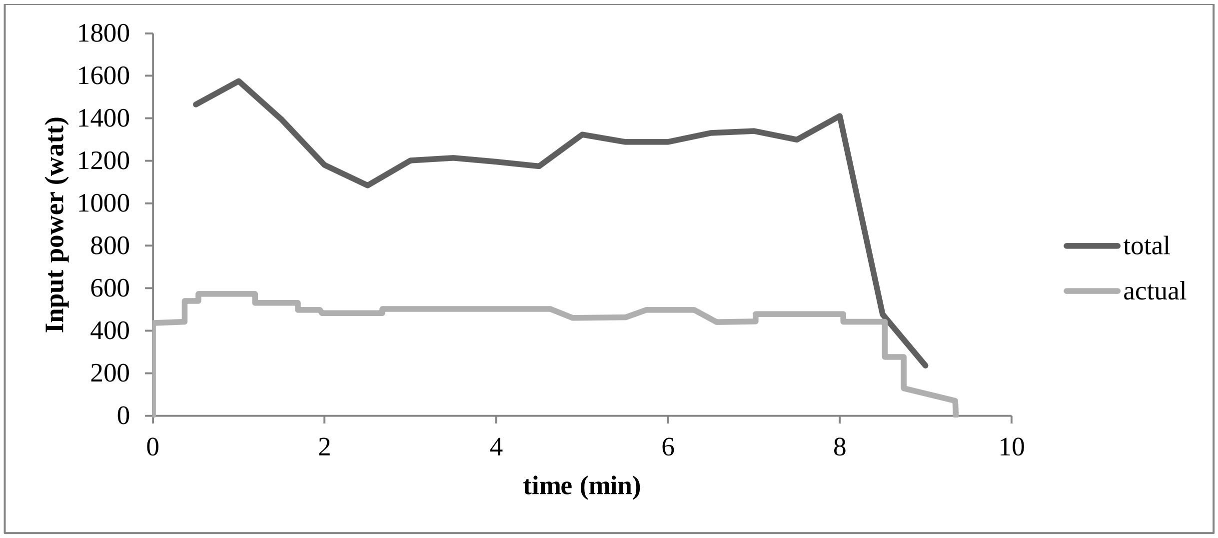

Figure C.5 Total power used and actual power delivered to sample for MW pretreatment of 450 gr of dewatered sludge cake (17.5% TS) to 80^{o}C.

