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HIGH TEMPERATURE MICROWAVE PRETREATMENT FOR ENCHANCEMENT OF ANAEROBIC SLUDGE DIGESTION

Işıl TÖRECİ

Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies

Under the supervisions of
Prof. Kevin J. Kennedy
Prof. Ronald L. Droste

In partial fulfillment of the requirements
for the PhD degree in Chemical and Biological Engineering

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ABSTRACT

Efficiency of anaerobic digestion (AD) for stabilization of 5 day sludge retention time (SRT) thickened waste activated sludge (TWAS) is limited by hydrolysis of the floc matrix and cell walls of bacteria in the sludge. Heating is an effective pretreatment to enhance the accessibility to intra and/or extra cellular TWAS organics. Microwave (MW) pretreatment was suggested as an alternative method to conventional heating as a result of its lower energy requirements and additional athermal effect from MW irradiation. This study evaluates the effect of high temperature (>100°C) MW irradiation on sludge solubilization and concomitant performance on subsequent mesophilic AD (MAD).

Effects of pretreatment conditions (temperature, MW intensity and TWAS concentration) on changes of sludge characteristics as well as AD biodegradability of whole TWAS (soluble + suspended) and the soluble portion only were evaluated. The highest increase in organic solubilization was observed for 175°C with 3.75°C/min MW intensity. sCOD/tCOD ratios were 4.5 ± 0.8 and 8.8 ± 0.9 fold greater than untreated TWAS for 6.0 and 11.8% TS concentrations, respectively. Biochemical methane potential (BMP) assays demonstrated acute short term methanogenic inhibition for all MW pretreated samples. However, this was accompanied by a longer exponential phase that enhanced the potential biogas production with increased MW pretreatment temperature once the inhibition was overcome. Additional culture acclimation suppressed the inhibition and for TWAS pretreated to 175°C at 0.83°C/min MW intensity, 31 ± 6% more biogas vs. the control was produced by the 18th day of the BMP assay. For digestion of soluble portion, pretreatment at 150°C at low MW

intensity produced the greatest potential increase in biodegradability resulting in 90% more biogas than that of the control at day 20 of the BMP.

Semi-continuous MAD of TWAS with single and dual stage digesters following MW pretreatment at 175°C at two MW intensities were compared to untreated control MAD systems. With MW pretreatment SRT was decreased from 20 to 5 days without significant changes in the effluent COD characteristics. Lower MW intensity resulted in less improvement on COD stabilization and biogas production for the MAD processes. With incorporation of MW pretreatment the single stage digesters performed better than the two stage system in terms of organics stabilization efficiency and biogas production improvement. Dewaterability of digestate improved with MW pretreatment.

MAD biodegradability and rates of degradation of soluble organic fractions at different molecular weight (Mw) intervals was assessed. MW intensity was found to influence the soluble Mw profile distributions as well as subsequent MAD performance and pathways assessed by BMP assay.

Energy calculations show that MW pretreatment requires approximately 944 MJ/m^3 WAS (6% TS). Although MW is an energy intense process, it was found that as long as the excess energy can be used efficiently, MW pretreatment could potentially decrease sludge management costs by up to 58% if treated sludge can be designated Class A which eliminates transportation and landfill tipping costs. At this time, it is recommended that to enhance WAS (5d SRT) solubilization and biogas production a single stage MAD with MW pretreatment at 175°C with 3.75°C/min MW intensity should be used.

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To my family,

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CHAPTER 1:

Introduction

In today's world, the consumption of natural resources, in particular, water and the production of contaminated wastewater continue to increase with economic development and the growing population. Regulations for effluent discharge from wastewater treatment plants (WWTPs) have become more stringent with the increase of water consumption which has led to the generation of more sludge solids in WWTPs that must be disposed. On account of this, WWTP sludge management has become a very important issue. Due to the danger of spreading diseases as a result of pathogens in the sludge and other environmental considerations such as heavy metal concentrations, sludge disposal is controlled very closely by regulations. Additionally, the availability of landfill space for sludge disposal decreases each year with concomitant increased tipping costs both in North America and in Europe. These problems have forced researchers to find alternate techniques to treat sludge and minimize sludge disposal volume in environmentally responsible and economical ways.

Anaerobic digestion is widely used for sludge stabilization since it is a practical, environmental and cost effective way to treat sludge from wastewater treatment plants. The main advantage of anaerobic digestion is the reduction of sludge volume which provides reduction of handling and transportation cost of sludge to landfills and less landfill volume for disposal. Additionally, during anaerobic digestion energy is produced in the form of biogas and in most cases the dewatering characteristics of treated sludge is improved.

In conventional anaerobic digestion of thickened waste activated sludge (TWAS), volatile solids (VS) reduction between 30-45% can be achieved which means more than 50% of the organics in the sludge are either non–biodegradable or not readily available for biodegradation (Gosset and Belser, 1982). This limitation in biodegradation is the result of the inability of the biological process to hydrolyze particulates and as a result is the rate limiting step in anaerobic digestion. Secondary sludge or TWAS consists mainly of microbial cell biomass. Cell walls are very resistant to degradation since they are physical and chemical barriers to exoenzyme degradation and hydrolysis (Baier and Schmidheiny, 1997). For total stabilization, destruction of the cell wall and the floc matrix which is composed of exocellular polymeric substances (EPS) and microbial cells are necessary. Enhancing the disintegration of the cell wall and improving the accessibility of intracellular components to biological degradation has been shown to increase the efficiency of anaerobic sludge digestion. Several conventional and innovative pretreatment methods have been studied to improve the rate and extent of biodegradation of municipal sludges. Pretreatment methods include thermal disintegration (Jolis *et al.,* 2004 and Skiadas *et al.,* 2005), mechanical disintegration (Kopp *et al.,* 1997 and Muller *et al.,* 1998), ultrasonic (Thiem *et al.,* 2001 and Barber, 2005), chemical disintegration (Knezevic *et al.,* 1995 and Navia *et al.,* 2002), ozonation (Goel *et al.,* 2003 and Scheminski *et al.,* 2000) and combination of these disintegration methods. Although all these pretreatments have been shown to increase the biodegradability of municipal sludge, thermal disintegration at high temperatures (160-175°C) and high pressures (6-8 bar) tends to produce better results in terms of increased VS destruction, increased biogas production as well as pathogen reduction than any of the other pretreatment methods (Barnard *et al.*, 2002; Abraham and Kepp, 2003).

As an alternative innovative method to conventional heating of sludge, microwave (MW) irradiation pretreatment may be a promising technology to conserve energy and enhance pathogen and VS destruction (Decareau, 1985). To date, the studies about the MW effect on sludge were reported for treatment temperatures lower than 100°C which were focused on solubilization, mesophilic digestion, fecal coliform destruction and the athermal MW effect. It was reported that MW is a promising technology as a pretreatment method of TWAS since it improves solubilization, efficiency of digestion and due to pathogen reduction it has potential to produce Class A sludge (Hong *et al.,* 2006, Park et al., 2004, Eskicioglu *et al.,* 2007a, Eskicioglu *et al.,* 2007b). In addition, the existence of the MW athermal effect on WAS solubilization and concomitant improvements in VS destruction and biogas production has recently been reported (Eskicioglu *et al.,* 2007c and Coelho *et al.,* 2008).

Another approach to TWAS management may be the separation of supernatant and biocake and digesting only the supernatant since most of the biodegradable components are in the supernatant of TWAS. In the literature there is only one example of this application. Sawayama *et al.* (1995) studied the efficiency of supernatant digestion of TWAS after pretreating TWAS thermally at 175°C with an electric furnace and holding it at 4 MPa (40 bar) for 1 hour in an autoclave. The anaerobic digestion of supernatant of pretreated sludge produced 70% of the biogas produced by pretreated TWAS digestion. Pretreating TWAS increases the solubility of sludge and by digesting only the supernatant the digester volume can be decreased and more efficient and rapid digestion can be achieved.

1.1 THE HYPOTHESIS

The aim of this study is to investigate the effect of high temperature (>100°C) MW irradiation on solubility of sludge and performance of mesophilic anaerobic digestion and the efficiency of anaerobic digestion of supernatant which can lead to a different perspective of handling the sludge. It is hypothesized that at temperatures above the boiling point the combination of thermal and orientation effects of microwaving cause the weak hydrogen bonds to break apart resulting in the unfolding and denaturation of complex organic molecules leading to smaller more biodegradable organic molecules and particles. It is also hypothesized, that due to extensive solubilization caused by high temperature (>100°C) MW pretreatment digesting only supernatant of TWAS by mesophilic anaerobic digestion can result in efficient biogas production in smaller reactors.

1.2 RESEARCH OBJECTIVES

This research will contribute to our fundamental research knowledge base and to the waste treatment industry with the following specific objectives:

- Determine the effects of high temperature/pressure, intensity, and sludge concentration on solubilization of municipal TWAS at different concentrations.

- Determine the effects of high temperature MW pretreatment on enhancement and/or inhibition (extent and rates) of biogas production, VS destruction, and sludge dewateribility for mesophilic anaerobic digestion.

- Determine the role of microwaving conditions on mesophilic anaerobic digestion of soluble compounds with various molecular weights.

- Determine the increase in hydrolysis rates of particulates following high temperature MW pretreatment.

- Determine the impact of high temperature MW pretreatment on anaerobic sludge digester kinetics.

- Determine the efficiency of mesophilic anaerobic digestion of only soluble compounds from TWAS following MW pretreatment.

1.3 THESIS ORGANISATION

This thesis is arranged as a paper format thesis. Chapter 2 gives brief information on literature review of fundamentals of anaerobic digestion, microwave technology and existing pretreatment methods. Results of this research are given as a journal manuscript format in Chapters 3-7. Overall conclusions and recommendations are given in Chapter 8.

Chapter 3 focuses on the effect of different operating conditions (MW temperature, MW intensity and sludge concentration) on TWAS characteristics such as solubilization sCOD, total COD (tCOD), soluble sugar, soluble protein and total volatile fatty acids (TVFA)). Statistical analysis with a three-factor fixed effect ANOVA model was used to analyze the significance of these conditions on solubilization. In addition, by using empirical modeling the effect of operating conditions on solubilization was illustrated. These results were presented at the 11th Conference on Process Integration, Modelling and Optimization for

Energy Saving and Pollution Reduction (PRES 2008) in Prague, Czech Republic, 24-28 August 2008. This manuscript has been selected for publishing at Heat Transfer Engineering Journal by the conference committee.

Chapter 4 presents the results obtained from biochemical methane potential (BMP) assays of TWAS pretreated at different MW pretreatment temperatures and intensities and using different sludge concentrations. It also presents the role and impact of inoculum acclimation on the short term and long term response of MAD. These results were presented at the 80th Annual Water Environment Federation Technical Exhibition and Conference (WEFTEC 2007) in San Diego, CA, USA, 13-17 October, 2007 and the manuscript was submitted to Journal of Water Environment Research (WER) for publication.

In the light of batch experiment results semi-continuous digestion experiments were conducted to mimic the full scale application. The results of these experiments are given in Chapter 5. Semi-continuous MAD experiment were undertaken to evaluate the effect of high temperature MW pretreatment and MW intensity on single stage MAD as well staged MAD performance. This manuscript was submitted to Water Research.

Chapter 6 presents in depth analyses of soluble organics exposed to MW pretreatment at different temperatures and intensities by examining the soluble organic distribution at different apparent molecular weight (Mw) cut offs. This paper focuses on exploration of soluble organics of TWAS at different Mw intervals as well as their biodegradability and rate of degradation in each interval. This manuscript was submitted to Environmental Engineering Science.

The final part of this research was on determination of efficiency of digestion of supernatant part of sludge that was pretreated with MW irradiation. Investigation of supernatant separation and efficiency of supernatant digestion is reported in Chapter 7. A brief energy analysis of sludge digestion with high temperature MW pretreatment is also given in this chapter. This manuscript will be submitted to Conference of Sustainable Management of Water and Wastewater Sludges in Harbin, China, August 8-11, 2009.

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CHAPTER 2:

Literature Review

2.1 BIOSOLID REGULATIONS

Biosolids that are produced from anaerobic digestion of municipal sludges can be used as fertilizer if the sludge meets the requirements of regulations instituted to protect public health. In the USA, the use and disposal of municipal biosolids are regulated under the 40 Code of Federal Regulations (CFR) Part 503. According to these regulations biosolids are classified in three categories: Class A, Class B and exceptional quality (EQ) biosolids. Classes A and B are differentiated from each other by bacteria and/or pathogen criteria. The criteria that are included in EQ biosolids are pathogens as well as more stringent heavy metal constraints (Spinosa and Vesilind, 2001). In Canada, the regulations and guidelines for use of biosolids are at the provincial/territorial level rather than the federal level. Some provinces refer to Part 503 for guidance.

Class B biosolids contain less than two million most probable number (MPN) of *fecal coliforms* per gram of total solids sludge (dry weight basis). For a biosolid to achieve the Class A category it has to meet the following requirements: it should contain *fecal coliforms* less than 1000 MPN/ 4 g - dry weight, *salmonella sp* less than 3 MPN/4 g - dry weight, enteric viruses less than 1 MPN /4 g - dry weight, and viable *helminth ova* less than 1 MPN/4 g - dry weight. Class B biosolids are restricted in their use as crop fertilizers, applications where animal grazing occurs and any applications where there is public access.

Class A biosolids on the other hand can be used for land applications (US EPA 1993). Class A biosolids production is an economical and environmental friendly alternative way for sludge disposal. Class A biosolids contain fewer viruses and pathogens as well as less heavy metals to protect public health, to prevent ground and surface water and soil from contamination. Pathogen reduction methods to achieve Class A biosolids are thermal treatment, modified thermophilic anaerobic digestion, modified composting process, modified sludge drying process, modified alkaline stabilization process and ozonation process. *MicroSludge*™ and CAMBI™ processes are two existing pretreatment methods of mesophilic anaerobic digestion that can destroy pathogens almost completely to achieve Class A biosolids. The studies of MW irradiation on primary and secondary sludges showed that to destroy all *fecal coliforms* the temperature to be reached with MWs is 65 and 85°C for primary and secondary sludges, respectively (Hong *et al.*, 2004).

US EPA Rule 40 also regulates organic pollutant concentrations that can be in Class A and B biosolids. These pollutants include such chemicals as aldrin/dieldrin (total), benzene, benzo(a)pyrene, bis(2-ethylhexyl)phatalate, chlordane, DDT/DDE/DDD (total), heptachlor, hexachlorobenzene, hexachlorobutadiene, lindane, n-nitrosdimethylamine, polychlorinated biphenyls, toxaphene, trichloroethylene and heavy metals such as arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel and selenium.

In Ontario, there is no specific Class A or B classification; however, regulation 347 of the Environmental Protection Act regulates biosolids. In general our regulations and guidelines follow a similar characterization as the USA Class A or B designations. A certificate of

approval from the Ministry of the Environment (MOE) is necessary for biosolids to be used on agricultural land (MOE and MAFR, 1996).

2.2 ANAEROBIC DIGESTION FUNDAMENTALS

Anaerobic digestion is the oldest biological wastewater treatment method. Anaerobic digesters imitate the processes occurring naturally in landfills. It reduces organic matter to more stable solids by complex biochemical reactions carried out by several microorganisms that require absence of oxygen. Anaerobic treatment is widely used in sludge stabilization due to its low cost, energy recovery and minimized biosolids production.

In anaerobic digestion, a small fraction of total energy content of the incoming pollutants is used for generation of biomass yielding less sludge production. Production of methane during digestion is a potential energy source that can reduce the energy requirements of the system.

The microbial community of the anaerobic process is very complex. There are two prokaryotic kingdoms that closely interact with each other: *Bacteria* and *Archaea*. There are three basic steps of anaerobic digestion. The first step involves hydrolysis of complex organic matter into simpler compounds. The second step is the acidogenesis of these organics to form organic acids and hydrogen. The final step is methane and carbon dioxide production from organic acids and hydrogen by *archael methanogens*. Figure 2.1 shows the process summary of anaerobic digestion.

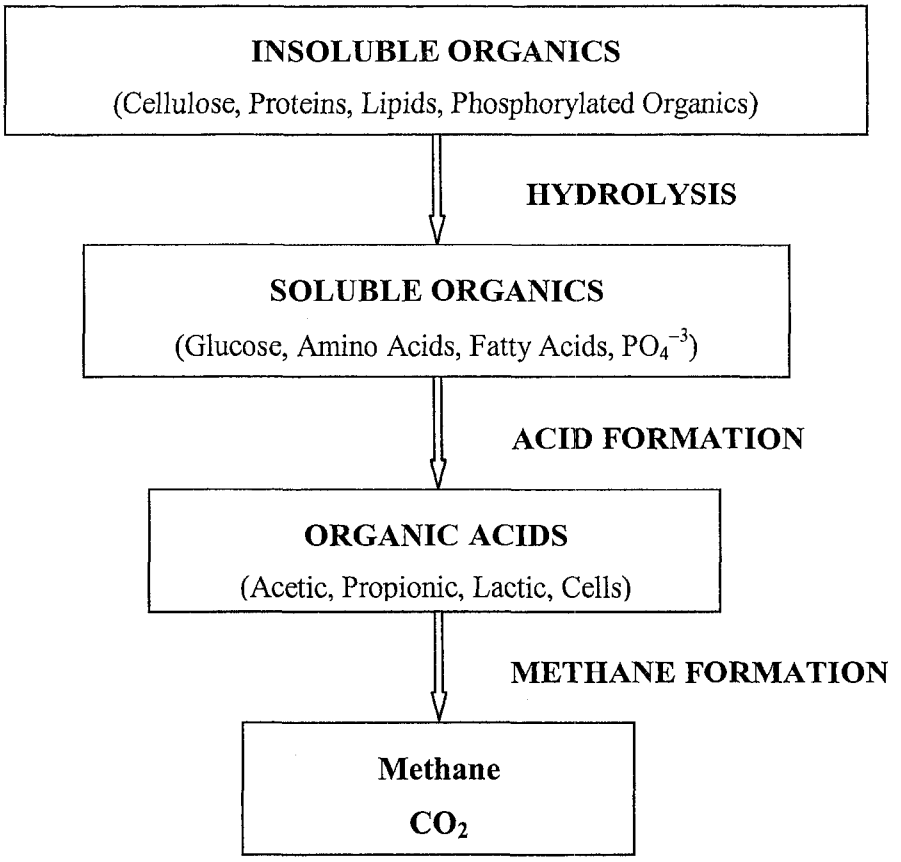

Figure 2.1: Simplified process summary for anaerobic digestion (WEF, 1991)

Acetogenic bacteria can function best at pH between 5 and 6, but they can also tolerate a wider range of pH. For methanogens however, the optimum pH is around 7 and they have less tolerance to different conditions. It is for this reason that anaerobic digestion is operated under the conditions that are favorable to methanogens. The optimum operating conditions for mesophilic anaerobic digestion are temperature of 33-35°C and pH of 7-7.2. The desired alkalinity level in anaerobic reactors is usually in the range of 2000-3000 mg/L as $CaCO_3$ and volatile fatty acid (VFA) concentration is in the range of 50-500 mg/L as acetic acid. In general VFA concentrations should be kept below 2000 mg/L as acetic acid. The ratio of

VFA/alkalinity should be kept below 0.3. The typical operating conditions for primary and secondary sludge anaerobic digestion are given in Table 2.1

Table 2.1: Environmental factors effecting anaerobic digestion (Metcalf and Eddy, 2003 and Parkin and Owen, 1986)

Variable	Optimum operational condition	Extreme operational condition
pH	6.8 - 7.4	6.3 – 7.9
Volatile acids (mg/L as acetic)	50-500	2000
Alkalinity (mg/L as $CaCO_3$)	2000-3000	1000-5000
Organic loading rate as volatile solids ($kg/m^3/d$):		
Mesophilic digestion	0.8-2.0	0.4-6.4
Thermophilic digestion	1.5-5.0	1.05-7.5
Temperature (°C):		
Mesophilic digestion	32-37	20-42
Thermophilic digestion	50-56	45-65
Hydraulic retention time (HRT) (days)	12-18	7-30

2.3 ANAEROBIC DIGESTION OF PRIMARY AND SECONDARY MUNICIPAL SLUDGE

Anaerobic digestion of primary sludge differs from that of secondary sludge or waste activated sludge (WAS) in terms of rate and extent of digestion as well as dewateribility of digested sludge.

In digestion of municipal sludge, acidogenesis and methane formation occur fast and the rate limiting step is usually the hydrolysis step. For primary sludge the hydrolysis step is relatively faster than that of secondary sludges because the main constituent of primary sludge is carbohydrates. Secondary sludge on the other hand is mainly composed of microbial cells which are very difficult to hydrolyze or degrade due to their cell walls and cell membranes. Primary sludge is more readily degradable than secondary sludge; therefore, total VS destruction of primary sludge is typically higher than that of secondary sludge. Typical values of VS reduction, chemical oxygen demand (COD) removal, biogas yield and composition of primary and secondary sludges are given in Table 2.2. In Figure 2.2, it can be seen that the rate and extent of biodegradability of primary sludge has been shown to be much higher than that of WAS. An equal mixture of primary and secondary sludge gives treatment results in between as expected. Increasing the readily degradable compounds in secondary sludge would increase the extent and also possibly increase the rate of anaerobic digestion. In order to do so there is a need for pretreatment.

Studies showed that reduction of particle size by pretreating sludge is accompanied with cell rupture leading to an increase in degradation rate and extent of degradation for pretreated sludge in anaerobic digestion (Palmowski and Muller, 2003).

Another important characteristic of sludge treatment that may be improved by pretreating and digesting is dewateribility. Sludge dewatering reduces transportation costs, eases the manipulation of sludge and biosolids and renders them with fewer odors. However it is important to note that during pretreatment especially thermal pretreatment the odor release from the sludge may increase.

Four different types of water are associated with sludge. Free water or the non-bound water to the particles that is easy to remove mechanically. The interstitial water is the water between particles and microorganisms and it is bound by capillary forces. Extreme pressure is needed to be applied to sludge to remove interstitial water. Surface water is the water that covers the surface of sludge particles and it is bound by adsorptive and adhesive forces. Surface water also includes the chemically bound water around exo-polymers which is the most difficult to remove from sludge. Intracellular water is the water in the cells. It is usually referred to as bound water and is included as part of the surface water and interstitial water. Only by pretreatment can the bound water be removed from sludge. Due to the microbial nature of the secondary sludge it is more difficult to dewater it than primary sludge. Pretreating WAS before anaerobic digestion to breaking up the cell walls has the potential to improve the dewateribility characteristic of WAS or blends of WAS and primary sludge.

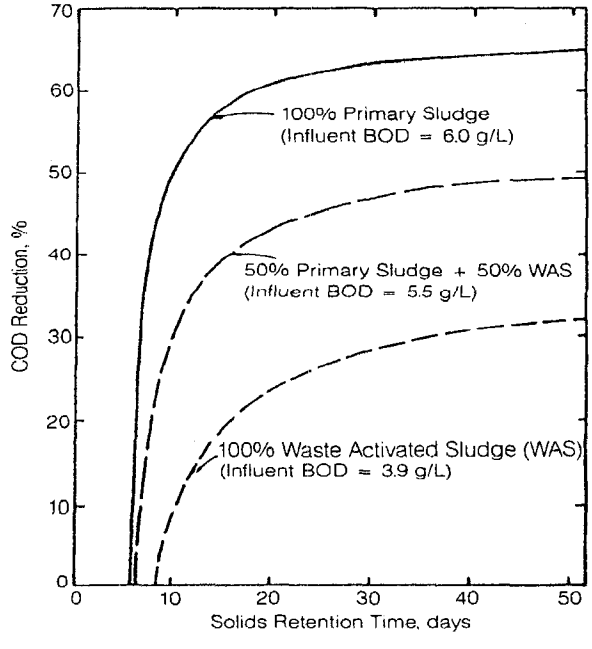

Figure 2.2: The effect of sludge type on anaerobic digestion (Adapted from ASCE, 1991)

Table 2.2: Typical values for mesophilic anaerobic digestion of WAS and primary sludge (Parkin and Owen, 1986 and Malina and Pohland, 1992)

Parameter	Typical values for mesophilic digestion
VS destruction (%)	
WAS	30-50
Primary sludge	40-70
COD removal (%)	
WAS	30-45
Primary sludge	40-60
Biogas yield (L/g VS destroyed):	
WAS	0.75
Primary sludge	1.00
Biogas composition (CH_4% volume):	
WAS	65-70
Primary sludge	30-35

2.4 EXISTING PRETREATMENT METHODS

2.4.1 Thermal Pretreatment

To enhance the hydrolysis of TWAS researchers first tried conventional thermal pretreatment prior to anaerobic digestion. The main advantages of thermal pretreatment were found to be improvements in VS biodegradability and biogas production, better

dewateribility of the treated sludge, as well as increased pathogen reduction and odor control (Gavala *et al.*, 2004 and Haug, 1977).

Continuous mesophilic digestion of TWAS pretreated at low temperatures in the range of 60 to 100°C increased methane production by 30-52% (Wang *et al.,* 1997) over controls. Similar results for mesophilic digestion were also reported by Hiraoka *et al.* (1985) who used unthickened WAS. For digester volumetric organic loading rates of 3 kg VS/m^3.d, biogas production increased by more than 30% when sludge was pretreated at 60 to 80°C. At lower digester organic loads they reported a 50% increase in biogas over controls when WAS was pretreated to 100°C. At high temperatures of 120 and 180°C it was found that although methane production increased the increase was relatively small. It was speculated that either inhibitory compounds were being formed that inhibited digestion or that a majority of the readily biodegradable solids had already been digested. Beyond 180°C a sharp decrease in methane production was observed. This phenomenon was attributed to a Maillard reaction that occurred between amino acids and low molecular weight sugars in the sludge, producing inhibitory and difficult to degrade end products (Pinnekamp, 1989). Interestingly Stuckey and McCarty (1984) also reported inhibition of anaerobic digestion following pretreatment of TWAS at elevated temperatures. They attributed the decrease in VS destruction to caramelization of sugars in the waste.

Haug (1978) reported that optimum pretreatment temperature for activated sludges in terms of the greatest increase in biodegradability for mesophilic digestion was near 175°C. Later studies by Haug (1978) showed that at pretreatment temperatures higher than 175°C, COD removal increased for thermophilic digestion. Thermally pretreated WAS at 204°C that was

thermophilically digested had COD removal between 37-43% whereas COD removal was 33% for nonpretreated mesophilic and 31% for nonpretreated thermophilic digestion, respectively (Haug *et al.,* 1983). Huag's studies indicated that different microbial flora for mesophilic and thermophilic digestion may result in differences in optimum pretreatment conditions.

Continuous digestion experiments done with sludge collected from a wastewater treatment plant which received both domestic and industrial wastewater showed very high improvement with high temperature thermal pretreatment (Bougrier *et al.,* 2006a). In this study sludge was pretreated at 130 and 170°C by using an autoclave and held at the desired temperature for 30 minutes. At 20 day SRT, TS and VS removal was improved 72 and 81% for pretreatment temperature of 150°C and 108 and 106% for 170°C pretreatment temperature, respectively. The same experiment was conducted with a different type of sludge as well. In this case sludge was collected from a plant that receives only urban wastewater. The results for sludge pretreated at 170°C showed 85 and 74% TS and VS removal, respectively. It was concluded that 150 and 170°C pretreatment temperatures both gave very high organic matter removal and feed sludge concentration and heat exchangers needs to be considered to choose the best pretreatment temperature.

None of these articles mentioned above except Bougrier et al. (2006a) specified whether sludge was held at the desired temperature for extended periods after being heated to the desired temperature. The only information about thermal pretreatment temperature holding time was found for research done on primary and secondary sludge by Skiadas *et al.* (2004). In this study, sludge was preheated to 70°C and held at that temperature for 2 days.

Preheated sludge digestion was compared to the untreated sludge; however; there was no comparison between heating to 70°C and temperature holding with just heating to 70°C with no holding time. Continuous experiments showed that methane production was increased with thermal pretreatment with temperature holding by 42 and 47% compared to controls for primary and secondary sludge, respectively. Holding the sludge at high temperatures can increase the heating effect and forces the cell membranes to break apart potentially allowing the sludge to be more biodegradable; however, this can also cause formation of toxic compounds when the contents of the cells are released from the sludge and held at elevated temperatures.

2.4.2 Mechanical Pretreatment

Cutting mills, jetting-and-colliding, high-pressure homogenizers, shear-gap homogenizers and stirred ball mills are the most commonly used equipment for mechanical disintegration. The effects of ball milling and cut milling on sludge degradation were investigated by Baier and Schmidheiny (1997). Ball milling was found to be better at enhancing the proportion of soluble COD (sCOD) in the sludge than cut milling. Ball milling increased soluble VS (sVS) from 38 to 51% and during mesophilic anaerobic digestion biogas production increased by 10% indicating an increase in sludge biodegradability. Kopp *et al.* (1997) compared a high-pressure homogenizer, shear gap homogenizer, stirred ball milling and ultrasound homogenizer. Each of these processes was able to increase the sVS/VS ratio (disintegration ratio) to above 90% except the shear gap homogenizer which achieved a 45% disintegration ratio. Among these methods, the high pressure homogenizer was found to have the lowest energy requirements for the same degree of disintegration. Continuous mesophilic digestion

of the high pressure homogenizer pretreated sludge resulted in volatile suspended solids (VSS) removal of 57.5% whereas it was 41% for stirred ball milling and 37% for the control (untreated) after 4 days. At longer HRTs the advantage of pretreating the sludge with mechanical methods was observed to decrease and after 15 days of digestion it was seen that VSS removal efficiency of both untreated and pretreated sludge became almost the same. This indicated that while the rate of digestion may be increased there was no increase in the ultimate degradability of the sludge. This is in contrast to what has been observed with other pretreatments such as the thermal pretreatment discussed above. Another important observation reported in this study was that mechanical pretreatment resulted in a decrease in sludge dewaterability which was manifest in increased polymer dosing to maintain dewatering characteristics similar to the control. Muller *et al.* (1998) also reported the same increase in polymer demand with the same mechanical disintegration equipment and postulated that the disruption of particle structure increased particle area and charge density which disrupted particle-particle interaction. Again in contrast to thermal pretreatment and others discussed later, mechanical sludge disruption seemed to have a negative impact on dewaterability. In their study Muller *et al.* (1998) reported that stirred ball milling and high pressure homogenizer gave the best results and resulted in a 10 to 20% increase in the extent of biodegradation. This is in contrast to Kopp *et al.* (1997) but more in agreement with other pretreatment methods.

Dohanyos *et al.* (1997) concluded that smaller sludge particle size; whether it was primary or secondary sludge had an effect on enhancing biodegradability. They used a special thickening impact centrifuge that had a special impact gear (required no additional energy) and they observed an increase in methane yield of 31.8% with TWAS only whereas a 50/50

(v/v) mixture of TWAS and primary sludge resulted in a methane yield increase of 13.6%. This is in agreement with conventional studies that show that primary sludge is readily degradable while secondary sludges (WAS and TWAS) are rate limiting both in terms of the extent and time required for sludge digestion (see section 2.3 above).

Hwang *et al.* (1997) reported on a WAS pretreatment study done with mechanical jetting-and-colliding under pressurized conditions. Using pressure gradients of 5 to 50 bar they reported a cell rupture ratio (sVS/VSS) of 40% at 30 bar. Using mesophilic digesters they found that pretreating the sludge at 30 or 50 bar gave similar VS destruction of about 50% whereas the control (untreated) had 40% VS destruction. Similar WAS experiments were done by Choi *et al.* (1997). They observed that the average particle size decreased from 69.1 μm to 37, 21.6 and 18.7 μm by pretreating the sludge at 10, 30 and 50 bar, respectively. sCOD increased by factors of 6.5 and 8 with pretreatment at 30 and 50 bar as compared to the control. Jetting-and-colliding of WAS sludge under pressure was also investigated by Nah *et al.* (2000) and it was seen that soluble protein concentration increased from 40 to 120 mg/L with pretreatment at 40 bar. Similarly sCOD increased from 200 to 800 mg/L and total suspended solids (TSS) decreased from 20650 to 19350 mg/L at the same conditions. The increases in soluble components and decrease in average particle size indicate that both cell disruption and cell wall fractionation occur under mechanical disintegration. Except for one report, mechanical pretreatment of secondary sludge led to an increase in the rate and extent of anaerobic biodegradation and a decrease in dewatering characteristics.

2.4.3 Chemical Pretreatment

2.4.3.1 Acids and Bases

High pH has been reported to enhance anaerobic digestion of WAS by improving COD solubilization by more than 45% (Rajan *et al.,* 1989). The most commonly used compounds in chemical pretreatment are sodium hydroxide (NaOH) and calcium hydroxide ($Ca(OH)_2$). In order to compare their efficiency in enhancing WAS anaerobic digestion several experiments have been performed (Chiu *et al.,* 1997, Ray *et al.,* 1990 and Knezevic 1993). For 1% total solids (TS) sludge with contact times of 12 and 24 hours, it was found that NaOH gave better results with sCOD percentages increasing to 28 and 42% of the total COD (tCOD), respectively (Chiu *et al.,* 1997). Solubilization of WAS under different chemical dosages of NaOH at different mixing times (3, 4 and 5 hours) was conducted and found that for dosages less than 15 meq/L all reactors had the same performance in terms of VS and COD reduction during mesophilic digestion at 7.5 or 20 day SRT. From pilot scale experiments the best biogas production was observed when WAS at 1% TS was pretreated with 12.5 meq/L NaOH. Mesophilic digestion sludge retention time (SRT) was reduced from 25 to 10 days without effecting the process performance and effluent quality (Knezevic *et al.,* 1995).

In recent studies it was observed that after 24 hours of chemical pretreatment with 60 meq/L dose of NaOH not only was sCOD increased but soluble protein concentration in WAS increased 6 times the original concentration and VSS concentration decreased by 21%

(Navia *et al.,* 2002). For 3% TS WAS, the optimum dosage of NaOH was found to be 45 meq/L to increase WAS solubilization.

Thermal and chemical (NaOH) pretreatments were combined and their effect on solubilization was also examined and it was found that as temperature was increased the extent of solubilization also increased. It was reported that after reacting 45 meq/L NaOH with 3% TS WAS sludge for 4 hours at 25, 35 and 55°C, solubilization (sCOD) increased to 27.2, 31.4 and 38.3% of tCOD and methane production was increased by 66, 73 and 88%, respectively, over the control. While the rates of VS destruction were not reported these experiments indicated that the combination of chemical and thermal pretreatment increased the extent of anaerobic WAS biodegradation (Heo *et al.,* 2003).

2.4.3.2 Ozonation

Another chemical that can be used to enhance hydrolysis (solubilization) of WAS is ozone. Ozone treatment prior to anaerobic digestion has been reported to result in the disruption of large polysaccharides, lipids and proteins which are the main constituents of microbial cells into their smaller compounds. Due to this, researchers have investigated the effect of ozone as a pretreatment prior to anaerobic digestion.

Weemaes *et al.* (2000) subjected WAS to ozone doses of 0.05 and 0.1 g O_3/g COD and reported methane production increased by factors of 1.5 and 2.2, respectively, compared to the untreated sludge. Elevated methane production with ozone pretreatment was also reflected in the elevated VS removal. Ozone pretreatment of WAS at doses of 0.05 , 0.1 and

0.2 g O_3/g COD combined with mesophilic anaerobic digestion resulted in average total VS removal efficiencies of 46, 68 and 62%, respectively.

Goel *et al.* (2003) used ozonation in two different process configurations and compared their treatment efficiencies. The first configuration was with ozone pretreatment of WAS followed by continuous mesophilic digestion. Before the pretreatment pH was adjusted to 2 with HCl and after pretreatment pH was readjusted to 7-7.2 with NaOH prior to digestion. In the second configuration, which was called closed loop, digested sludge was centrifuged for solids recovery and post ozonation was performed on digested sludge which was returned to the digester. From the first configuration it was found that with the dose of 0.015 g O_3/g TS, there was a slight increase in VS reduction efficiency (10-30% higher than the control) using a 28 day SRT. As the dose increased to 0.05 g O_3/g TS, the efficiency of total VS reduction improved to 85 and 90% over the control when SRT was 28 and 14 days, respectively. A slight increase was observed in specific methane production with the dosage of 0.015 g O_3/g TS (from 0.2 to 0.21 L CH_4/g VS at 28 days SRT and from 0.12 to 0.14 L CH_4/g VS fed at 14 day SRT). This slight increase was not significant and was associated with variation of the data. With dose of 0.05 g O_3/g TS, specific methane production doubled compared to the untreated sludge with all SRTs and was significant. From the closed loop experiments, it was reported that in order to have the most benefit out of post-ozonation, the ozone dose had to be higher than 0.45 g O_3/g TVS fed to obtain better gas recovery and better effluent quality. The experiment showed the benefits of WAS pretreatment by ozone over post treatment.

Improvement in methane production with ozone pretreatment was also reported by Benitez *et al.* (1997). Treating olive mill wastewater under mesophilic conditions average methane production was increased from an average of 194 mL CH_4/g COD without pretreatment to 266 mL CH_4/g COD with ozonation. Unfortunately, the ozone dose was not quantified.

Although improvement in biodegradability and sludge reduction as well as methane production was observed with ozonation, there are some drawbacks of this pretreatment. The increase in energy demand for sludge treatment and deterioration of dewatering characteristics are the most important disadvantages of ozonation. Additionally, it has been observed that there is an increase of COD and ammonium concentration in the effluent stream (Scheminski *et al.,* 2000).

2.4.4 Ultrasound Pretreatment

The frequency range for ultrasound is between 20 kHz and 10 MHz. In an aqueous environment application of ultrasound at lower frequencies between 20 to 40 kHz results in the formation of small bubbles due to localized pressure decreases below the evaporation pressure in the aqueous phase which causes cavitation. These bubbles oscillate, grow and collapse in a nonlinear manner. Cavitation causes strong mechanical shear forces and extreme temperature increases inside and around the bubble (Chu *et al.,* 2001). This phenomena can be used to disrupt the cellular structure of WAS leading to solubilization of biomass material.

Initial research found that 96 seconds of ultrasound pretreatment of WAS at 3.6 kW increased VS reduction from 45.8 to 50.3% at a 22 day SRT with mesophilic anaerobic

digestion. VS reduction of 44.3% could also be achieved by ultrasound treatment with SRT as low as 8 days (Thiem *et al.,* 1997).

In another study, WAS subjected to 9 kHz ultrasound pretreatment for 30 minutes resulted in a 64% increase in methane production over the control. In the same study it was also found that extending the pretreatment contact time to longer than 30 minutes resulted in no significant increase in methane production (Wang *et al.*, 1999). This finding suggested that an optimum or upper boundary existed for ultrasound pretreatment conditions and concomitant increased digester biogas production and VS destruction.

It was also reported that with alkaline treatment only of WAS with 40 meq/L NaOH, the VFAs to tCOD ratio (percentage basis) increased from 10 to 66% within 21 hours. However: when alkaline treatment was combined with ultrasonic pretreatment the VFA to tCOD ratio increased by 84% in 21 hours (Chiu *et al.*, 1997). This work suggests that combinations of pretreatments work together synergistically to increase hydrolysis of WAS.

In work presented by Tiehm *et al.* (2001) it was found that at frequency of 41 kHz, the degree of WAS disintegration (based on sCOD/tCOD) was observed to be 80% and as the frequency increased the degree of disintegration decreased indicating that lower frequencies were better for pretreatment. Other important observations of this study were that ultrasound treatment time had an important effect on WAS cell disintegration and improved mesophilic digestion. After ultrasound pretreatment for 7.5 minutes, VS reduction was improved 22% over the control with floc deagglomeration but no cell disintegration was observed. After 150 minutes of ultrasound pretreatment VS reduction improved to 33.7% and cell disruption was observed (Tiehm *et al.,* 2001). This finding suggests that an optimum between the

benefits of improved digestion (VS removal, improved biogas production, dewaterability, etc.) and costs of pretreatment must eventually be determined.

Research on floc size disruption showed that after 0.22 W/mL power was applied to WAS sludge with 98.9 μm floc size, floc size starts to decrease. Sludge treatment done at 0.33 W/mL causes a size reduction to 22 and 4μm (average) when contact time was 20 and 120 minutes, respectively. The smallest floc size was observed to be 3 μm after treating the WAS sludge at 0.44 W/mL for 20 minutes. During these experiments no change was observed on the settling properties of the sludge (Chu *et al.,* 2002). At lower frequencies close to 20 kHz, it was recommended that in order to enhance biogas production, ultrasound contact treatment time should be increased in conjunction with increased sludge concentrations up to 5% TS (Onyeche *et al.,* 2002).

At 160 kJ/L ultrasound application (20 kHz for 1 hour with 260 W power) it was found that for low WAS loading (1.2-3.2 g TS/L), COD solubilization increased in the range of 9 to 20% (Gonze *et al.,* 2003).

Studies done at plant scale showed that biogas production increased about 50% with 15% reduction of VS when ultrasound pretreatment was applied to WAS at 20 kHz for a minimum of 1.5 seconds when compared to the untreated control. While not actually stated it is believed that the 15% reduction of VS was actually a 15 point reduction (i.e., 30 to 45%) if biogas production increased by 50% (i.e., 50 to 75 L/d). Additionally, sludge dewatering improved by 2.6% percentage points (i.e., 17 to 19.6% solids concentration in biosolid cake) without changing the polymer dosage (Brown *et al.,* 2003). Similar results with WAS were also reported by Barber (2002). Barber reported a 25-50% increase in

biogas production and hydrolysis rate after ultrasound pretreatment. With the addition of ultrasound pretreatment the HRT was reduced by 30% while maintaining the same removal as the control. Barber suggested that by maintaining the same HRT the organic loading rate to the mesophilic digester could be increased by 20-50% (Barber, 2002) without loss of efficiency.

The effect of ultrasound pretreatment was compared with ozonation and thermal pretreatment by Bougrier *et al.* (2006b). Operating frequency and supplied power for ultrasound pretreatment were 20 kHz and 225 W, respectively. The pretreatment conditions were 6250 and 9350 kJ/kg TS for ultrasound, 0.1 and 0.16 g O_3/kg TS for ozone and 170 and 190°C for thermal pretreatments. COD and TS solubilization for each technique found to be very similar in the range of 15% for sonication, 20-25% for ozonation and 40-45% for thermal treatment. Although ozonation showed better solubilization than ultrasound, methane production was higher with ultrasound. Capillary suction time (CST) measurements before and after treatments showed that only thermal treatment improved the dewateribility compared to other methods. The reported methane productions were as 334, 272 and 333 mL CH_4/g COD added and biodegradabilities were 95, 78 and 95% for ultrasound (9350 kJ/kg TS), ozone (0.16 g O_3/g TS) and thermal (170°C) pretreatments, respectively. Although ultrasound and thermal pretreatment showed very similar biodegradability it looked like thermal pretreatment had an advantage of improving dewaterability.

2.4.5 Thermochemical Pretreatment

The combined effects of chemical and thermal pretreatment of WAS sludge on anaerobic digestion were studied by Tanaka and coworkers (1997). Three different pretreatment conditions were tested which included chemical pretreatment with 0.6 g NaOH/g VSS, thermal pretreatment at 180°C for 5 min and thermochemical pretreatment at 130°C for 5 min with a dose of 0.3 g NaOH/g VSS. Tanaka reported that thermochemical pretreatment of WAS, resulted in a 70-80% and 30% increase in VSS solubilization and methane production respectively, which was the best result among the pretreatment techniques tested.

The change in sludge characteristics with thermochemical pretreatment by using acid was studied by Neyens *et al.* (2003a). The effect of temperature was tested between temperatures of 80 and 155°C while keeping pH at 2 by adding H_2SO_4. It was seen that higher the temperature the better dewaterability in terms of CST and lesser volume of solid residual. Similar tests were also conducted with alkaline addition in terms of $Ca(OH)_2$ and it was concluded that thermochemical pretreatment with acid (at 120°C and pH of 3) performed better than thermochemical pretreatment with alkali (at 100°C and pH of 10) (Neyens *et al.*, 2003b). Additionally alkaline thermochemical pretreatment introduces salts containing Ca^+ which has a negative impact on dewaterability.

Thermochemical pretreatment WAS followed by mesophilic digestion was also reported by Vlyssides and Karlis (2004). A combination of heating to 90°C and NaOH addition to pH 11 for 10 hours resulted in a 46% decrease in VSS concentration versus the control and improved methane product yield by 0.28 L/kg of initial VSS.

Another extensive research on thermochemical pretreatment was done by Valo et al. (2004). In this study thermal pretreatment (130, 150 and 170°C), alkali pretreatment (30 (pH 10) and 65 (pH 12) meq dm^{-3} KOH), oxidant pretreatment with hydrogen peroxide and Fenton's reagent (150 and 300 mmol dm^{-3} H_2O_2 and 5 mmol dm^{-3} $FeSO_4$) and thermochemical pretreatment (temperatures 130 and 170°C and pH 10 and 12) were compared. It was reported that only thermal pretreatment improved solubilization better than only alkaline pretreatment. sCOD/tCOD ratio was improved from 2.7% to 25.3 at 130°C , 59.5% at 170°C and only 9.3% at pH 10 and 30.7% at pH 12. Experiments with 150 mmol dm^{-3} H_2O_2 at 130°C showed less than 5% improvement on solubilization and due to temperature sensitivity of hydrogen peroxide other experiments were performed at 90°C; however, even with 300 mmol dm^{-3} H_2O_2 addition had only 7% improvement in solubilization. The highest improvement was observed with thermochemical pretreatment. The reported COD solubilization rates varied from 30.6 to 63.1% at 130°C at pH 7 and 10 and from 59.5 to 83.0% at 170°C at pH 7 and 12.

Batch experiments were also performed to investigate the effect of these pretreatment methods on biodegradability. The highest biodegradability was observed with thermal pretreatment at 170°C and thermochemical pretreatment at 130°C with pH 10 which showed 45 and 23% improvement in biodegradability, respectively. Continuous digestion experiments were also conducted to compare these two pretreatment methods at 20 day SRT. COD removal was increased from 44% to 71 and 60% and VS removal from 35 to 67 and 60% for digesters with thermal pretreatment and with thermochemical pretreatment, respectively. Although digester with thermochemical pretreatment produced more biogas

(54% increase compare to control), digester with thermal pretreatment showed better COD degradation (71%) and TS removal (59%).

2.4.6 CAMBI^{TM} Process

The CAMBI^{TM} process which was developed by the Norwegian Company CAMBI, consists of chemical pulping (17% TS) followed by heating thickened sludge (14% TS) to 165°C at a pressure of 12 bar in a reactor followed by mesophilic digestion. The main advantages of the CAMBI^{TM} process are sludge sterilization (Class A sludge), destruction of foaming organisms, enhanced methane production, less sludge generation, surplus energy production and an automated process (Barnard *et al.*, 2002). It was reported that by heat recirculation management that the process was economical but exact details could not be found. In 2001, a full scale CAMBI^{TM} plant was built in Dublin, Ireland. The process diagram of this plant is shown in Figure 2.3.