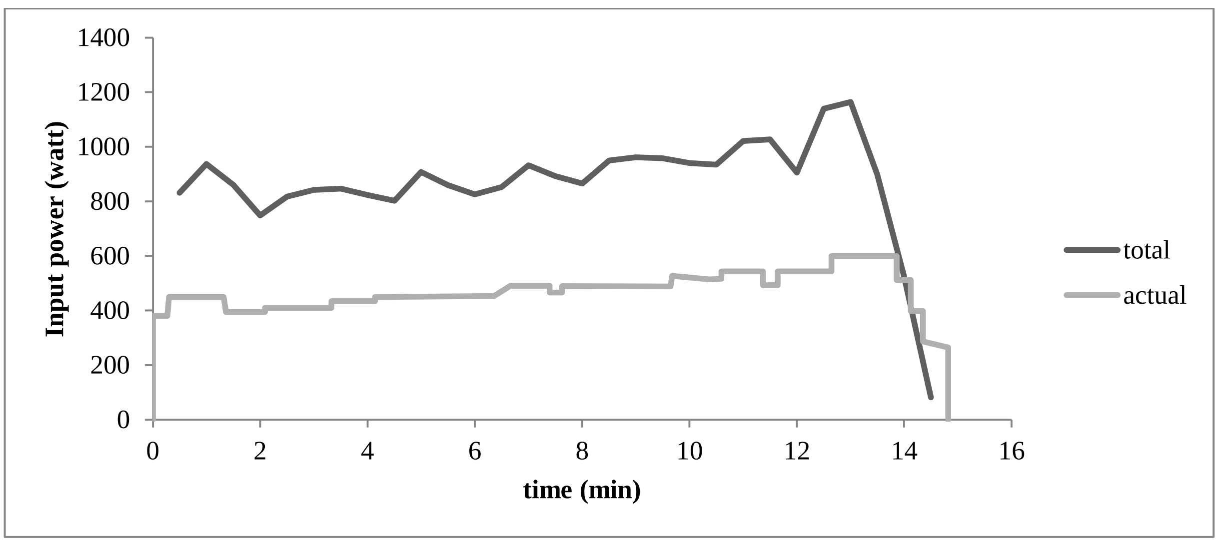

Figure C.6 Total power used and actual power delivered to sample for MW pretreatment of 450 gr of dewatered sludge cake (17.5% TS) to 120^{o}C.

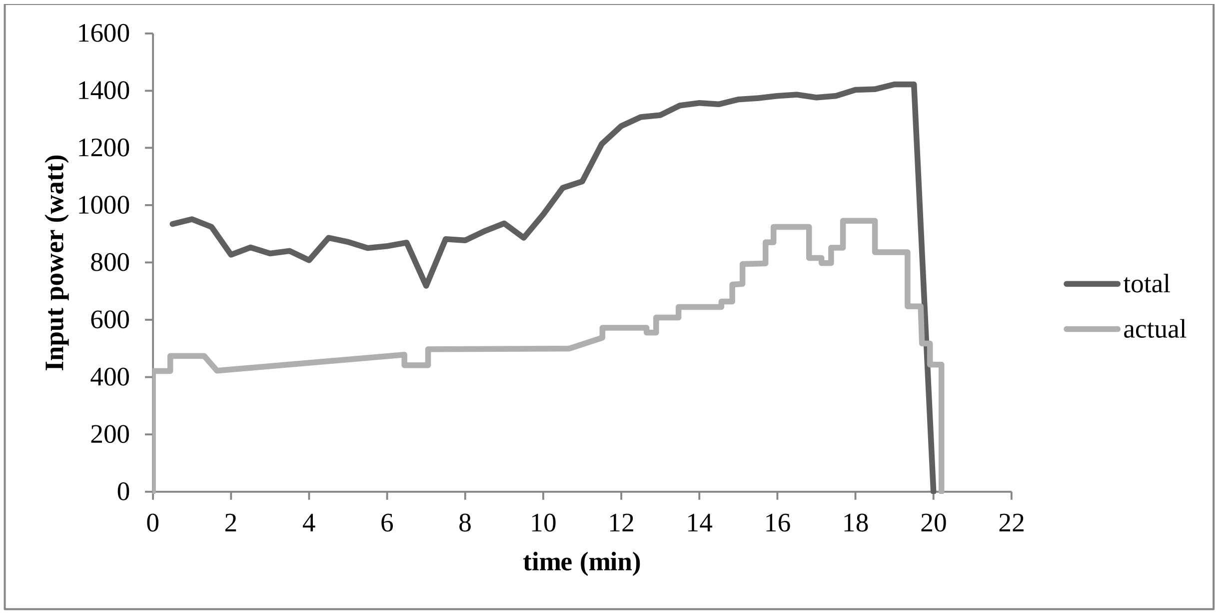

Figure C.7 Total power used and actual power delivered to sample for MW pretreatment of 450 gr of dewatered sludge cake (17.5% TS) to 160°C.

C.3 Comparison of input energy for MW and CH

The total and actual amount of energy delivered to the sludge samples during cooking are presented in Table C.2. The amount of energy used by MW is higher than CH for the pretreatment temperatures of 80, 120 and 160^{o}C.

Table C.2 Total and actual input energy (KWh/Tonne TS heated) for batch pretreatment of dewatered sludge cake with 17.3%TS by weight

Sample	**Total input energy** (kWh/Tonne TS heated)	**Efficiency (%)**	**Actual energy delivered to sample** (kWh/Tonne TS heated)
Control	-	-	-
MW-80	2296.9	42	964.7
MW-120	2662.6	54	1437.8
MW-160	4539.3	57	2587.4
CH-80	1684.2	43	724.2
CH-120	2887.2	43	1241.5
CH-160	4491.2	43	1931.2