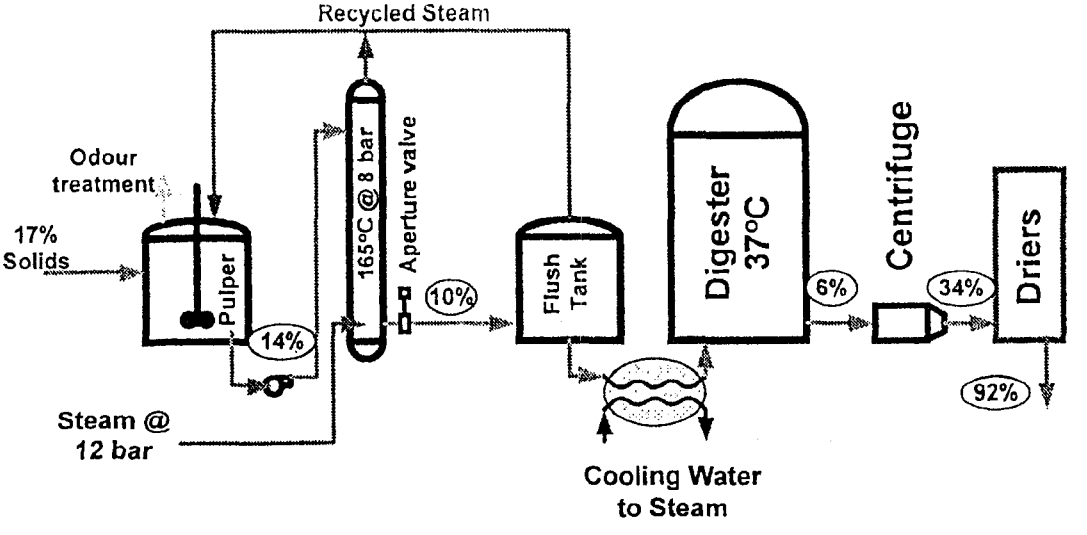

Figure 2.3: Diagram of the Dublin Bay sludge treatment train (Adapted from Barnard *et al.*, 2002)

At start-up it was found that the initial sludge solids concentration was lower than the expected 17% TS concentration. The problem was overcome by mixing hydrolyzed sludge with digester cake sludge (concentrated digested sludge) at ratios of 33 and 67% by volume, respectively. With this modification the plant was reported to operate with VS destruction of approximately 70% (Abraham and Kepp, 2003). It was unclear if this value was 70% of virgin material or the sludge/biocake mixture. Pickworth et al. (2006) reported 62% VS reduction with 15-18 day HRT for this system at WWTP at Dublin, Ireland. The digested sludge was able to be dewatered to 34% with the end product of Class A cake. The net energy production was calculated to be 3 MWs. It was concluded that CAMBI process integrated with the existing digestion and drying plant reduced the operating cost for energy.

2.4.7 Steam Explosion Pretreatment

Steam explosion technology designed by Super Blue Box Recycling Corporation, to pretreat municipal solid waste (MSW) has been applied to pretreat TWAS (6% TSS) and digested biocake solids (30% TSS) prior to anaerobic mesophilic digestion. Sludge is treated in a pressurized reactor at 10.3-41.4 bar and 180-260°C for five minutes and then cooked sludge is released through a small orifice causing an explosion. This explosion causes extreme shearing conditions and causes microbial cell wall disruption. BMP tests conducted following various steam explosion pretreatment conditions to TWAS and biocake were used to evaluate changes in sludge characteristics and enhanced biogas production (Dereix *et al.*, 2005). TWAS that was used for this research had a solids concentration of 6% which was low for steam explosion pretreatment; therefore, it was enriched with biosolids that had a concentration of 30% TS. The recommended minimum sludge concentration for steam

explosion was 15%. After steam explosion treatment at pressures of 10.3, 20.7 and 41.4 bar, sCOD/tCOD ratios were found to be increased from 7% control (no pretreatment) to 13, 40 and 33%, respectively. VS destruction during digestion increased from 28% (control) to 38, 37 and 40%, respectively. It was indicated that results of experiments conducted using 20.7 bar pressure were questionable due to the fact that the tCOD value for this experiment was found to be lower than the other experiments. Biogas production was improved by 28, 41 and 68% over the control for pretreatment at 10.3, 20.7 and 41.4 bar, respectively.

Semi-continuous anaerobic digestion (35°C) experiments at SRT of 8 days with steam explosion pretreatment at 300 psi showed that VS destruction was improved from 30 to 35% and biogas production increased by 31% over control reactors. For a SRT of 14 days, VS destruction was improved by 34% and biogas production was increased by 48%. It was also reported that dewateribility of digested sludge (based on CST test) with pretreatment was improved slightly. The average CST value of pretreated sludge was 205 s while that of control was 310 s.

2.4.8 MicroSludge™

MicroSludge™ increases the extent of WAS degradation and rate of methane production by applying pressure and chemical pretreatment to WAS. Cell membranes are weakened by alkaline pretreatment and with the use of an industrial scale homogenizer sudden and gross pressure change applied to the WAS causes disruption of cell structure (i.e., burst).

The *MicroSludge*™ process claims many advantages as a pretreatment option for mesophilic digestion of WAS. It reduces pathogens concentrations close to US EPA Class A Biosolids

(US EPA, 1994) and the combination of better dewaterability of digested sludge mass and high VSS removal results in significantly reduced amount of a significantly drier and better stabilized sludge for disposal. It was also reported to reduce odours compared to controls.

Pretreatment experiments followed by mesophilic digestion performed on mixed primary sludge and WAS (ratio of 40:60, respectively) resulted in 97% sCOD destruction being achieved whereas with conventional mesophilic anaerobic digestion (no pretreatment) sCOD destruction was observed to be only 17% after 15 days of digestion. The mixed sludge pretreated with *MicroSludge*™ process after 5 days of digestion also showed 90% reduction in sCOD.

VS reduction was increased from 41 to 85% with the *MicroSludge*™ process after 15 days of digestion. In the first 5 days of digestion, most of all VFA produced during this time is converted to biogas and within 10 days almost 97% of VFA produced are converted to biogas. During the experiments no changes in ammonia concentrations in the digesters were observed which would cause ammonia inhibition (Stephenson *et al.,* 2003). Full scale demonstration plants are in operation or under construction in Chilliwack, B.C. and Los Angeles, CA. However results have not yet been released to the general public.

2.5 Microwave Technology as a Pretreatment Method

2.5.1 Theory of Microwave

Microwaves are electromagnetic radiation. Their frequencies and corresponding wavelengths range from 300 MHz to 30 GHz and from 1 to 0.01 m, respectively (Figure

2.4). To prevent interference between MW heating and telecommunication, ISM bands (Industrial Scientific and Medical frequencies) which are 27.12, 915 MHz and 2.45 GHz, are used for MW heating. 2.45 GHz frequency with a 12.3 cm wavelength is taken as the standard frequency for MW irradiation for domestic and industrial ovens (Loupy, 2002) (In this study, 2450 MHz frequency with 12.3 cm wavelength will be used)

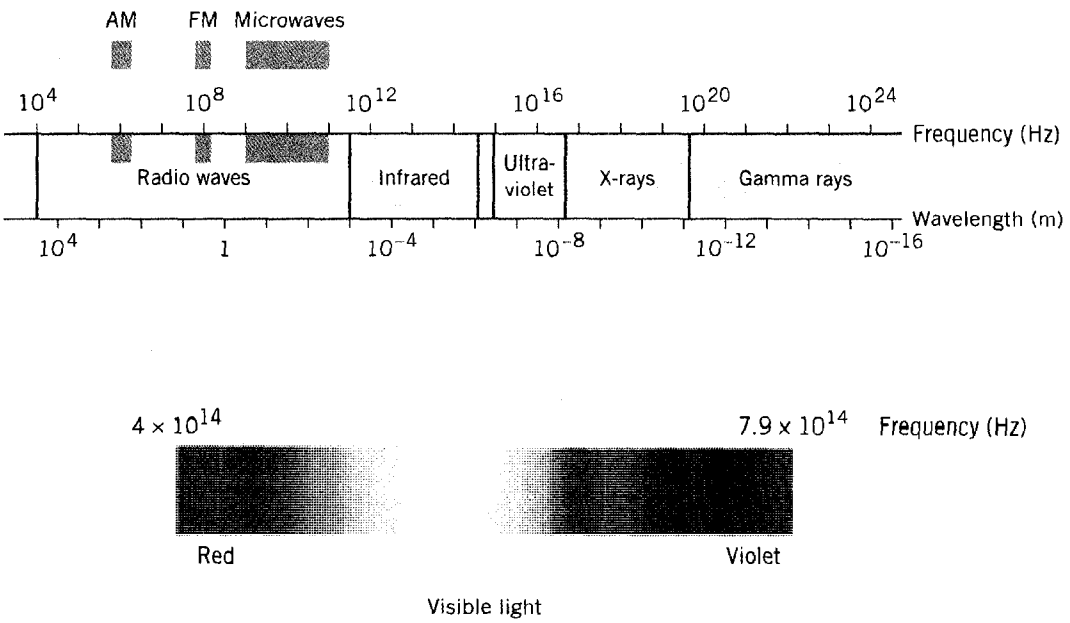

Figure 2.4: The electromagnetic spectrum (www.valdosta.edu/~pbaskin/phys1112ch24notes.doc)

The electromagnetic field produced by microwaving causes polarized molecules to align which is referred to as dipole rotation. A decrease in electromagnetic field leads to the restoration of disorder and thermal energy is released (Figure 2.5). The time required for molecules to return to disorder is called relaxation time. At 2.45 GHz frequency, the time required for field changes between the relaxation time of permanent dipoles and electric field oscillation occurs 4.9×10^9 times per second. The temperature of reagents or solvents

increases rapidly due to absorption of MWs that oscillate between aligned dipoles (order) and relaxation (disorder) (Kingston and Jassie, 1988).

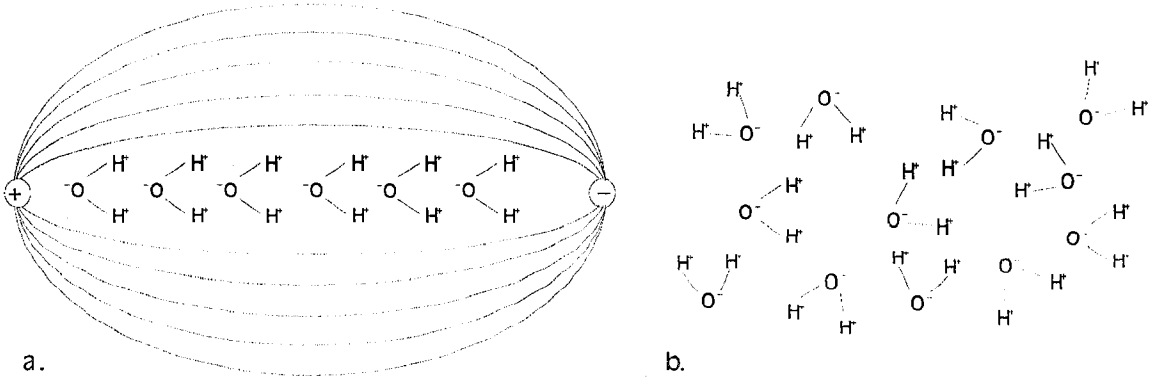

Figure 2.5: Schematic of the Molecular Response to an Electromagnetic Field. (a) Polarized Molecules Aligned with the Poles of the Electromagnetic Field; (b) Thermally Induced Disorder as Electromagnetic Field is Removed (Adapted from Kingston and Jassie, 1988)

Some solids and liquids also have the ability to transform electromagnetic energy into heat. This is called the dissipation factor (Equation 1) which differs from material to material. The dissipation factor is a function of the dielectric loss factor and dielectric constant of the material and is formulated as:

$$\tan \Delta = \frac{\varepsilon''}{\varepsilon'} \qquad (1)$$

Where $\tan \Delta$ is the dissipation factor

ε'' is the dielectric loss factor

ε' is the dielectric constant of the material

A material's efficiency to transform the electromagnetic energy into heat is referred to as the dielectric loss factor whereas the dielectric constant is related to the polarization ability of the molecule under an electric field. At 2.45 GHz, the heating rate of water by microwaving is maximized as the dielectric constant of water increases with decreased frequency. The dielectric constant of water drops to zero very rapidly when frequency reaches 30 GHz (Fini and Breccia, 1999).

2.5.2 Thermal and Athermal Effects

Microwave heating is different than conventional heating. In addition to the thermal heating of water, during MW irradiation, side chains of macromolecules can be polarized and they can line up in the direction of the electric field and this can cause hydrogen bonds to break which cannot be achieved by conventional heating (Hong et al, 2004). These hypothetical effects are called athermal effects which are unique to electromagnetic irradiation. Some authors have rejected the athermal effect of microwaving (Pollington *et al.,* 1991, Mijovic *et al.,* 1992 and Raner and Strauss, 1992). Jahngen *et al.* (1990) reported that the increase in hydrolysis rate of adenosine triphosphate (ATP) by microwaving which was observed by Sun *et al.* (1988) was only due to conventional temperature heating effects and the increase was not attributable to athermal effect of MW irradiation. Plazl *et al.* (1995) have also concluded that MW irradiation had no extra effect on the kinetics of sucrose hydrolysis compared to conventional temperature heating during catalysis using a strong cationic ion exchange resin. MW experiments on permeability of liposomes by Bergqvist *et al.* (1994) reached a similar conclusion: there is no athermal effect of MW irradiation on liposome permeability.

On the other hand, other researchers claim the existence and advantages of the non-thermal effect of MW irradiation. Shin and Pyun (1997) concluded that the membrane structure of *L. plantarum* was significantly more irreversibly damaged by MW treatment than when conventional heating was applied. They also observed that microwaved microbial cells were more sensitive to salt inhibition than conventionally treated (heated) cells. Similar conclusions were also reported by Kozempel *et al.* (1998) who used MW radiation to kill microorganisms (sterilization or die off studies) in different fluid media. They observed that in some fluids microorganisms were killed at sublethal temperatures by MW treatment but survived at similar and higher treatment temperatures using conventional heating. It was interesting to note that athermal effects seemed to be reported for more complex systems (i.e., sucrose hydrolysis vs. cellular membrane damage).

Although there is no concise agreement on whether there is or not a non-thermal effect of MW irradiation on biological systems, the importance of MWs as an alternative way of introducing energy to biochemical and chemical systems is well appreciated by all these researchers.

There are other benefits of using MW heating. Microwaved materials are heated directly internally so there is no heat loss through convection or conduction (Figure 2.6). Large amounts of materials can be heated more efficiently. Heating rates through microwaving can be much faster than conventional heating so with a proper MW applicator the energy efficiency can be increased dramatically. Since the power source is remote from the applicator, a clean heating environment can be achieved (National Research Council, 1994).

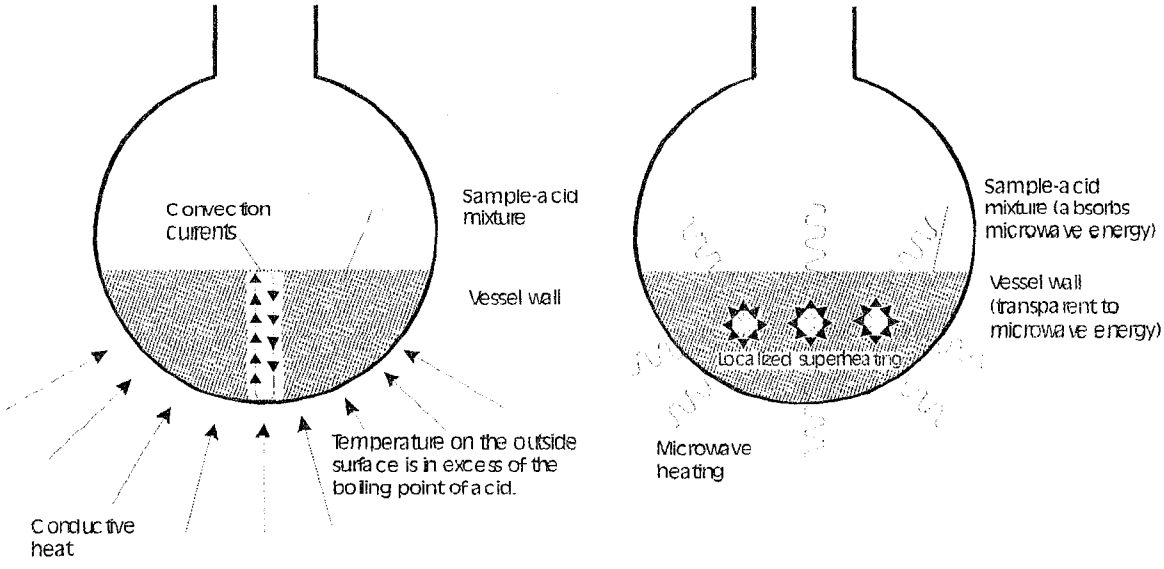

Figure 2.6: Schematic of Sample Heated by Conventional (on the left) and by MW Technology (on the right) (Adapted from Kingston and Jassie, 1988)

2.5.3 Application Fields of Microwave Irradiation

Microwaves are involved in kitchens mostly for heating or cooking purposes. For commercial purposes MWs have been used mostly in food processing, ceramic and mineral processing, sterilization, analytical chemistry and heating and vulcanization of rubber.

In ceramic processing, process time reduction as well as uniformity and improved microstructure of the products with the ability to synthesis new materials are some advantages of MW applications. In the metallurgy industry, MW processing reduces energy consumption substantially and decreases the negative impact of the industry on the environment. In analytical chemistry laboratories MWs have been used since the mid-1970s. Initially MWs were used primarily for sample preparation, and then it expanded into esterification, drying, extraction, acid dissolution, hydrolysis and synthesis of radiopharmaceuticals or labelled drugs (National Research Council, 1994).

Applications to biological systems have also shown that MW irradiation has benefits (Roy and Gupta, 2003). Vaid and Bishop (1998) reported that the effect of MW irradiation on spore disruption was greater than conventional heating at any given temperature (another athermal effect). As an example it was shown that spores of *Cl. Sporogens* were disrupted when heated with MWs at 100°C for 8 minutes where as boiling for the same length of time showed no effect on the structure of the spores. They observed similar results when applying MW irradiation to other spore forming species. It was also mentioned that no other mechanical disruption method produced similar results. It was hypothesized that generation of internal pressure in the spore's core rather than external pressure generation which is the case of most other thermal and mechanical treatment methods caused spore lysis and death. Similar results were found by Salvatorelli *et al.* (1996) with *Bacillus Subtilis* spores. Another interesting work by Celandroni *et al.* (2004) observed that conventional heating caused swelling of the cortex of the nucleoid where as irradiating with the MW showed no modification of this layer compared to untreated controls. Although the release of nucleotides was observed with both conventional and MW treatment, the lack of cortex swelling shows a non-thermal effect of MW irradiation.

In application of MWs to sterilisation, work done by Papadopoulou *et al.* (1995) showed that conventional heating and MW irradiation give the same results on *B. marcerans*. However when applied to *Escherichia coli,* death rates were greater with MW irradiation than conventional heat sterilisation at temperatures higher than 45°C (Banik *et al.*, 2003).

Another important study was done on denaturation of enzymes and proteins (Porcelli *et al.*, 1997). Experiments conducted with *S-adenosylhomocysteine hydrolase* and *5-*

methylthioadenosine showed that MW irradiation caused irreversible and time dependent enzyme inactivation which was ascribed as a non-thermal effect of MW irradiation whereas conventional heating did not result in the same degree of inactivation and denaturation.

Experiments with MW pretreatment applied to secondary WAS showed release of sCOD up to 22% of tCOD when sludge was heated with MW to boiling temperature (Park *et al.*, 2004). The main thrust of the work was determination of pathogen reduction. It was reported that the effect of MW irradiation on pathogens had the potential to produce Class A sludge (Hong *et al.*, 2004). It was mentioned that the energy requirement of MW pretreatment would be much less than other leading pretreatments such as sonication.

The effect of MW irradiation on various municipal sludges has been investigated in the Water Pollution Laboratory at University of Ottawa. All research was done at temperatures lower than 97°C.

First, primary sludges with different concentrations were pretreated with MW at temperatures of 35, 60 and 90°C at different MW intensities (Zheng, 2006). It was observed that sCOD/tCOD ratio increased from 2% (control) to approximately 7% when 2% suspended solids (SS) (w/v) primary sludge was treated at 90°C with 80% MW intensity. Figure 2.7 shows the complete diagram for sCOD/tCOD ratio vs. sludge concentration and MW temperature. It shows that higher temperature results in greater solubilization. No MW tests were reported for extended temperature holding time scenarios.

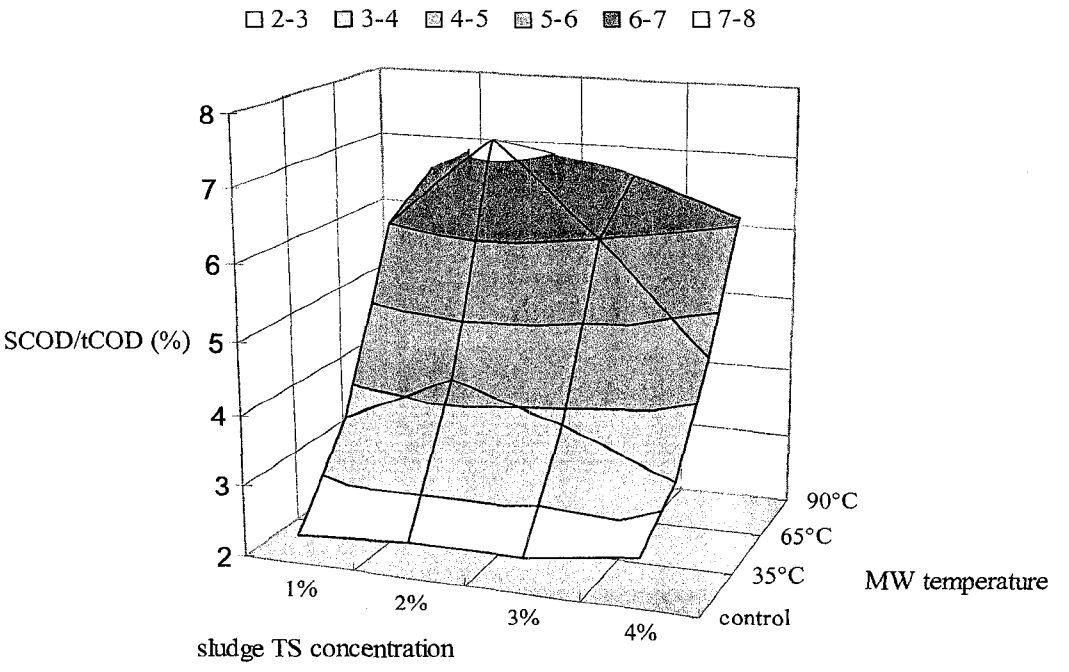

Figure 2.7: Effect of solubilization rate with 80% intensity (Adapted from Zheng, 2006)

Microwave pretreatment with combined primary and secondary sequencing batch reactor (SBR) sludge was also investigated at different temperatures (45, 65 and 85°C), MW intensity and sludge concentration (1.2-4.3%) (Thibault, 2006). In this study the highest sCOD/tCOD ratio was also found to be 7% by microwaving to 85°C at 4% SS concentrated sludge (Figure 2.8). When the same sludge was pretreated with a strong dose of NaOH, the sCOD/tCOD ratio was found to be 57% which indicates that MW irradiation at 85°C or lower still does not improve the solubilization of primary and secondary mixed SBR sludge to the extent possible with strong chemical pretreatment methods. Partial sludge treatment and low MW intensity did improve the extent of biodegradability. The maximum biogas production over the control was reported to be 16.2%. Again no MW tests were reported for extended temperature holding time scenarios.

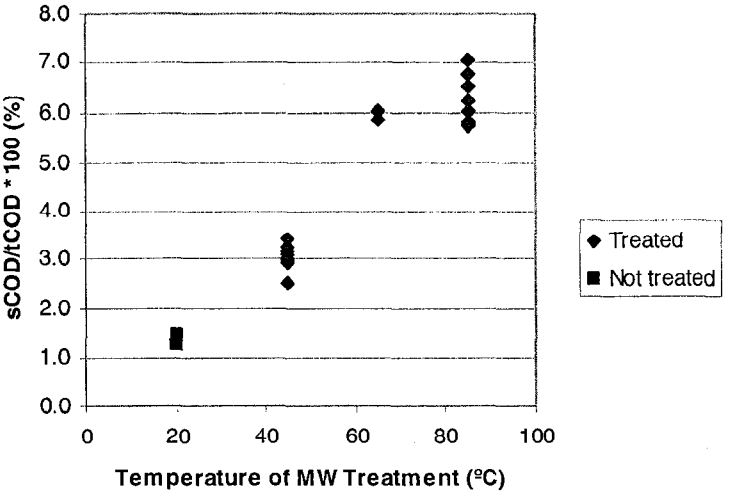

Figure 2.8: Effect of the temperature of MW treatment on COD solubilization (Adapted from Thibault, 2006)

In another study, low temperature (lower than the boiling point) MW irradiation of secondary sludge was investigated (Eskicioglu, 2005). Results showed that microwaved WAS had 3.6 and 3.2 fold increases in sCOD/tCOD ratio (Figures 2.9 and 2.10) and 13 and 17% increase in cumulative biogas production (CBP) (Figures 2.11 and 2.12) at concentrations of 1.4 and 3% TS, respectively. Low MW intensity to a set temperature was observed to be more effective in increasing the degradability of WAS than high intensity to a set temperature indicating that exposure time to set conditions could improve results. This result is contrary to the results obtained by Thibault (2006) who found effects of MW intensity to be negligible. This may be the result of differences in the types of sludge tested. It was also observed that the initial difference between the CBP of treated and untreated WAS sludges was negligible. Microwave pretreatment at low temperatures (<100°C) accelerates hydrolysis and extends the time of methanogenesis and also impacts the extent of WAS digestion (Figures 2.9-2.12).

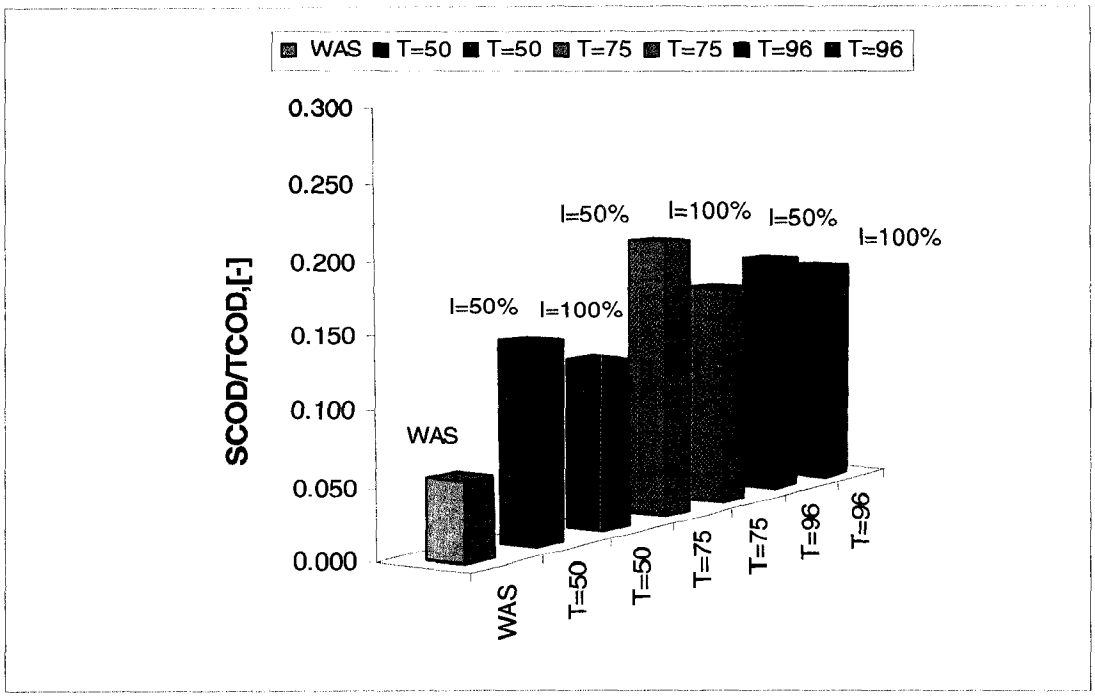

Figure 2.9: Solubilization Effect of MW on WAS (5.4% TS) (Adapted from Eskicioglu, 2005)

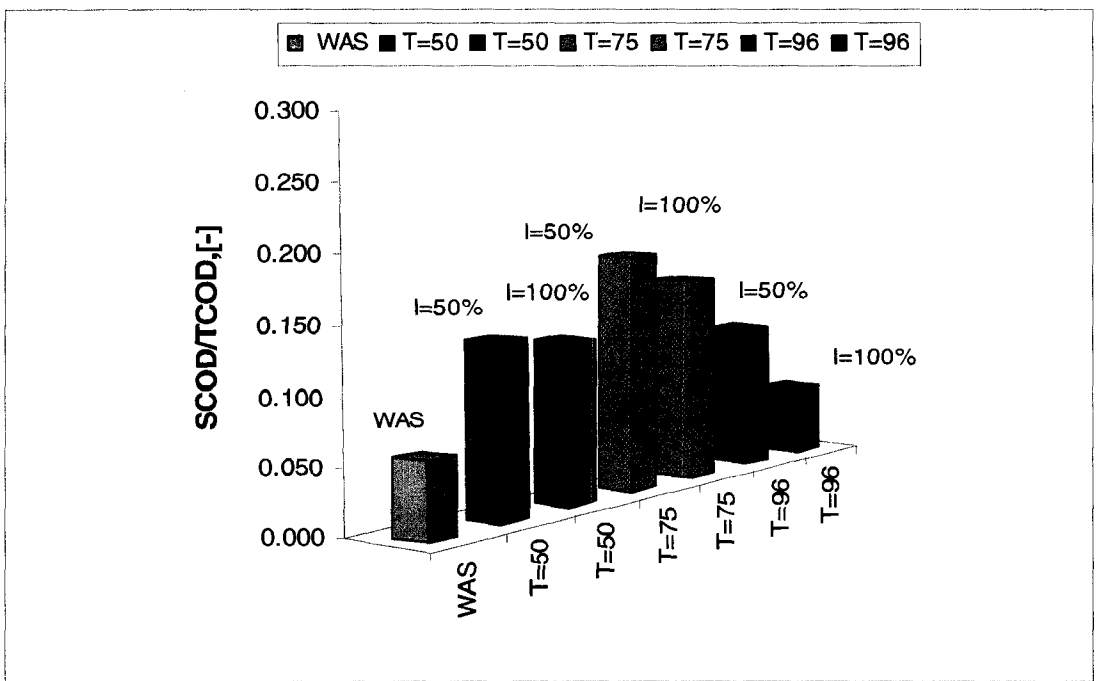

Figure 2.10: Solubilization Effect of MW on WAS (1.4% TS) (Adapted from Eskicioglu, 2005)

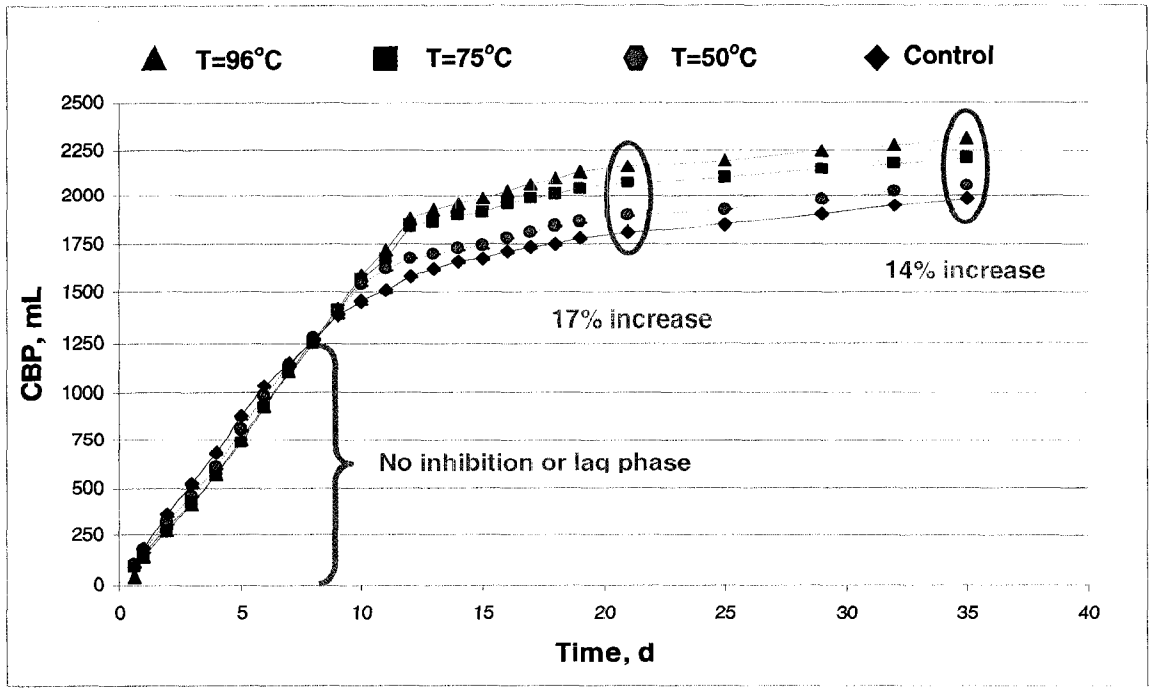

Figure 2.11: CBP from Batch Reactors with WAS (3% TS) (Adapted from Eskicioglu, 2005)

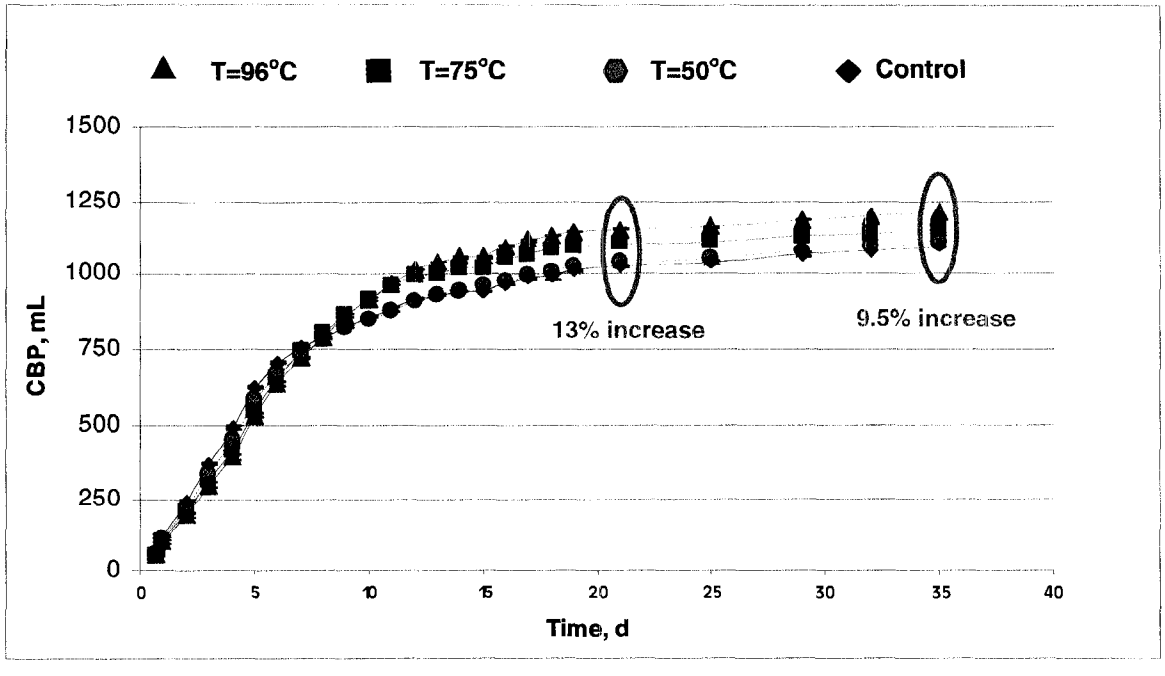

Figure 2.12: CBP from Batch Reactors with WAS (1.4% TS) (Adapted from Eskicioglu, 2005)

The experiments on semi-continuous anaerobic digestion with low temperature MW pretreatment showed less than 5% improvement in biogas production at 10 day SRT from digestion of sludge MW pretreated at 96°C. However more significant improvements in biogas production were observed when the SRT was decreased to 5 day and was reported to be 15 and 28% for sludge MW pretreated at 50 and 96°C, respectively (Eskicioglu *et al.* 2007). CST results indicated that digested sludge dewaterability improves by 39% with MW pretreatment at 96°C.

A summary of the work that has been done is shown in Table 2.3. While results tend to indicate that higher temperature and exposure time may be important, no MW tests were reported or were planned for various extended temperature holding time scenarios at temperatures above or below 100°C.

Table 2.3: Summary of recent work at University of Ottawa

Sludge Type	MW Pretreatment Temperature	Tests done	Operating conditions that are tested	Observations
Primary	35, 65, 90	Pre-digestion Batch digestion	Temperature MW intensity Sludge concentration	* temperature ↑, biodegradability ↑
Primary + Secondary	45, 65, 85	Pre-digestion Batch digestion	Temperature MW intensity Sludge concentration Partial pretreatment Multiple microwaving	* high intensity and full treatment have better results * multiple microwaving does not have advantages over single one
TWAS	50, 75, 96	Pre-digestion Batch digestion Semi-continuous digestion	Temperature MW intensity Sludge concentration Partial pretreatment	* MW pretreatment increase the rate of digestion * low intensity is slightly better than high intensity *MW pretreatment enables reduction of SRT for continuous digestion *Dewaterability improves with MW pretreatment

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CHAPTER 3:

Effect of High Temperature Microwave Irradiation on Municipal Thickened Waste Activated Sludge Solubilization

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3.1 INTRODUCTION

Sludge production at wastewater treatment plants causes significant economical and environmental problems since sludge stabilization governs a large portion of plant operational costs and its disposal is also expensive and causes environmental degradation. It is important to decrease sludge volume and increase its dewateribility to decrease its transportation cost. Removing pathogens and heavy metals while stabilizing sludge can convert sludge into a useful product for field applications. Anaerobic digestion is the most commonly used method to achieve all of these objectives.

In conventional anaerobic digestion (AD) of thickened waste activated sludge (TWAS), volatile solids (VS) reduction between 30-45% can be achieved; thus more than 50% of the

organics in the sludge are either non–biodegradable or not readily available for biodegradation (Gosset and Belser, 1982). This limitation in biodegradation in anaerobic digestion results from the slow rate of hydrolysis of particulates. Secondary sludge or TWAS consists mainly of microbial cell biomass and extracellular floc matrix. Cell walls in association with the floc matrix are very resistant to degradation since they are physical and chemical barriers to exoenzyme degradation and hydrolysis (Baier and Schmidheiny, 1997). Disintegration of the floc matrix and/or cell walls would increase the accessibility of intracellular components to biological degradation which would improve the efficiency of anaerobic digestion.

Many pretreatment methods have been studied to enhance anaerobic digestion, which include thermal, chemical, physical disintegration and combinations of these methods. Although all of these pretreatments have been shown to increase the biodegradability of municipal sludge, thermal disintegration at high temperatures (160-175°C) and high pressures (6-8 bar) tends to produce better results than any of the other pretreatment methods in terms of increased VS destruction, increased biogas production as well as pathogen reduction (Barnard *et al.*, 2002; Abraham and Kepp, 2003).

As an alternative innovative method to conventional heating of sludge, microwave (MW) irradiation pretreatment may be a promising technology to conserve energy and enhance pathogen and VS destruction (Decareau, 1985). The electromagnetic field produced by microwaving causes polarized molecules to align which is referred to as dipole rotation. A decrease in electromagnetic field leads to the restoration of disorder and thermal energy is released. MW irradiation can produce rapid focused heating effects from both thermal and

athermic (non-thermic) molecule orientation effects. Athermic effects can result in the disruption of the tertiary and quaternary structure of complex organic molecules due to dipole rotation of polar molecules. It is hypothesized that the combination of thermal and orientation affects of microwaving causes the weak hydrogen bonds to break apart resulting in the unfolding and denaturation of complex organic molecules leading to smaller more biodegradable organic molecules and particles. Although there is no universal agreement on whether or not there is a non-thermal effect of MW irradiation on biological systems, the importance of MWs as an alternative method of introducing energy to biochemical and chemical systems is well agreed on. Due to the fact that materials are directly heated internally by MWs, heat loss through convection and conduction can be minimized. Since the power source is remote from the applicator, a clean heating environment can be achieved (National Research Council, 1994).

Experiments with MW pretreatment applied to secondary TWAS showed a release of soluble chemical oxygen demand (sCOD) up to 22% of total COD (tCOD) when sludge was heated with MW to boiling temperature (Park *et al.,* 2004). The main thrust of their work was determination of pathogen reduction. It was reported that MW irradiation of pathogens had the potential to produce Class A sludge (Hong *et al.,* 2004). It was also mentioned that the energy requirement of MW pretreatment would be much lower than other leading pretreatments such as sonication.

Another study using conventional kitchen type MW as a pretreatment method for mesophilic anaerobic digestion (MAD) of WAS showed that MW treated WAS (temperatures between 50-96°C) had 3.6 ± 0.6 and 3.2 ± 0.1 fold increases in sCOD/tCOD and 13 and 17% increases

in cumulative biogas production (CBP) (in batch digestion) at sludge concentrations of 1.4 and 3% total solids (TS), respectively. MW pretreatment at low temperatures (<100°C) impacts the extent of WAS digestion; however, no change was observed in the rate of methanogenesis for WAS (Eskicioglu et al., 2006).

In conventional thermal pretreatment it was observed that increasing pretreatment temperature up to 175°C gives better solubilization and biogas production. Beyond 180°C methane production was observed to decrease sharply and it was ascribed to a Maillard reaction which occurred between amino acids and low molecular weight sugars in the sludge producing inhibitory and difficult to degrade end products (Pinnekamp, 1989). Stuckey and McCarty (1984) also reported inhibition of anaerobic digestion following pretreatment of TWAS at elevated temperatures. They attributed the decrease in VS destruction to caramelization of sugars in the waste.

At temperatures higher than the boiling point there is no information on the effect of MW on solubilization and efficiency of anaerobic digestion of WAS. The objective of this paper is to investigate the properties of TWAS exposed to MW irradiation at temperatures higher than 100°C at different conditions.

3.2 EXPERIMENTAL SETUP

TWAS (approx. 5% w/v; 80% VSS) was obtained from the centrifuge thickener at the Robert O. Pickard Environmental Center (ROPEC) located at Gloucester, ON Canada. The average sludge retention time in the activated sludge basins at ROPEC was 5 days. MW pretreatments were carried out with a Mars 5© (MW Accelerated Reaction System; CEM Corporation) MW

oven. Mars 5© has a frequency of 2450 MHz and can deliver 1200 W±15% of MW energy at full power with complete MW penetration of the sample vessels. With its temperature and pressure sensors it is possible to monitor and control operating conditions up to 250°C and 34.5 bar.

A multilevel factorial design was used to investigate the variables affecting efficacy of pretreatment which were chosen to be: (i) pretreatment temperature, (ii) intensity of microwaving (the MW intensity was programmed such that the temperature change in unit time is constant) and (iii) concentration of sludge. Table 3.1 shows the variables and their levels.

Table 3.1: Variables and their levels used in the statistical design

Variables → / Levels ↓	Temperature °C	Temperature Change Rate °C/min	Sludge Concentration %
1	110	3.75	6
2	150	7.5	11.85
3	175		

Highly concentrated sludge was obtained by centrifuging raw TWAS at 7000 rpm for 20 minutes. The TWAS concentration increased from 6 to 11.85% TS.

The effects of high temperature MW irradiation on ammonia, pH, HCO_3^- alkalinity, TS, VS, sCOD, tCOD, soluble protein and soluble reduced sugars were investigated. Ammonia was measured using an ORION model 95-12 ammonia gas sensing electrode with Fisher Accumet

pH meter 750 according to Standard Methods 4500D procedure. Alkalinity and VS/TS analysis were done according to Standard Methods 2320B titration and 2540D procedures, respectively. sCOD and tCOD measurements were conducted according to Standard Methods 5220C colorimetric method using a Coleman Perkin-Elmer spectrophotometer model 295. To asses dewaterability of digested WAS, the 2710G capillary suction time (CST) method was used (APHA, 1995). For soluble protein and soluble reduced sugar concentrations in the supernatant, Bradford (1976) and Miller (1959) methods were used, respectively. Total volatile fatty acids (TVFA) (acetic acid, propionic acid and butyric acid) measurements were done by using a HP 5840A capillary column GC.

3.3 RESULTS

The raw sludge was microwaved at different conditions to determine changes in sludge properties. TWAS concentrations of 6 and 11.85% TS were studied. The effect of MW on sludge characterization is summarized in Table 3.2. All samples were analyzed in duplicate.

It was observed that as the pretreatment temperature increased, the sCOD content of the sludge also increased (Figures 3.1 and 3.2). The concentration of sludge before the treatment has significant importance on sCOD release. Increase in sCOD of treated sludge compared to the untreated TWAS (control) was greater for more concentrated sludge. The highest impact of MW intensity on sCOD release was observed when 11.85% TWAS was treated to 175°C with the microwaving rate at 3.75°C/min. For both sludge concentrations, the highest increase in sCOD was observed at 175°C with the lowest MW intensity (3.75°C/min). Sludge treated at 175°C with the lowest MW intensity had 0.46 ± 0.06 and 0.57 ± 0.04 sCOD/tCOD ratios

which were 4.5 ± 0.5 and 8.8 ± 0.6 fold higher than their controls (untreated TWAS) for 6 and 11.85% TS concentrations, respectively (Figures 3.1 and 3.2). The improvement in transferring materials from the solid phase to the soluble phase was higher with elevated temperatures (T>100°C) than for pre-treatment temperatures below the boiling point. When TWAS was treated with conventional MW to 96°C at concentrations of 1.4 and 3%, the highest improvements were only 3.6 ± 0.6 and 3.2 ± 0.1 fold more than the control, respectively (Eskicioglu et al., 2006). It is important to note that improvement in sCOD/tCOD ratio was greater for low sludge concentration when the pretreatment temperature was lower than boiling temperature however above boiling temperature high sludge concentration had shown greater improvement in enhancing sCOD/tCOD ratio. Figure 3.3 shows the sCOD/TS values for all conditions studied. For MW temperatures 110 and 150°C, sCOD/TS values were very similar for sludge with 11.85% TS and increasing MW temperature to 175°C showed further improvements in sCOD concentration. On the other hand, for 6% TWAS increasing temperature from 110 to 150°C also showed improvement in sCOD concentration.

It was found that the intensity of MW also had an important effect on the solubilization of sludge at elevated temperature MW pretreatment (Figures 3.1 and 3.2). For sludge with a 6% concentration, lower MW intensity (3.75°C/min) resulted in average 25 ± 0.04% higher sCOD/tCOD ratio than high MW intensity (7.5°C/min) for all temperatures tested. The difference between sCOD/tCOD ratios of 6% TWAS treated at low and high MW intensities decreased as pretreatment temperature increased. For 11.85% TWAS, the effect of intensity on solubility was not significant for treatment temperatures of 110 and 150°C; however, it

was more pronounced when sludge was heated to 175°C which resulted in 47% higher sCOD/tCOD ratio than low MW intensity.

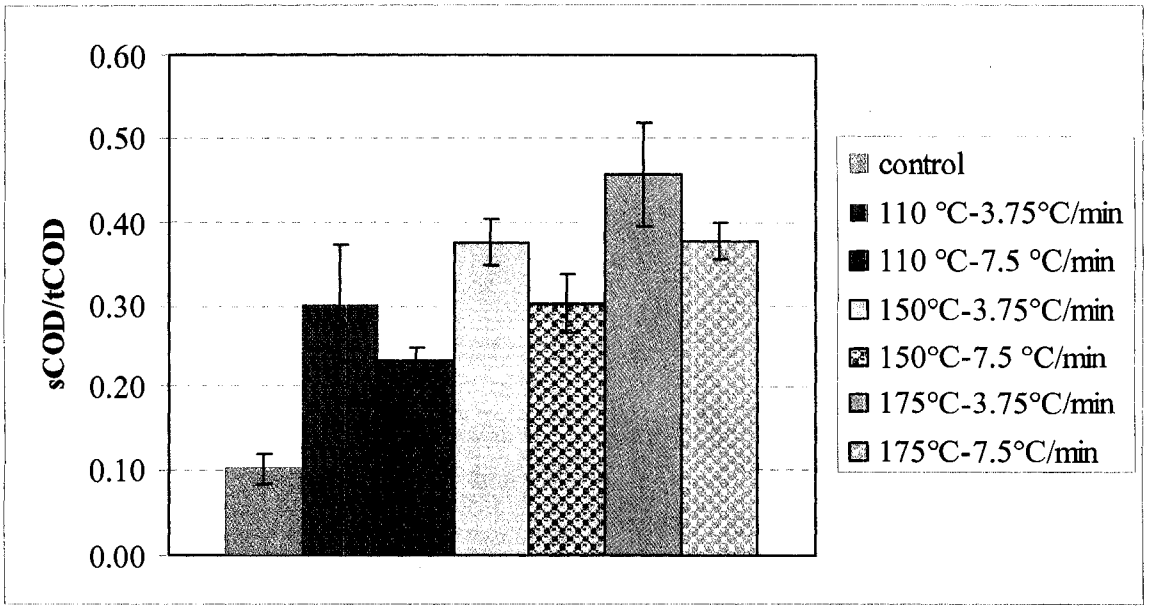

Figure 3.1: sCOD/tCOD ratios for 6% TWAS treated at different temperatures and MW intensities

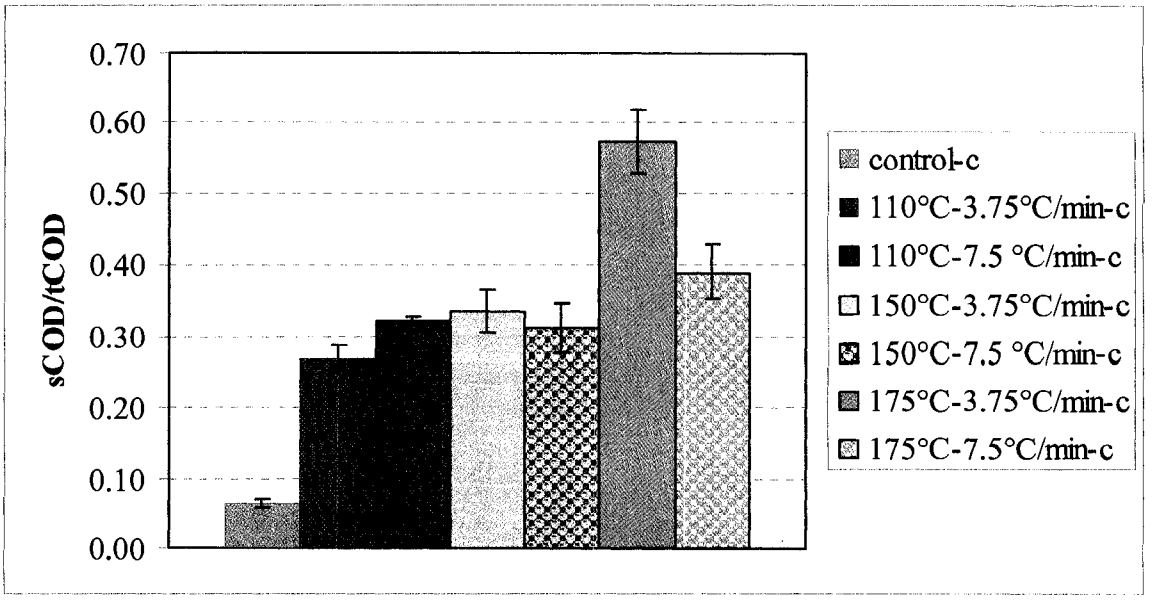

Figure 3.2: sCOD/tCOD ratios for 11.85% TWAS treated at different temperatures and MW intensities

Table 3.2: Sludge properties before and after MW treatment

Properties	TWAS conc. %	Raw TWAS	MW treated TWAS					
			110°C		150°C		175°C	
			3.75°C/min	7.5°C/min	3.75°C/min	7.5°C/min	3.75°C/min	7.5°C/min
pH	6	7.12	7.10	7.08	7.20	8.47	6.92	6.83
	11.85	7.49	7.05	6.97	6.82	6.96	6.56	6.61
sCOD/tCOD	6	0.10±0.02	0.30±0.07	0.23±0.02	0.38±0.03	0.30±0.04	0.46±0.06	0.38±0.02
	11.85	0.07±0.01	0.27±0.02	0.32±0.01	0.34±0.03	0.31±0.04	0.57±0.04	0.39±0.04
VS/TS	6	0.71±0.0	0.72±0.0	0.73±0.0	0.73±0.0	0.73±0.0	0.73±0.0	0.74±0.0
	11.85	0.73±0.0	0.72±0.0	0.72±0.0	0.72±0.0	0.72±0.0	0.71±0.0	0.71±0.0
NH_3-N (mg/L)	6	1081±53	1122±20	1050±39	1020±3	1151±16	1229±54	1079±3
	11.85	1181±65	2057±32	1786±93	1222±11	1593±42	2041±101	1616±41
Alkalinity (mg $CaCO_3$/L)	6	3322±441	3139±32	2900±24	2492±35	2692±12	2400±24	2458±35
	11.85	3850±118	3467±24	4224±154	3675±59	4167±47	3667±0	2968±26
TVFA (mg/L)	6	371±19	4835±2	3748±34	0±0	5912±22	4159±126	4766±122
	11.85	979±36	6042±219	7233±30	6426±401	6172±76	6717±219	4873±634
Soluble Protein (mg BSA/L)	6	202±4	402±29	260±5	723±33	283±14	850±27	322±28
	11.85	278±14	456±1	479±8	445±5	484±1	721±3	684±1
Soluble Sugar (mg/L)	6	168±7	408±75	304±7	607±1	481±13	607±6	621±22
	11.85	165±25	847±18	667±24	466±19	733±7	402±3	430±1

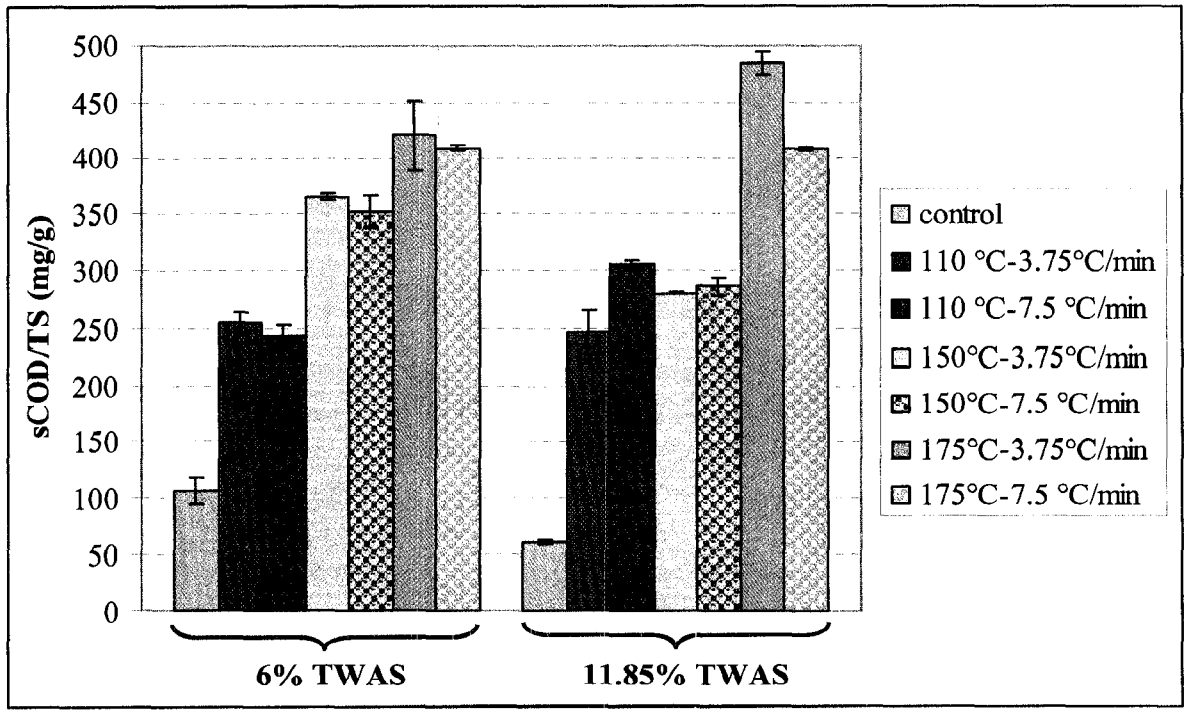

Figure 3.3: sCOD concentration per g TS at different operating conditions

When other characteristics of sludge were considered, the effect of MW pretreatment was more notable on soluble protein and soluble sugar concentrations. The change in soluble protein and sugar concentrations of TWAS after pretreating with MW concur with the change in sCOD of TWAS at 6% TS (Figures 3.4 and 3.6). As pretreatment temperature increased, soluble protein concentration as well as sugar concentration increased. Lower MW intensity produced a greater release of proteins and sugars from the exocellular polymeric matrix and/or inside of cells to the supernatant compared to higher MW intensity. For concentrated TWAS, protein concentration in the supernatant increased with temperature and soluble protein concentrations of samples treated with low MW intensity were also greater than that of samples treated with high MW intensity (Figure 3.5).

Soluble sugar concentration of concentrated TWAS showed a mixed trend (Figures 3.6 and 3.7). Soluble sugars increased with pretreatment temperature with the 6% TWAS. However, for the 11.85% TWAS, with low MW intensity soluble sugar concentration increased for MW treatment temperatures up to 110 and 150°C, then decreased when concentrated TWAS was treated at 175°C. For high MW intensity when the treatment temperature was set at 110°C, a high increase in soluble sugar concentration was observed (from 165 ± 25 to 847 ± 18 mg/L); however, at higher treatment temperature soluble sugar concentration decreased (466 ± 19 and 402 ± 3 mg/L at 150 and 175°C, respectively) (Figure 3.7). The decrease in soluble sugar concentration of concentrated TWAS pretreated at 175°C could not be attributed to a Maillard reaction since there was no decrease in soluble protein concentration for this condition. Additionally, the decrease in soluble sugar concentration can not be caused by caramelization because 6% TWAS did not show a decrease in soluble sugar concentration at 175°C MW pretreatment condition and the difference in water content between 6 and 11.85% is not significantly different to effect the activation energy of any reaction step that occurs during caramelization.

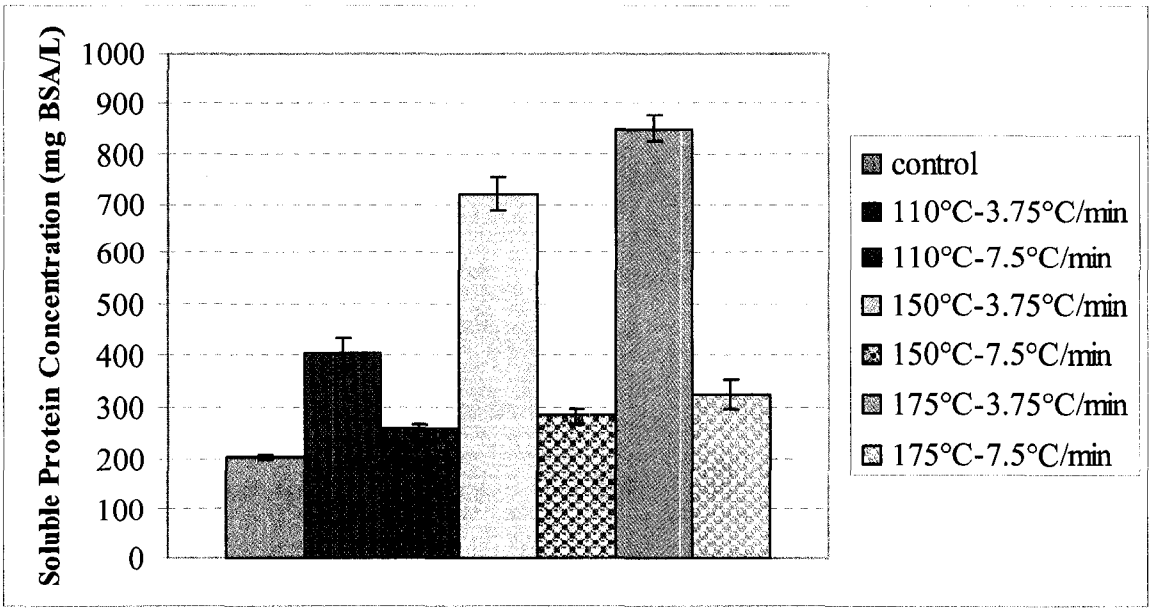

Figure 3.4: Soluble protein concentration of 6% TWAS treated at different temperatures and MW intensities

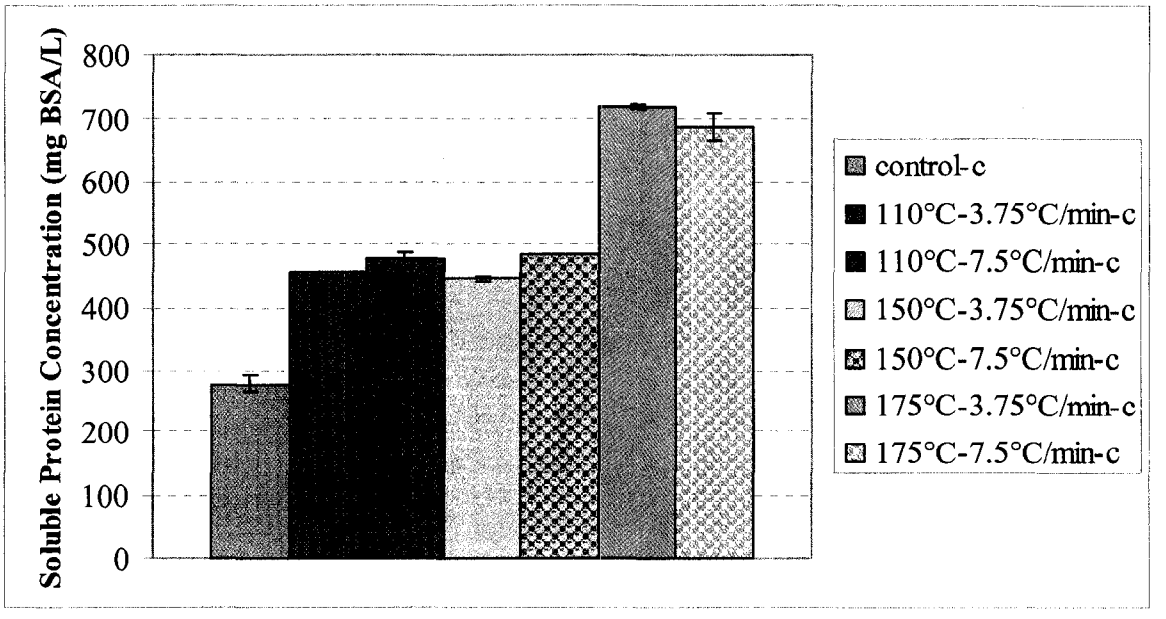

Figure 3.5: Soluble protein concentration of 11.85% TWAS treated at different temperatures and MW intensities

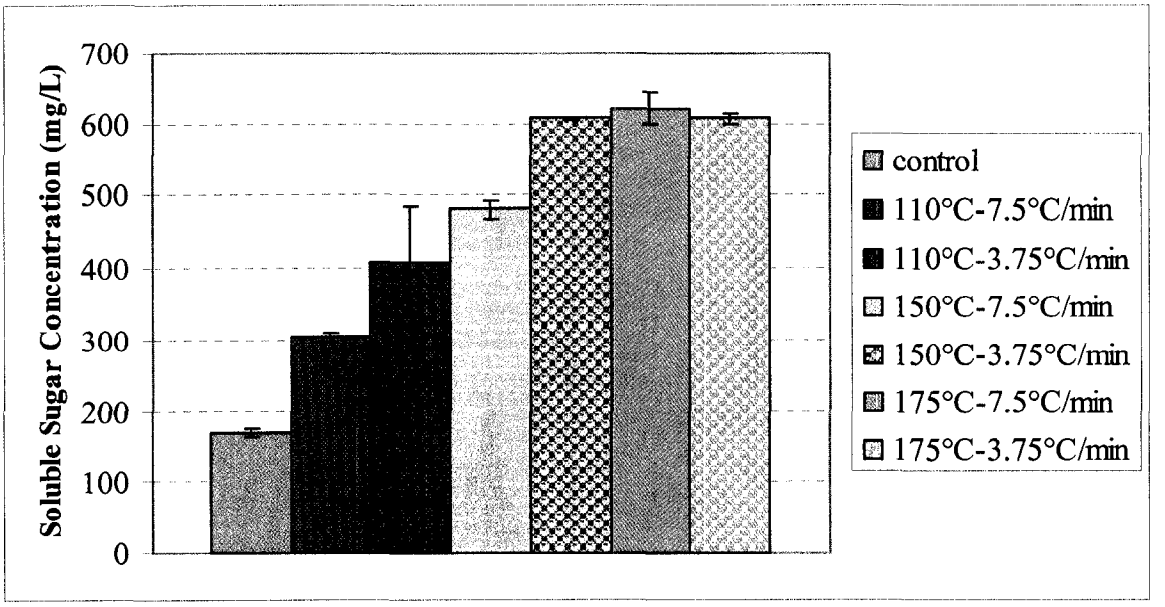

Figure 3.6: Soluble sugar concentration of 6% TWAS treated at different temperatures and MW intensities

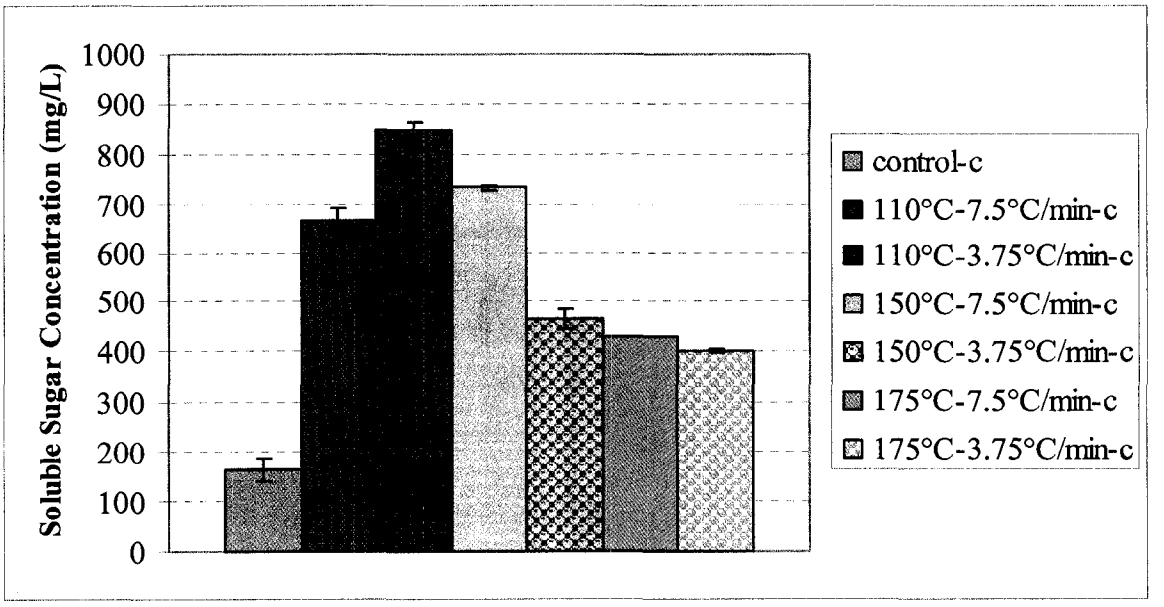

Figure 3.7: Soluble sugar concentration of 11.85% TWAS treated at different temperatures and MW intensities

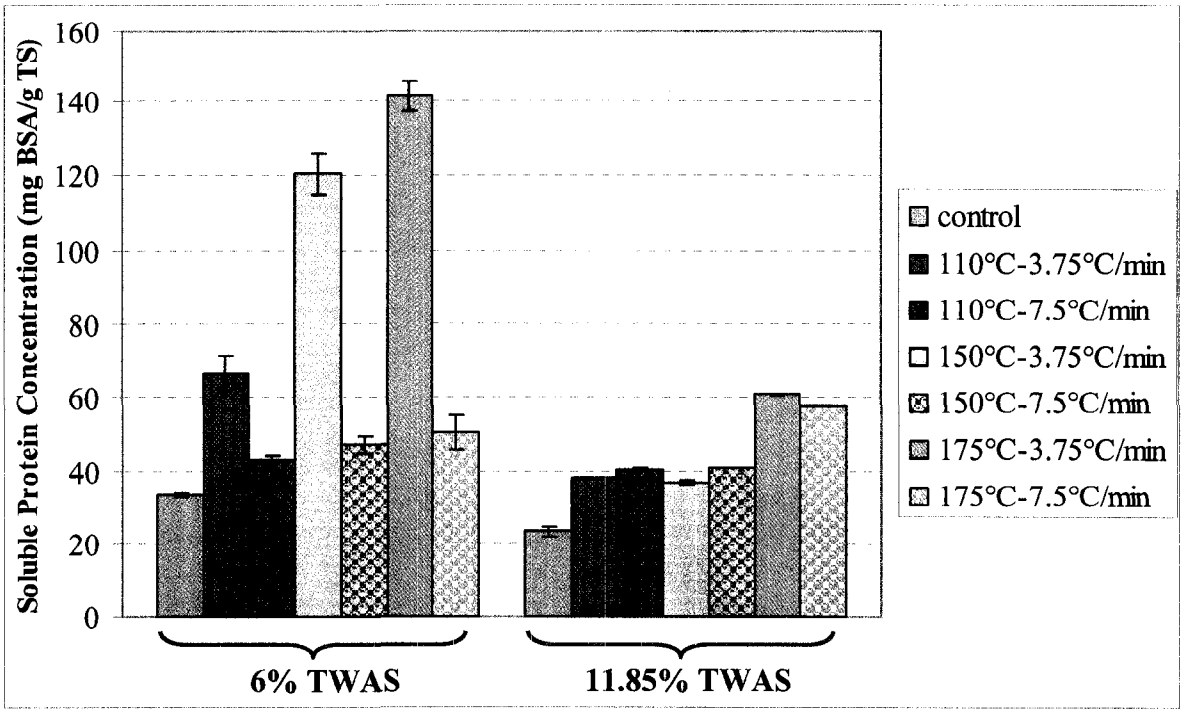

Figure3.8: Soluble protein concentration per g TS at different operating conditions

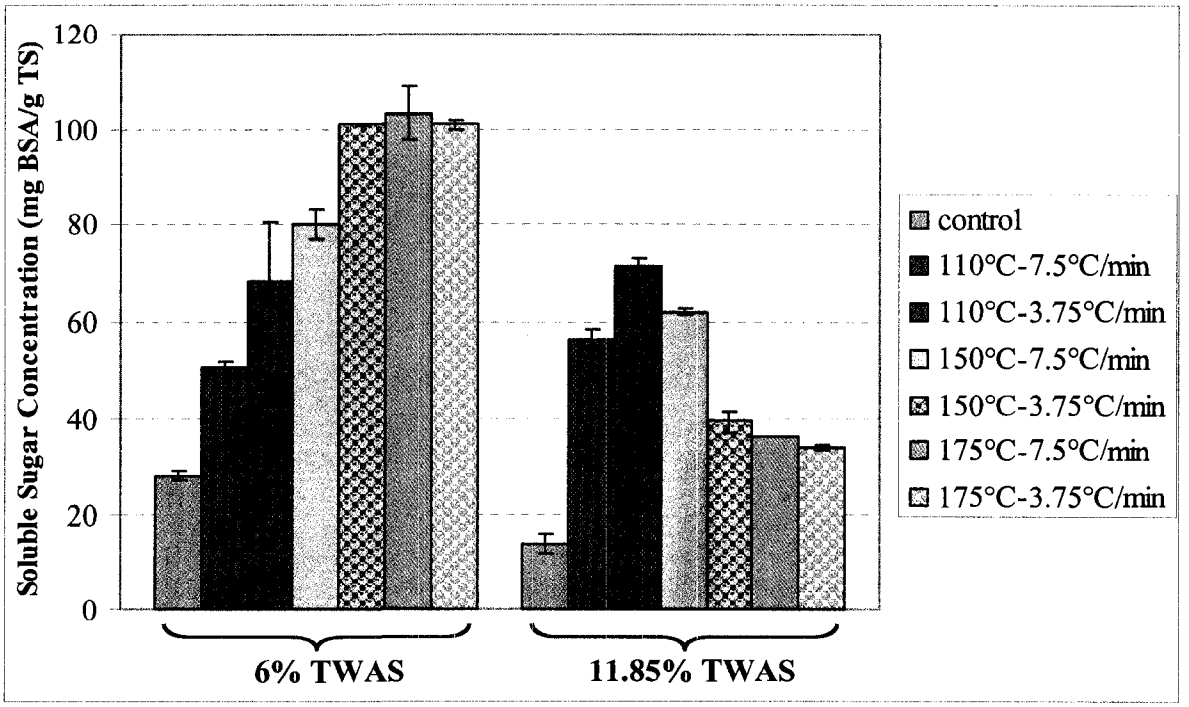

Figure 3.9: Soluble sugar concentration per g TS at different operating conditions

To be able to compare the results of different sludge concentrations, soluble protein and glucose concentrations were converted to a per gram TS base (Figures 3.8 and 3.9). Counter intuitively it was observed that soluble protein and soluble sugar concentrations released from pretreatment of concentrated sludge were much lower compared to that of lower concentrated sludge.

VFAs were measured in terms of acetic acid, butyric acid and propionic acid concentrations (Figure 3.10). It was observed that pretreating sludge with MW at higher temperatures than the boiling point increases TVFAs dramatically; yet, increasing pretreatment temperature above this point did not result in further improvement in TVFA concentrations per g of sludge TS. Pretreating 6% sludge with MW resulted in 12-fold increase in specific TVFA concentration whereas pretreating 11.85% sludge caused only a 6-fold increase in specific TVFA concentration.

The ammonia concentration which was 1080 ± 50 mg NH_3-N/L for 6% TWAS pretreated to a temperature of 175°C did not change after microwaving, but for TWAS with 11.85% TS concentration an increase in ammonia concentration from 1180 ± 60 to around 1620 ± 40 mg NH_3-N/L occurred. MW pretreatment temperature or intensity did not have a significant effect on ammonia concentration of the sludge. Comparing these results with protein solubilization, it is apparent that although proteins were solubilized, they were not broken down by the pretreatment.

MW pretreatment did not have an effect on the alkalinity level of the sludge. The alkalinity level for 6% TWAS was 2772 ± 360 mg $CaCO_3$/L and 3831 ± 514 mg $CaCO_3$/L for 11.85% TWAS.

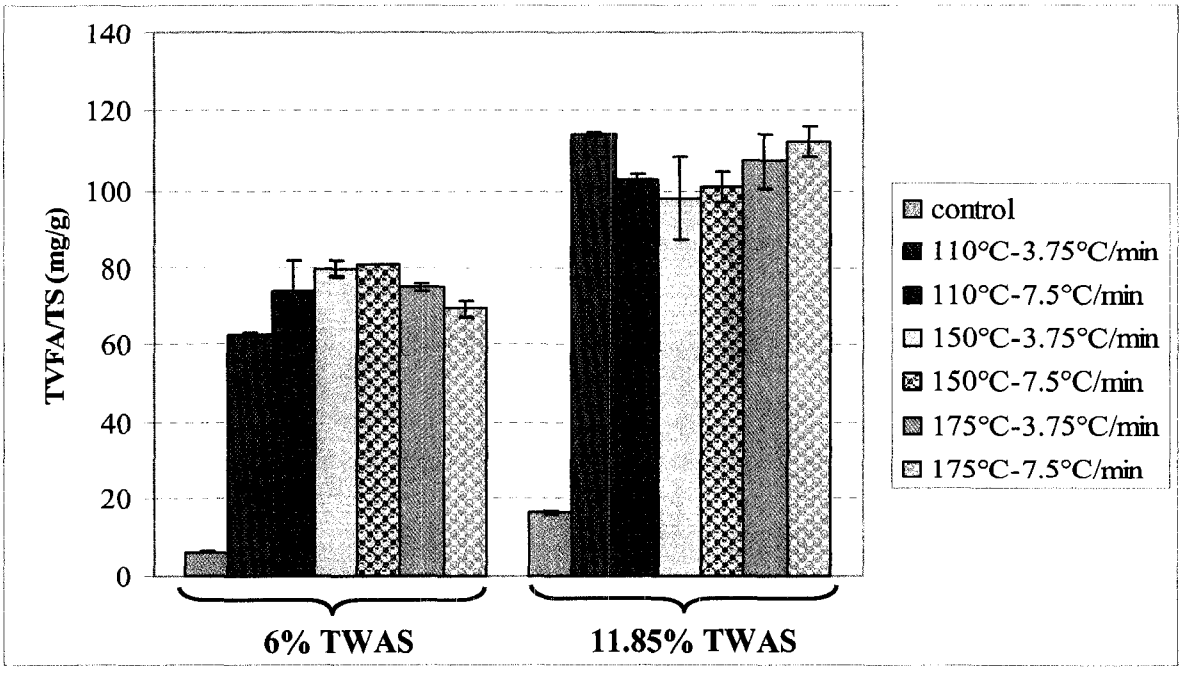

Figure 3.10: TVFA (sum of acetic acid, propionic acid and butyric acid) concentration per g TS at different operating conditions

3.4 STATISTICAL ANALYSIS

In order to understand the significance of main effects of temperature (T), MW intensity (I) and sludge concentration (C) on solubilisation, a three-factor fixed effect ANOVA model was used. sCOD/tCOD ratios for each condition tested were divided by sCOD/tCOD ratio of their control ($sCOD/tCOD^{*}=sCOD/tCOD_{sample}/sCOD/tCOD_{control}$). The statistical package called S-plus 2000 was used to perform ANOVA. Results of the analysis are given in Table 3.3.

Table 3.3: Results of three factor fixed effect ANOVA for sCOD/tCOD*

Source	Degrees of freedom	Sum of Squares	Mean of Squares	F Value	Probability of F value
T	2	16.22886	8.11443	54.1082	0.0000010
I	1	6.24240	6.24240	41.6253	0.0000315
C	1	40.30042	40.30042	268.7292	0.0000000
T:I	2	3.46597	1.73299	11.5558	0.0015936
C:I	1	0.24402	0.24402	1.6271	0.2262394
T:C	2	3.31836	1.65918	11.0637	0.0018901
T:I:C	2	4.82411	2.41205	16.0839	0.0004022
Residuals	12	1.79960	0.14997		

F-value results showed that only the sludge concentration- MW intensity interaction (C:I) is not significant. The main effects of temperature- MW intensity (T:I) and temperature- sludge concentration (T:C) interactions as well as three factor interactions (T:I:C) are significant and necessary in the model.

Model parameters for different linear models without and with two and three factor interactions were tested. For this analysis X values were centered to have better precision in parameter values since X values used in this analysis are far from zero. Another advantages of centering X values is that it prevents any round off errors that may occur when the system

is solved by computer methods. X values can be centered by subtracting the averaged values from the data. Therefore if the model is considered as

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \varepsilon \quad (1)$$

Then the model becomes the following with centered X values:

$$Y = \beta_0^* + \beta_1^* (X_1 - \overline{X}_1) + \beta_2^* (X_2 - \overline{X}_2) + \varepsilon \quad (2)$$

To be able to compare different models with different parameters, coefficients of multiple determination (R^2) were adjusted to balance the improvement in R^2 value by introducing more parameters. Adjusted R^2 (R_a^2) can be calculated as:

$$R_a^2 = 1 - \frac{n-1}{n-(k+1)}(1-R^2) = \frac{(n-1)R^2 - k}{n-1-k} \quad (3)$$

Where n is the sample size and $(k + 1)$ is the number of parameters in the model (β_0, β_1, β_2, ..., β_k). Table 3.4 shows the empirical models and their R^2 and R_a^2 values. Here Y represents sCOD/tCOD* ratios and the variables, pretreatment temperature, MW intensity and sludge concentration were represented as X_1, X_2 and X_3, respectively.

Table 3.4: Linear models and their R^2 and R_a^2 values

	Linear models	R^2	R_a^2
1)	$Y=\beta_0^*+\beta_1^*(X_1-\overline{X}_1)+\beta_2^*(X_2-\overline{X}_2)+\beta_3^*(X_3-\overline{X}_3)$	0.788	0.756
2)	$Y=\beta_0^*+\beta_1^*(X_1-\overline{X}_1)+\beta_2^*(X_2-\overline{X}_2)+\beta_3^*(X_3-\overline{X}_3)+\beta_{12}^*(X_1-\overline{X}_1)(X_2-\overline{X}_2)$ $+\beta_{13}^*(X_1-\overline{X}_1)(X_3-\overline{X}_3)$	0.850	0.808
3)	$Y=\beta_0^*+\beta_1^*(X_1-\overline{X}_1)+\beta_2^*(X_2-\overline{X}_2)+\beta_3^*(X_3-\overline{X}_3)+\beta_{12}^*(X_1-\overline{X}_1)(X_2-\overline{X}_2)$ $+\beta_{13}^*(X_1-\overline{X}_1)(X_3-\overline{X}_3)+\beta_{23}^*(X_2-\overline{X}_2)(X_3-\overline{X}_3)$	0.853	0.802
4)	$Y=\beta_0^*+\beta_1^*(X_1-\overline{X}_1)+\beta_2^*(X_2-\overline{X}_2)+\beta_3^*(X_3-\overline{X}_3)+\beta_{12}^*(X_1-\overline{X}_1)(X_2-\overline{X}_2)$ $+\beta_{13}^*(X_1-\overline{X}_1)(X_3-\overline{X}_3)+\beta_{123}^*(X_1-\overline{X}_1)(X_2-\overline{X}_2)(X_3-\overline{X}_3)$	0.906	0.872
5)	$Y=\beta_0^*+\beta_1^*(X_1-\overline{X}_1)+\beta_2^*(X_2-\overline{X}_2)+\beta_3^*(X_3-\overline{X}_3)+\beta_{12}^*(X_1-\overline{X}_1)(X_2-\overline{X}_2)$ $+\beta_{13}^*(X_1-\overline{X}_1)(X_3-\overline{X}_3)+\beta_{23}^*(X_2-\overline{X}_2)(X_3-\overline{X}_3)+\beta_{123}^*(X_1-\overline{X}_1)(X_2-\overline{X}_2)(X_3-\overline{X}_3)$	0.909	0.869

Results indicate that introducing two factor interaction parameters improved overall fit; however, addition of MW intensity-sludge concentration interaction parameters decreased R_a^2 values slightly. Addition of three factor interactions (model numbers 4 and 5) increased the complexity of the model but also resulted in an overall improvement in fit compared to two factor interactions. Additionally, $Pr(>|t|)$ values for MW intensity-sludge concentration coefficient were calculated to be more than 0.45 which indicates that the confidence interval for this coefficient is less than 0.55. This result concurs with ANOVA analysis which showed that this two factor interaction does not have a significant effect on the response. Therefore, model number 4 was selected as the best model to describe this set of experimental results

and the parameter to parameter interactions. Coefficient values obtained for this model are given in Table 3.5.

Table 3.5: Estimated coefficient values

Coefficients	Value	Std Error	t value	Pr(>|t|)
β_0^*	4.4517	0.1330	33.4784	0.0000
β_1^*	0.0282	0.0050	5.6787	0.0000
β_2^*	-0.2720	0.0709	-3.8354	0.0013
β_3^*	0.4438	0.0455	9.7452	0.0000
β_{12}^*	-0.0070	0.0026	-2.660	0.0165
β_{13}^*	0.0034	0.0017	2.0232	0.0591
β_{123}^*	-0.0029	0.0009	-3.1621	0.0057

Pr(>|t|) values for all estimated coefficients are less then 0.06 indicating that these values are estimated within a 94% confidence interval. By using these values, sCOD/tCOD values were estimated for 6% TS sludge concentration at different temperatures and MW intensities (Figure 3.11). It is clearly seen from this figure that increasing treatment temperature and decreasing MW intensity produces better solubilization. Another interesting estimation from this graph is that microwaving sludge to 180°C with 7°C/min MW intensity results in the same solubilization as treating it to 105°C with 1°C/min intensity. However it is important to note that calculations for above 175°C and 7.5°/min and below 110°C and 3.75°C/min are made by extrapolating the model determined by data obtained in the range of 110 and 175°C

MW temperatures and 3.75 and 7.5 °C/min MW intensities. For verification of these comparisons further experimental data is required.

During selection of operating parameters it is important to account for the effect of these parameters on other properties of sludge (such as methanogenic inhibition effects of high temperature heating) as well as on the cost analysis. At 3.75°C/min constant MW intensity, the model estimated that treatment temperature had more impact on solubilization when applied to concentrated sludge (Figure 3.12).

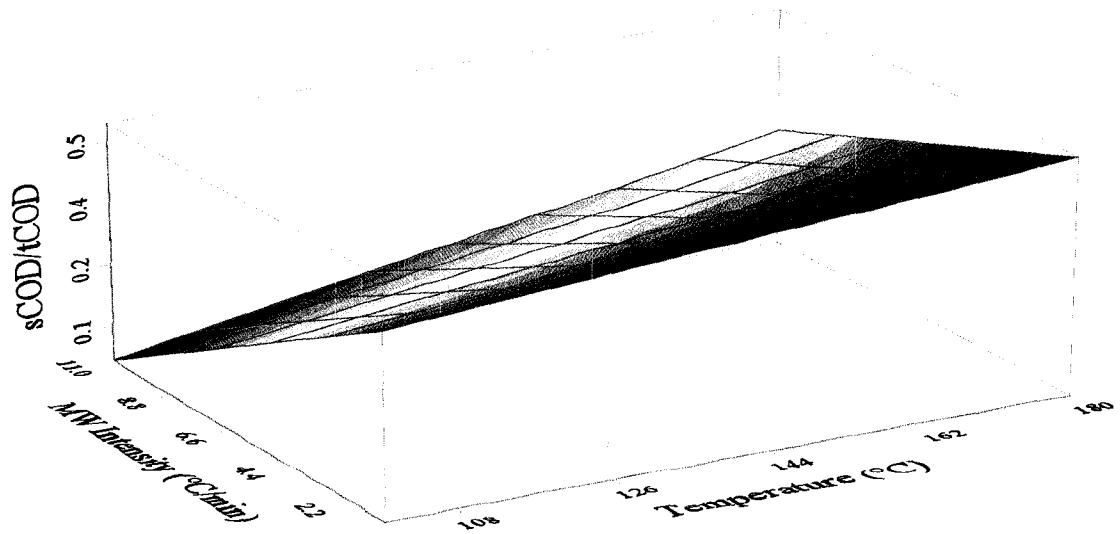

Figure 3.11: Estimated sCOD/tCOD values as a function of temperature (°C) and MW intensity (°C/min) when sludge concentration is 6%

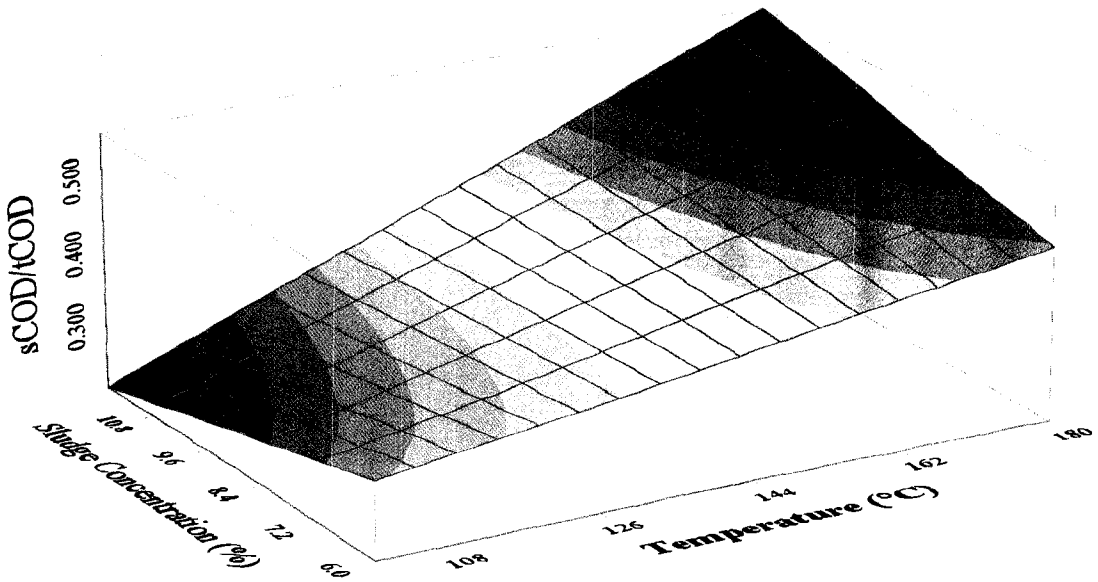

Figure 3.12: Estimated sCOD/tCOD values as a function of temperature (°C) and sludge concentration (%) when MW intensity is 3.75°C/min

3.5 CONCLUSIONS

The effect of high temperature MW treatment on sludge character was investigated at different treatment temperatures, with different MW intensity using two different sludge concentrations.

It was observed that as treatment temperature increases the solubilization of TWAS increases. MW intensity has also positive impact on solubilization with more impact realized on sCOD concentration with concentrated TWAS.

MW treatment at 175°C with 3.75°C/min intensity had the greatest improvement on solubilization of sludge. Sludge treated at these conditions had 0.46 ± 0.06 and 0.57 ± 0.04 sCOD/tCOD ratios which were 4.5 ±0.8 and 8.8 ± 0.9 fold more than untreated TWAS for 6 and 11.85% TS concentrations, respectively.

Soluble protein and sugar concentrations had similar improvement as the solubilization for 6% sludge concentration, yet with 11.85% concentrated sludge improvements in these concentrations were less than for 6% sludge.

Three-factor fixed effect ANOVA determined that T, I, C are the main effects and T:I and T:C interactions as well as T:I:C interaction are significant at a 94% confidence interval.

3.6 REFERENCES

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CHAPTER 4:

Mesophilic Anaerobic Digestion with High Temperature Microwave Pretreatment and Importance of Inoculum Acclimation

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4.1 ABSTRACT

Thickened waste activated sludge (TWAS) was pretreated with microwave (MW) irradiation to temperatures higher than the boiling point (between 110 and 175°C) using different MW intensities. Biochemical methane potential (BMP) assays demonstrated that although mesophilic anaerobic digestion (MAD) inoculum used was acclimated for 4 months with MW pretreated TWAS (to 175°C), acute methanogenic inhibition was observed. Additionally, the MW conditions applied increased the sCOD/tCOD ratio, however no significant enhancement in the rate or extent of TWAS stabilization was observed for the MW pretreated samples. MW pretreatment to between 110 and 175°C at lower MW intensity with a better acclimated MAD inoculum (acclimatized for an additional 3 months)

resulted in minimal methanogenic inhibition (improved acclimation) and improved the rate and extent of TWAS biodegradation as determined by VS removal and biogas production. TWAS pretreated to 175°C produced 31 ± 6% more biogas than the control (raw TWAS) by the 18th day of the BMP test whereas the highest improvement observed from the first set of BMP experiments was 13 ± 1%.

KEYWORDS

Microwave, high temperature, waste activated sludge, biodegradability, acclimation

4.2 INTRODUCTION

Hydrolysis is the rate limiting step for conventional AD of municipal sludges due to the cell structure of microbial biomass and extra-cellular polymeric substances that maintain the floc matrix of WAS (Baier and Schmidheiny, 1997). Pretreatment of WAS prior to AD offers several benefits for improved municipal sludge management and stabilization including: enhancing the rate of and extent of organics stabilization, production of a smaller quantity of undigested residuals for ultimate disposal, increasing the release and capture of energy contained within the sludge in the form of biogas, smaller reactor volumes, improved digested dewaterability, improved pathogen reduction and regrowth in residuals to be applied to the land and generally more stable digester operation (Park et al, 2005, Gavala et al., 2004). Many pretreatment methods have been proposed and evaluated to enhance AD, including conventional thermal, chemical, ultrasound, physical disintegration and combinations of them. It was reported that, ultrasound is an energy effective pretreatment method to enhance AD however it does not improve pathogen removal (Thiem *et al.*, 2001

and Barber, 2005). The same is true for mechanical pretreatment methods such as ball milling, high pressure homogenizer and jetting and colliding (Nah et al., 2000, Muller et al., 1998 and Kopp et al., 1997). Additionally, most physical disintegration methods required more polymer addition after digestion to improve dewaterability. Chemical pretreatment is a less energy effective way to treat sludge due to cost of chemicals used (Navia et al., 2002 and Knezevic *et al.,* 1995). Ozonation is another method showed improvement in degree of hydrolysis however the energy demand and deterioration in the dewateribility property of sludge as well as high concentrations of ammonia and COD in the effluent stream make this pretreatment method not feasible (Scheminski *et al.,* 2000).

Generally these pretreatments have been shown to increase the solubility and concomitant biodegradability of municipal WAS to various extents. However, conventional thermal pretreatment at high temperatures (160-175°C) and high pressures (6-8 bar) has been demonstrated to produce better digestion results than the other pretreatments in terms of increased volatile solids (VS) destruction as well as increased biogas production and pathogen reduction (Abraham and Kepp, 2003). Beyond 180°C, a decrease in methane production was observed which was ascribed to an inhibition caused by Maillard reactions that occurred between amino acids and low molecular weight sugars in the sludge (Pinnekamp, 1989). Methanogenic inhibition of TWAS pretreated at elevated temperatures was also reported by Stuckey and McCarthy (1984). Caramelization of sugars was indicated as the reason for decrease in VS destruction.

As an alternative innovative method to conventional heating of sludge, highly efficient microwave (MW) irradiation may be a promising technology to conserve energy and

enhance pathogen and VS destruction during AD (Decareau, 1985). Recent studies have shown that MW pretreatment of WAS at temperatures below 100°C can increase VS solubilization and biogas production using conventional MAD as well as destroy pathogens (Eskicioglu *et al.*, 2007a, Hong et al., 2004 and Park et al, 2004). Additionally, it has also been demonstrated that at temperatures below 100°C MW pretreatment showed improvements in AD performance over identical conventional heating scenarios. AD improvements of MW over conventional thermal heating were proven to be a result of the athermal effects of MWs. (Coelho *et al.*, 2008, Eskicioglu et al., 2007b). Further improvements in digestion of WAS may be realized from the combination of MW pretreatment at elevated temperatures and pressures combined with a potential advantages of the associated MW athermal effect. Presently, no MAD studies have been conducted with WAS to evaluate the effect of MW pretreatment at temperatures above boiling point. No information is available on the effect of these conditions on solubilization and efficiency of MAD using TWAS.

The objectives of this study are to evaluate the effects of high temperature (>100°C) MW irradiation of TWAS on biogas production from MAD and to investigate the role and impact of inoculum acclimation on the short term and long term response of MAD. It is hypothesized that MW pretreatment at higher temperatures and pressures can liquefy more of the organics in sludge, further increasing the availability of biodegradable substrate resulting in increased rates and/or extent of MAD. However, more rapid hydrolysis or acidogenesis due to MW pretreatment or the release of high concentrations of inhibitory compounds from the microbial matrix could sour or at least retard digestion. The impact of proper inoculum acclimation to overcome possible acute or chronic inhibition was studied.

4.3 MATERIALS AND METHOD

TWAS [approx. 6% w/v; 80% volatile suspended solids (VSS)] was obtained from the thickener centrifuge at the Robert O. Pickard Environmental Center (ROPEC) located in Gloucester, ON Canada. ROPEC is a conventional activated sludge plant with an average sludge retention time (SRT) of 5-7 days. TWAS was stored at 4°C until used then warmed to room temperature before being MWed. MW pretreatments of TWAS were carried out batch wise with a programmable Mars 5© (MW Accelerated Reaction System; CEM Corporation, 0-1250 W, 2450 MHz frequency) MW oven equipped with online fiber optic temperature and pressure monitoring probes and 100 ml pressure sealed vessels with full MW penetration. Pressure vessels were filled with 70 mL of TWAS and a temperature and pressure profile was programmed and monitored to obtain temporal heating profiles up to 250°C and 34.47 bar as desired.

In the first set of pretreatment experiments, a multilevel factorial design coupled to biochemical methane potential (BMP) assay was used to investigate the following factors: (i) pretreatment temperature, (ii) intensity of microwaving (MW intensity was programmed such that the temperature change per unit time was constant. Temperature was the final temperature achieved with 1 minute hold time.) and (iii) concentration of TWAS (Table 4.1 and Figure 4.1).

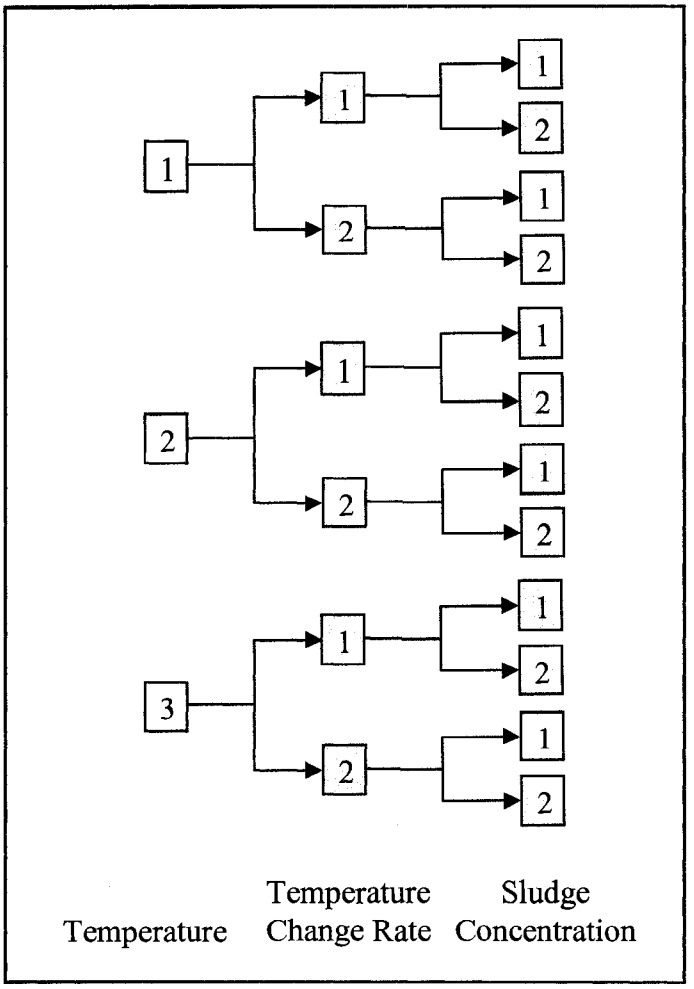

Figure 4.1: Illustration of multilevel factorial design used in this set of experiments

Table 4.1: Variables and levels used in statistical experimental design

Variables → / **Levels ↓**	**Temperature[a] °C**	**Temperature Change Rate °C/min**	**Sludge Concentration %**
1	110	3.75	6
2	150	7.5	11.85
3	175		

[a] Final temperature achieved with 1 minute hold time.

For acclimation, one 10 L anaerobic semi-continuous reactor, fed with MW-irradiated sludge, was run at approximately 20 d SRT by gradually increasing the influent flow rate over a period of 4 months (Ekama *et al.*, 1986). The initial source of inoculum was from effluent line of the MAD at ROPEC where primary sludge and TWAS are treated in a 58/42 (v/v) ratio at a SRT of 15- 20 days. Organic loading rate (OLR) of acclimation reactor was 2.0 ± 0.04 g tCOD/ L. d. MW toxicity effect on secondary sludge was expected to increase with MW temperature (Hong, 2002); therefore 175°C was used to pretreat feed sludge for the acclimation reactor. The concentration of feed was 3% TS (w/w), which can be considered as a typical sludge concentration in a full-scale sludge digester. When the inoculum was being acclimatized to the MW-irradiated WAS, daily biogas production, biogas composition and VFA readings reached a stable value and BMP reactors were set-up with this acclimatized inoculum which had a specific activity of 0.12 ± 0.01 g tCOD/ g VSS. d.

Concentrated sludge for tests was obtained by centrifuging raw TWAS at 6513 relative centrifugal force (RCF) for 20 minutes. The BMP analysis was performed using 500 mL Kimax glass bottles with butyl rubber stoppers as reactors. The concentration of TWAS used in the BMP reactors was set at 3% which necessitated diluting the sludge distilled water after pretreatment. A 280 mL volume of diluted (as needed), pretreated TWAS was added to 70 mL of acclimated inoculum in each reactor and mixed. Nitrogen was bubbled through the BMP mixture to prevent air exposure. An equal volume mixture of potassium and sodium bicarbonate was added to provide 4000 mg/L of bicarbonate alkalinity and the reactors were sealed. BMP tests were performed in duplicate at 35 ± 1°C on a New Brunswick rotary shaker at a speed of 95 rpm. BMP assays were done on raw non-pretreated TWAS and MW

pretreated TWAS and acclimatized inoculum. Chemical characterizations of these samples were conducted before and at the conclusion of BMP assays.

Biogas production was measured daily. Once weekly, pH of the reactor, total volatile fatty acids (VFA) concentrations and biogas composition were monitored during the BMP assay. The effect of high temperature MW irradiation on ammonia, pH, HCO_3^- alkalinity, total solids (TS), VS, soluble chemical oxygen demand (sCOD), total COD (tCOD), dewaterability, soluble protein and soluble reduced sugars before and after the BMP was also evaluated. Ammonia was measured using an ORION model 95-12 ammonia gas sensing electrode with Fisher Accumet pH meter 750 according to Standard Method procedure 500D. Alkalinity and VS/TS analysis were done according to Standard Methods 2320B-titration and 2540D procedures, respectively. sCOD and tCOD measurements were conducted according to Standard Method's colorimetric method 5220C using a Coleman Perkin-Elmer model 295 spectrophotometer. Before SCOD determination, sludge samples were centrifuged (20 min at 7,000 rpm, 5856 RCF) and filtered through GN-6 Metricel S-Pack membrane disc filters with 0.45 μm pore size To assess dewaterability of digested WAS, the capillary suction time (CST) method 2710G was used (APHA, 1995). For soluble protein and soluble reduced sugar concentrations in the supernatant, the methods of Bradford (Bradford, 1976) and Miller (Miller, 1959) respectively were used. TVFAs were determined using a HP 5840A GC with glass Chromosorb 101 column (Chromatographic Specialties Inc., Brockville, ON, Canada, mesh size: 80/100, column length × ID: 304.8 cm × 2.1 mm) and a flame ionization detector according to van Huyssteen (1967). Biogas composition was determined with a HP 5710A GC with Porapak T packed column

(Chromatographic Specialties Inc., Brockville, ON, Canada, mesh size: 50/80, column length × OD: 304.8 cm × 6.35 mm) and thermal conductivity detector (Ackman, 1972).

The second set of BMP experiments was done in a similar manner but there were two important differences: TWAS samples were exposed to a decreased intensity of MW irradiation and the MAD inoculum was acclimatized for an additional 3 months (Total of 11 SRTs). TWAS samples were heated from room temperature to 90°C at a higher intensity (4.6°C/min) then MW intensity was lowered to 0.52°C/min, with an overall average rate of 0.83°C/min. Figure 4.2 shows the heating time for all MW intensities used in both sets of experiment in this study. It was hypothesized that longer exposure time to the combined thermal and athermal effects of MW would improve MAD. Three pretreatment temperatures were used: 120, 150 and 175°C. The concentration of TWAS in the BMP reactors was set at 3% as in the first set of experiments. Dilution was required to maintain a 3% concentration in each serum bottle. A volume of 70 mL pretreated TWAS was added with 15 mL of acclimated inoculum in each serum bottle that had a total volume of 125 mL. Properties of TWAS used in both sets of experiments are shown in Table 4.2.

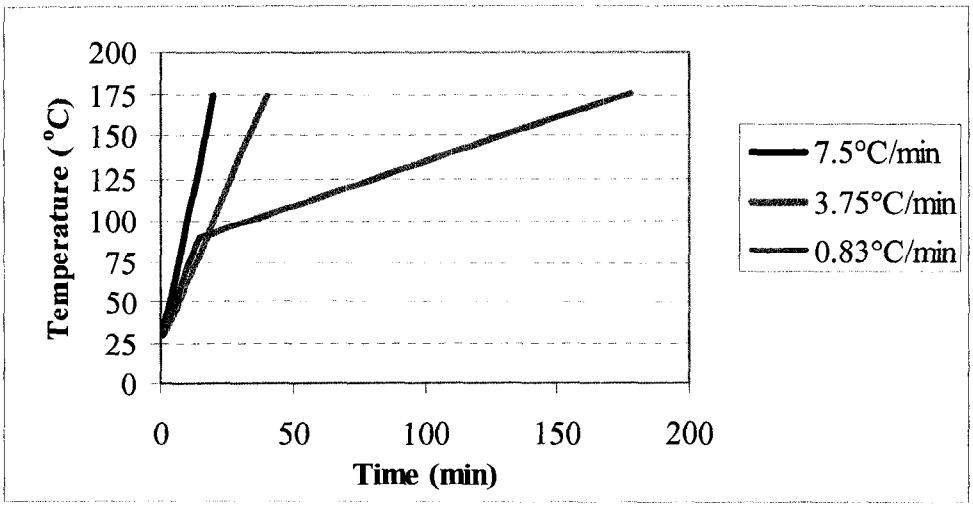

Figure 4.2: Heating profile for different MW intensities

Table 4.2: Characteristics of TWAS used in the BMP tests

Properties	Raw TWAS for the 1st set of experiments		Raw TWAS for the 2nd set of experiments
TS, %(w/w)	6±0.1	11.85±0.2	4.6±0.2
VS/TS	0.71±0.0	0.73±0.0	0.67±0.00
sCOD/tCOD	0.1±0.01	0.06±0.0	0.09±0.00
NH_3-N, mg/mL	1081±53	1181±65	547
Protein, µg/mL	202±4	278±14	41
Sugar, mg/mL	168±7	165±25	94

4.4 RESULTS

4.4.1 Effect of temperature, concentration and MW intensity on BMP (Test 1)

Preliminary characterization results of pretreated TWAS showed that MW treatment to the highest temperature (175°C) at the lowest MW intensity and rate of temperature change of 3.75°C/min resulted in the highest degree of sludge solubilization. Sludge treated at these conditions had sCOD/tCOD ratios of 0.46 ± 0.06 and 0.57 ± 0.04 which were 4.5 ± 0.8 and 8.8 ± 0.9 fold greater than untreated TWAS for 6 and 11.85% TS concentrations, respectively. A similar trend was observed for low MW temperatures. The sCOD/tCOD ratios for 1.4 and 5.4% TS concentrations increased 3.6 ± 0.6 and 3.2 ± 0.1 fold respectively when sludge was pretreated at 95°C with MW (Eskicioglu et al., 2007a). Increasing MW pretreatment temperature from 150 to 175°C further improved sCOD/tCOD ratios from 0.30 ± 0.04 to 0.38 ± 0.02 with high MW intensity and from 0.38 ± 0.03 to 0.46 ± 0.06 with low MW intensity.

Despite the enhancement in sCOD/tCOD ratio, BMP results compared to the control showed less improvement in overall biogas production both in the short term and long term compared to what might be expected by the increase in liquefied sludge components as measured by the increased concentration of sCOD. All BMP tests performed with the MW pretreated sludge showed acute inhibition in the early stage of the assay as indicated by lower biogas production despite use of acclimatized inoculum. For 6% TWAS with high MW intensity acute inhibition was observed in the first 14 days of the batch test (Figure 4.3)

compared to the control. Figure 4.3 indicates that ultimate biogas production for all samples was similar suggesting that MW pretreatment had no benefits. Digestion of 6% TWAS MW pretreated to 110 and 150°C with low MW intensity also showed acute inhibition in the first 11 days; however, for 6% TWAS pretreated at 175°C with low MW intensity, the inhibition continued until the 23rd day (Figure 4.4). Again ultimate biogas production after 60 days was approximately similar for all samples indicating little advantage for high intensity high temperature MW pretreatment of TWAS. Results for concentrated TWAS (11.85%) also exhibited inhibition during the BMP test. In reactors having sludge pretreated at high MW intensity, inhibition ended at the 18th day (Figure 4.5). Sludge treated at low intensity with pretreatment temperatures of 110 and 150°C showed inhibitions until the 20th day; whereas when the pretreatment temperature increased, the inhibition phase extended until the 23rd day (Figure 4.6). An interesting observation had been made with sludge pretreated at 175°C with low MW intensity. At this pretreatment condition, regardless of the sludge concentration an initial inhibition zone was observed between days 5-8 followed a distinct secondary inhibition period from days 15-20.

Although the rate of biogas production was only slightly slower for MW pretreated samples compared to the control (caused by mild inhibition), the exponential phase of gas production lasted longer for pretreated samples resulting in more biogas production in a shorter period of time. It was observed that MW intensity has a significant impact on the extension of the exponential phase time. Lowering MW intensity (increasing the exposure time of the sample to reach the set temperature) increased the duration of the exponential phase and increased biogas production. The greatest difference in biogas production between MW pretreated

sludge and the control was seen with 6% TWAS pretreated at 175°C at MW intensity of 7.5°C/min which was recorded as a 13% improvement over the control at the 21st day of the BMP test. Decreasing MW intensity from 7.5 to 3.75°C/min improved biogas production slightly (Figure 4.4). However due to secondary inhibition observed with low MW intensity at a pretreatment temperature of 175°C, increase in cumulative biogas production (CBP) during the exponential phase was suppressed.

A number of conclusions were drawn from the BMP data. Rapid TWAS temperature changes (20 and 40 min, room temperature to 175°C at high and low heating rate) using MW irradiation increased SCOD concentrations but in general did not result in an improvement in the rate or overall biogas production compared to the control. Since MW pretreatment with low MW pretreatment temperatures has been shown to increase biogas yield, it can be surmised that the irradiation settings used provided insufficient thermal and athermal exposure to affect the biodegradability of the substrate or increase the amount of biodegradable material in the pretreated samples that may cause toxicity. In fact MW pretreatment resulted in release of materials that produced acute inhibition. It may be concluded that the initial acclimation period for the inoculum was insufficient and or that levels of exposure to inhibitory substances can be reduced below the inhibitory concentration in a semi-continuous reactor. This could not be stopped from occurring in non-steady state batch culture. The fact that inhibition was acute and occurred in the first days of the BMP assay when concentrations are greatest concurs with this scenario. It should be kept in mind that BMPs were run at 3% solids and that if higher concentrations were applied in BMP or continuous reactors the inhibition zones could be extended. From this initial study it was concluded that greater improvements in CBP could be obtained if the

TWAS samples were treated with longer MW exposure times and if the acute inhibition that was seen in the early stages of BMP tests could be circumvented.

The BMP assay ran for 60 days and at the conclusion the CBPs of all samples were very similar to their controls indicting little or no increase in the biogas yield. This shows that MW pretreatment at high temperatures at the irradiation rates used had little or no effect on the overall degradability of the sludge. Using the set conditions of MW heating organics in the sludge were simply converted from a less readily degradable solid form to a more readily degradable soluble phase. In other words, MW heating made organics more readily accessible to the anaerobes. This was also verified by the increase in the exponential phase duration of the pretreated samples by high temperature microwaving. However under the conditions applied, MW pretreatment did not convert any non-biodegradable materials in to readily or intermediate degradable substrates.

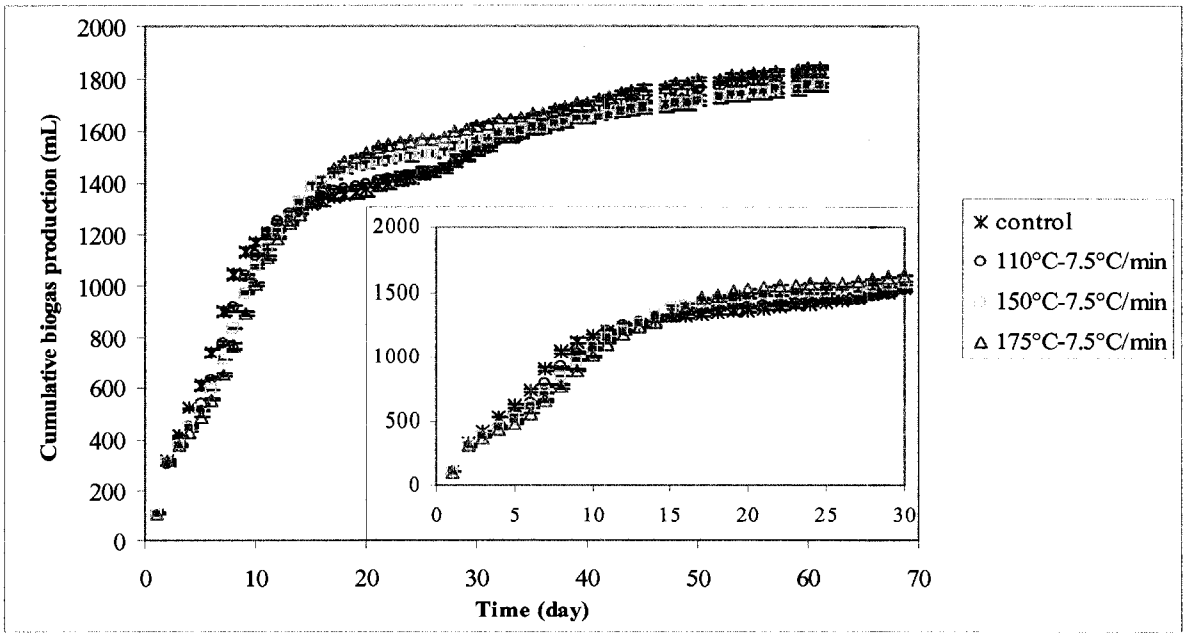

Figure 4.3: Biogas production for the control and 6% TWAS pretreated with high MW intensity (7.5°C/min) at different temperatures

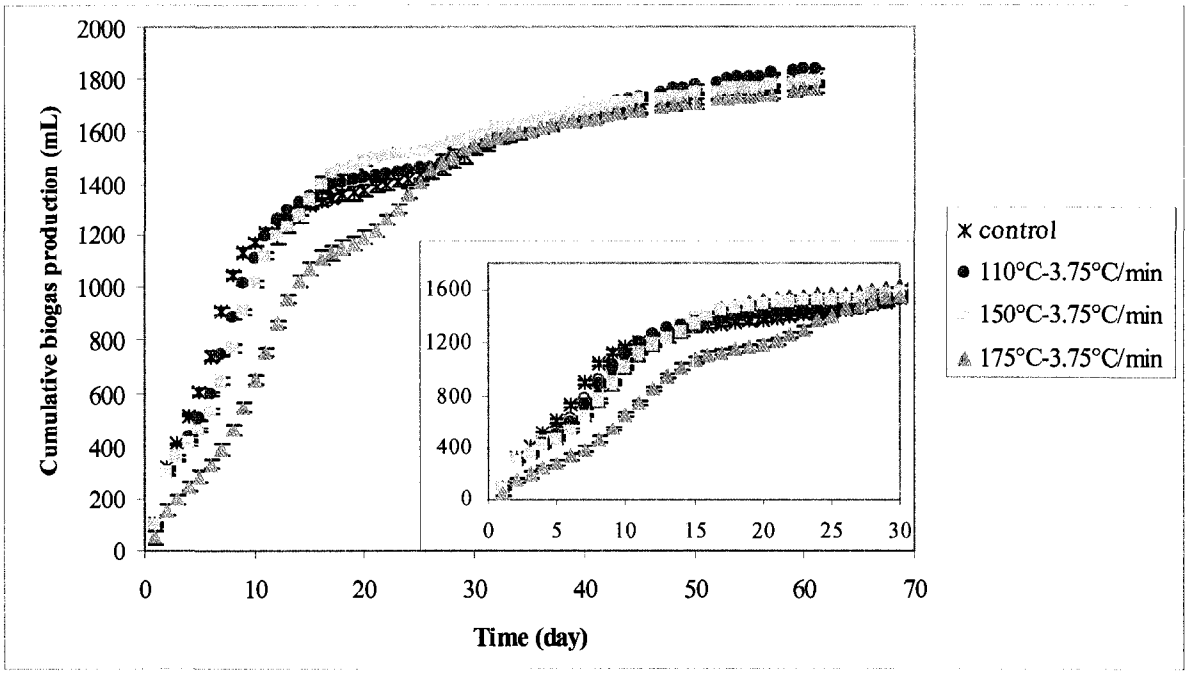

Figure 4.4: Biogas production for the control and 6% TWAS pretreated with low MW intensity (3.75°C/min) at different temperatures

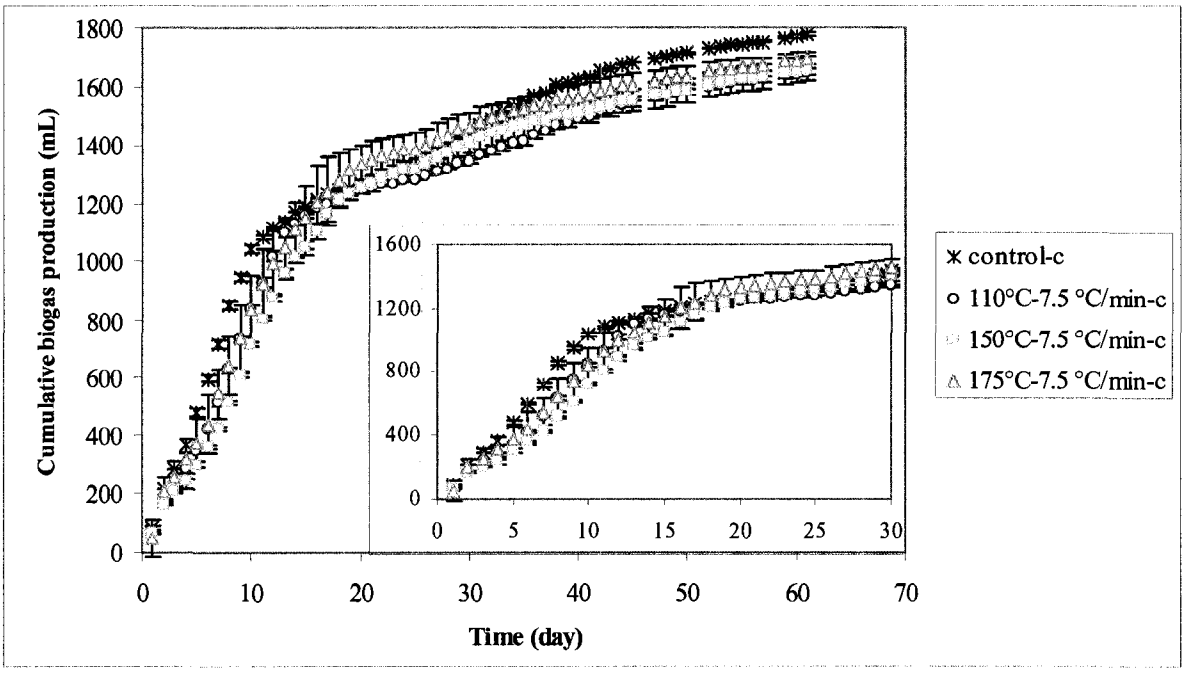

Figure 4.5: Biogas production for the control and 11.85% TWAS pretreated with high MW intensity (7.5°C/min) at different temperatures

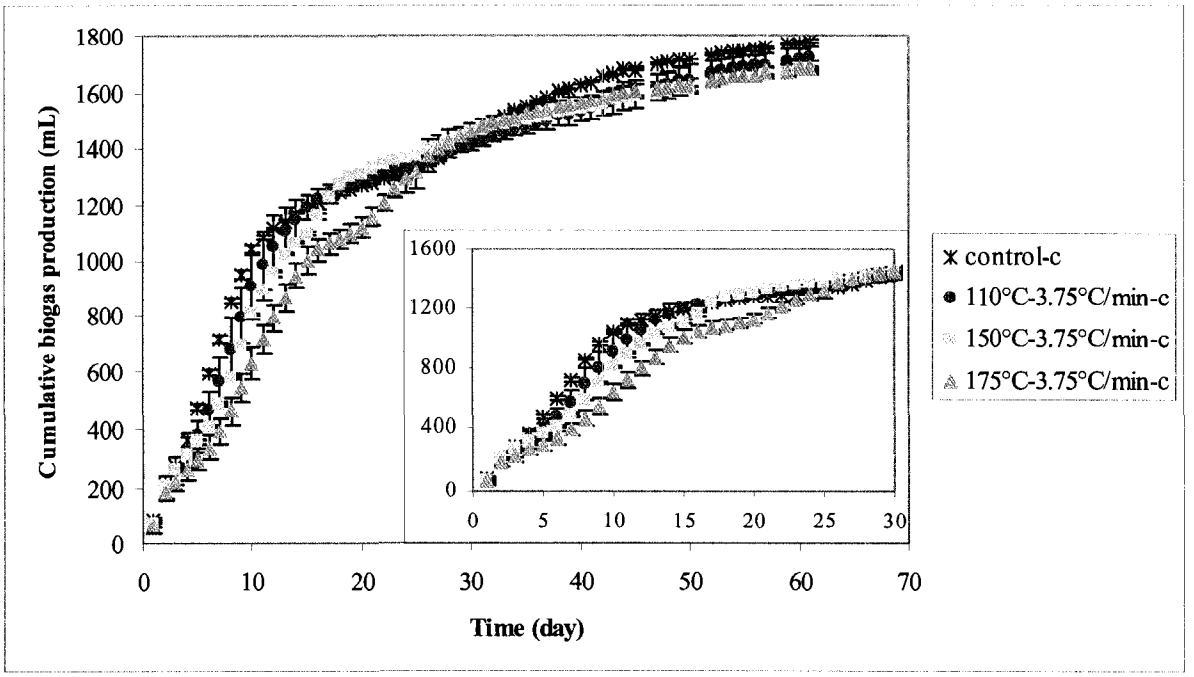

Figure 4.6: Biogas production for the control and 11.85% TWAS pretreated with low MW intensity (3.75°C/min) at different temperatures

Table 4.3 shows weekly VFA measurements for batch reactors. Data represented are the average values of duplicates and standard deviation of values from the mean are in parenthesis. Within the first three weeks of the BMP assay, total VFAs were completely absent in all bottles except in those containing both high and low concentrations of TWAS pretreated to 175°C at low MW intensity. For these bottles an additional week was required to consume all VFAs. After 61 days of incubation BMP assay bottles were opened and the characteristics of the digestates were determined.

Table 4.3: Weekly VFA measurements of batch reactors

	INITIAL				WEEK 1				WEEK 2				WEEK 3			
	AA*	BA	PA	TVFA	AA	BA	PA	TVFA	AA	BA	PA	TVFA	AA	BA	PA	TVFA
Control	172 (7)	13 (2)	-	**186 (9)**	1017 (73)	1097 (14)	71 (27)	**2185 (114)**	469 (441)	28 (35)	-	**497 (476)**	60			**30**
110°C high	1138 (26)	463 (7)	272 (2)	**1874 (17)**	2003 (17)	1112 (13)	-	**3114 (4)**	37 (24)	-	-	**37 (24)**	19 (1)	1 (0)	-	**20 (0)**
150°C high	1390 (154)	435 (51)	382 (41)	**2206 (245)**	2418 (92)	1199 (5)	344 (35)	**3960 (132)**	20 (7)	961 (99)	-	**981 (106)**	17 (0)	-	-	**17 (0)**
175°C high	1602 (40)	469 (10)	312 (11)	**2382 (61)**	2680 (43)	1169 (18)	558 (16)	**4407 (44)**	150 (102)	1447 (60)	-	**1597 (162)**	46 (39)	17 (0)	-	**54 (51)**
110°C low	1362 (1)	697 (0)	359 (1)	**2418 (1)**	2311 (152)	1126 (29)	296 (32)	**3733 (214)**	23 (0)	15 (15)	-	**39 (13)**	22 (2)	-	-	**22 (2)**
150°C low	1249 (21)	623 (7)	377 (4)	**2249 (31)**	2328 (34)	1102 (29)	464 (85)	**3894 (110)**	18 (2)	1353 (77)	-	**1371 (74)**	22 (1)	2 (0)	-	**22 (2)**
175°C low	1136 (43)	548 (14)	395 (7)	**2080 (63)**	2828 (85)	1063 (3)	639 (21)	**4530 (104)**	235 (111)	1397 (33)	41 (0)	**1652 (173)**	32 (3)	1669 (13)	-	**1702 (10)**
Control-c	152 (9)	53 (0)	43 (0)	**248 (9)**	1025 (5)	888 (23)	167 (137)	**2081 (165)**	37	44	-	**81**	10 (3)	5 (0)	-	**13 (6)**
110°C high-c	1119 (7)	430 (7)	282 (8)	**1831 (8)**	1666 (62)	919 (14)	273 (69)	**2858 (145)**	39 (1)	330 (266)	-	**369 (266)**	12 (0)	-	-	**12 (0)**
150°C high-c	1063 (18)	314 (3)	186 (4)	**1563 (19)**	2170 (35)	984 (8)	501 (13)	**3655 (56)**	37 (6)	1389 (67)	-	**1426 (61)**	21 (2)	-	-	**21 (2)**
175°C high-c	886 (112)	225 (33)	123 (15)	**1234 (161)**	1947 (243)	910 (1)	382 (73)	**3239 (317)**	13 (6)	1197 (128)	-	**1210 (134)**	16	-	-	**16**
110°C low-c	873 (36)	415 (11)	242 (9)	**1530 (55)**	1722 (45)	910 (10)	271 (146)	**2903 (181)**	43 (54)	463 (618)	-	**505 (672)**	11 (1)	-	-	**11 (1)**
150°C low-c	1176 (78)	316 (17)	134 (6)	**1627 (101)**	2169 (58)	1030 (14)	519 (31)	**3718 (103)**	135 (140)	1341 (100)	-	**1476 (240)**	13 (9)	-	-	**13 (9)**
175°C low-c	1089 (30)	419 (17)	193 (9)	**1700 (55)**	2491 (61)	933 (39)	518 (20)	**3942 (41)**	89 (21)	1069 (67)	-	**1185 (88)**	32 (5)	1421 (26)	-	**1453 (21)**

*AA=acetic acid, BA=butyric acid, PA=propionic acid, TVFA= total volatile fatty acids (AA+BA+PA), units are mg/L.

Table 4.4: Digestate properties after BMP tests

Property	TWAS conc., %	Raw Sludge	MW pretreated TWAS					
			110°C		150°C		175°C	
			3.75°C/min	7.5°C/min	3.7.5°C/min	7.5°C/min	3.7.5°C/mi	7.5°C/min
sCOD/tCOD	6	0.045±0.00	0.046±0.009	0.041±0.004	0.051±0.004	0.060±0.00	0.165±0.033	0.069±0.009
	11.85	0.069±0.00	0.053±0.002	0.064±0.009	0.083±0.003	0.074±0.08	0.1364±0.02	0.081±0.001
VS/TS	6	0.49±0.00	0.50±0.00	0.49±0.01	0.48±0.01	0.50±0.01	0.50±0.00	0.48±0.00
	11.85	0.49±0.01	0.50±0.01	0.48±0.02	0.48±0.00	0.49±0.01	0.46±0.03	0.47±0.01
NH_3-N, mg/L	6	1294±193	1391±31	1350±50	1469±54	1300±44	1430±0	1423±92
	11.85	1433±20	1452±78	1402±16	1486±38	1482±212	1519±26	1445±53
Alkalinity, mg $CaCO_3$/L	6	7041±663	7675±561	6440±362	6404±37	6554±25	7137±100	6652±412
	11.85	6157±362	6251±214	6042±350	6482±38	6060±25	6358±63	6019±63
Protein, mg BSA/L	6	27±0	32±14	25±1	74±1	34±10	54±3	40±1
	11.85	52±7	43±15	41±8	40±5	37±2	51±4	43±3
Sugar, mg glucose/L	6	22±2	20±6	55±2	90±9	56±8	81±11	66±1
	11.85	63±1	59±15	71±10	59±1	62±11	68±0	60±2
Total biogas produced,	6	3778±66	3900±11	3796±11	3966±0	3910±50	3969±5	4065±8
	11.85	3718±3	3636±79	3598±9	3724±20	3703±97	3671±72	3781±30
CH_4 composition, %	6	59±0	60±0	60±1	60±0	60±0	60±0	60±0
	11.85	59±0	60±2	58±0	60±1	60±0	58±0	59±0
VS removed, g	6	1.79±0.01	1.89±0.01	2.02±0.12	1.93±0.02	1.90±0.00	1.90±0.01	2.00±0.00
	11.85	1.87±0.00	1.99±0.02	1.97±0.00	2.00±0.01	1.97±0.06	1.97±0.00	1.94±0.03
TS removed, g	6	2.12±0.00	2.12±0.07	2.16±0.11	2.11±0.06	2.16±0.01	2.07±0.04	2.13±0.02
	11.85	2.11±0.02	2.25±0.17	2.26±0.02	2.39±0.01	2.30±0.01	2.38±0.03	2.27±0.08

Table 4.4 summarizes digestate characteristics at the conclusion of the BMP test. It was found that all bottles including the controls had ammonia and alkalinity concentrations near the average values of 1420 ± 67 mg NH_3-N/L and 6519 ± 476 mg $CaCO_3$/L, respectively. The similar ammonia concentrations indicate that pretreatment did not increase the ultimate degradation of protein from either the cellular structure or floc matrix EPS of the TWAS sample. This result is in agreement with the fact that the ultimate CBP of control and pretreated samples were also similar. For 11.85% MW pretreated TWAS the digestate in all bottles had very similar soluble protein and soluble sugar concentrations regardless of the pretreatment conditions. Average values for protein and sugar in all bottles were 44 ± 5 mg BSA/L and 63 ± 5 mg glucose/L, respectively. The soluble protein and sugar concentrations of 6% sludge pretreated to 175°C with low MW intensity had slightly higher values than the other pretreated sludge and control; however, concentrations were still very low for all 6% TWAS treated at different conditions. The average concentrations of soluble protein and soluble sugars for pretreated 6% TWAS were 41 ± 17 mg BSA/L and 56 ± 27 mg glucose/L, respectively.

The biogas and methane yields of TWAS were calculated in terms of VS removal instead of tCOD removal due to fact that tCOD measurements are less reliable since the dilution factor for 11.85% TWAS and even for 6% TWAS is usually higher than 100. Methane yield is usually in the range of 0.49 to 0.75 L CH_4/g VS removed depending on the sludge type (Metcalf and Eddy, 1991). From the BMP reactors, the ultimate methane yield was calculated to be 0.57 ± 0.07 and 0.52 ± 0.07 L CH_4/g VS removed for TWAS MW pretreated at 6 and 11.85% concentrations, at the various temperatures and MW intensities

respectively. Biogas yield for 6% pretreated TWAS was calculated as 0.91 L biogas/g VS removed and for 11.85% pretreated TWAS it was found to be 0.84 L biogas/g VS removed. The amount of COD solubilized per gram of VS initially present was slightly higher at the higher pretreatment TWAS concentration. However the yield of CH_4 produced per gram of VS initially present was slightly higher when the pretreatment TWAS concentration was 6% as opposed to 11.85%.

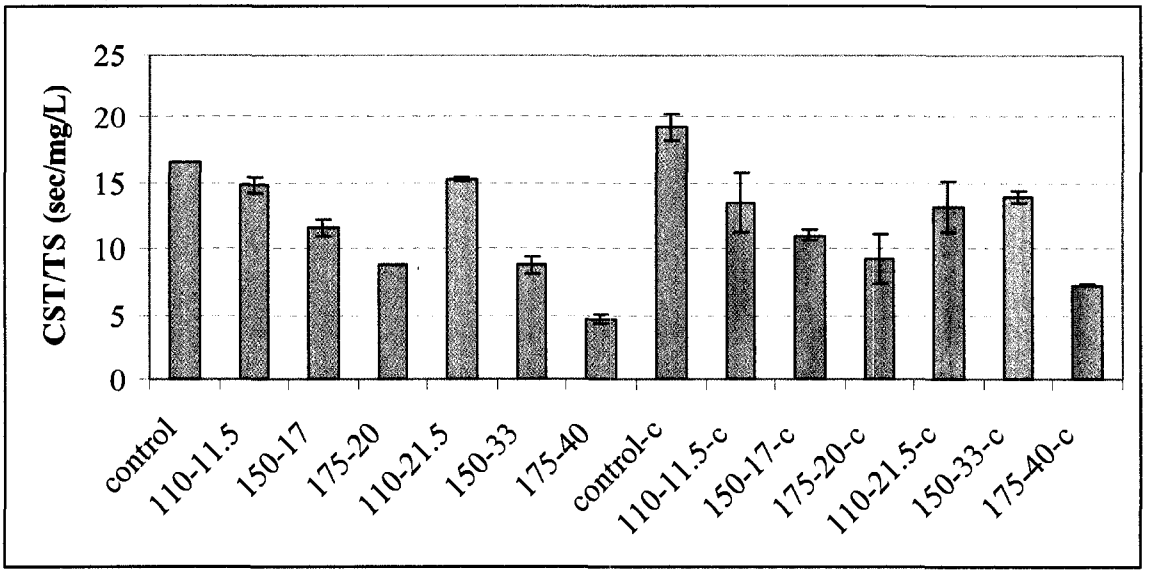

Figure 4.7: Dewaterability of sludge pretreated at different conditions after first set of BMP tests in terms of CST/TS

The dewaterability of digestate from control assays and MW pretreated sludge was investigated after the BMP test by using the CST method. The temperature and volume of samples were kept constant during CST analysis at 23 ± 1°C and 5 mL, respectively. CST values were reported per mg/L of TS concentration of digestate for each sample for better comparison (Figure 4.7). It was observed that with lower MW intensity and higher pretreatment temperature, a shorter time was required for water to be released from digestate

between two reference points. The greatest improvement in dewaterability was observed when both sludge concentrations were MW pretreated at 175°C with lower MW intensity corresponding to the lower temperature ramp profile. The corresponding percentage decreases in CST for these pretreatment conditions were 74 and 66% compared to the control for 6 and 11.85% sludge, respectively.

4.4.2 Inhibition

The level of inhibition observed in BMP assays with MW pretreated sludge was mild and of short duration indicative of an accumulation of a slowly degradable substance at an inhibitory concentration or lack of acclimation to the presence of the substance. In AD many organics and inorganics can cause inhibition. Most commonly seen inhibitions are due to high concentrations of ammonia (Fujishima *et al.,* 2000, Poggi-Varaldo *et al.,* 1997), long chain fatty acids (Pereira *et al.,* 2005, Shin *et al.,* 2003) and high concentrations of organics. It was found that high temperature MW pretreatment increases soluble organic content as well as VFAs dramatically. Sludge treated at 175°C with the 3.75°C/min MW intensity had 4.5 ±0.5 and 8.8 ± 0.6 fold more sCOD/tCOD ratios over untreated TWAS for 6 and 11.85% TS concentrations. It was observed that total VFA (TVFA) acids in terms of acetic acid, propionic acid and butyric acid in BMP serum bottles accumulated over the short term at the beginning of the assay after high temperature MW pretreatment. TVFA was approximately 12 times greater than the control with the MW pretreatment for 6% TWAS and it was around 6 times more for concentrated 11.85% TWAS prior to digestion (Table 4.3). In the first week of the BMP assay TVFA concentrations of pretreated samples were almost twice as much as the TVFA concentration of untreated sludge.

In terms of ammonia and long chain fatty acids concentrations of sludge, no significant increase was observed after MW pretreatment which concurs with the CBP results and final ammonia concentrations.

The anaerobic toxicity assay (ATA) was conducted to observe the threshold concentrations of VFA and/or sCOD concentrations leading to inhibition. In this assay, 150 and 175°C MW pretreatment temperatures and 3.75 and 7.5°C/min MW intensities were studied. For ATA test, untreated and MW pretreated sludges were centrifuged at 6513 RCF for 20 minutes and the supernatant were filtered through 1.2 μm glass filters. Five dilutions at 100, 50, 25, 12.5 and 6.25% were made with distilled water. ATA test was performed by using 150 mL serum bottles and plastic rubber stoppers as caps. In each bottles there were 21 g inoculum, 85 g supernatant and 0.256 mL acetic acid with equal amount of potassium carbonate and sodium carbonate (1.5 g/L supernatant) as pH buffer. Nitrogen was bubbled to remove air from the bottles. Experiments as always were performed in duplicate. Number of bottles used for ATA test including controls was 56. Biogas production was measured daily and biogas composition, pH and VFA concentrations were determined once a week.

Figure 4.8 shows cumulative biogas production of TWAS pretreated at 150°C at 3.75°C/min intensity as an example of results from this study. It was observed that in the early stage of digestion mild inhibition occurred in all dilutions. Similar inhibition was observed for all pretreatment conditions. This indicates that, acute inhibition observed in the early stage of BMP tests was not caused by high organic loads but rather presence of an inhibitory substance not familiar to the microbial consortia. It is known that by proper acclimation bacteria can adapt to toxic compound concentrations; therefore, in the second set of BMP

tests, the effects of a longer acclimation period on inhibition as well as slower MW temperature ramp (attempt to increase the MW effect on TWAS digestion) was studied.

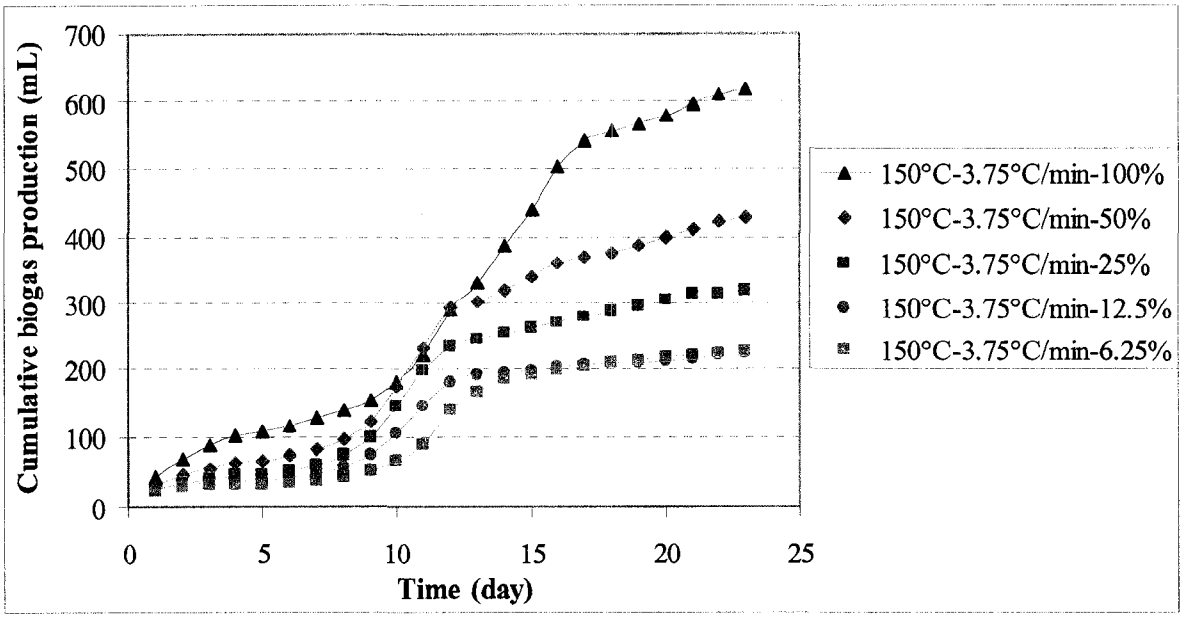

Figure 4.8: Cumulative biogas production of supernatant of TWAS pretreated at 150°C at 3.75°C/min intensity at different dilutions

4.4.3 Effect of improved acclimation and low intensity MW on BMP (Test 2)

BMP tests of MW pretreated TWAS with lower intensity and better acclimatized inoculum gave better results than the first tests reported above (Figure 4.9). The duration of inhibition was shortened and the intensity of the inhibition was decreased. CBP around the 20th day showed improved biogas production for sludge pretreated with MW. As MW pretreatment temperature increased biogas production increased.

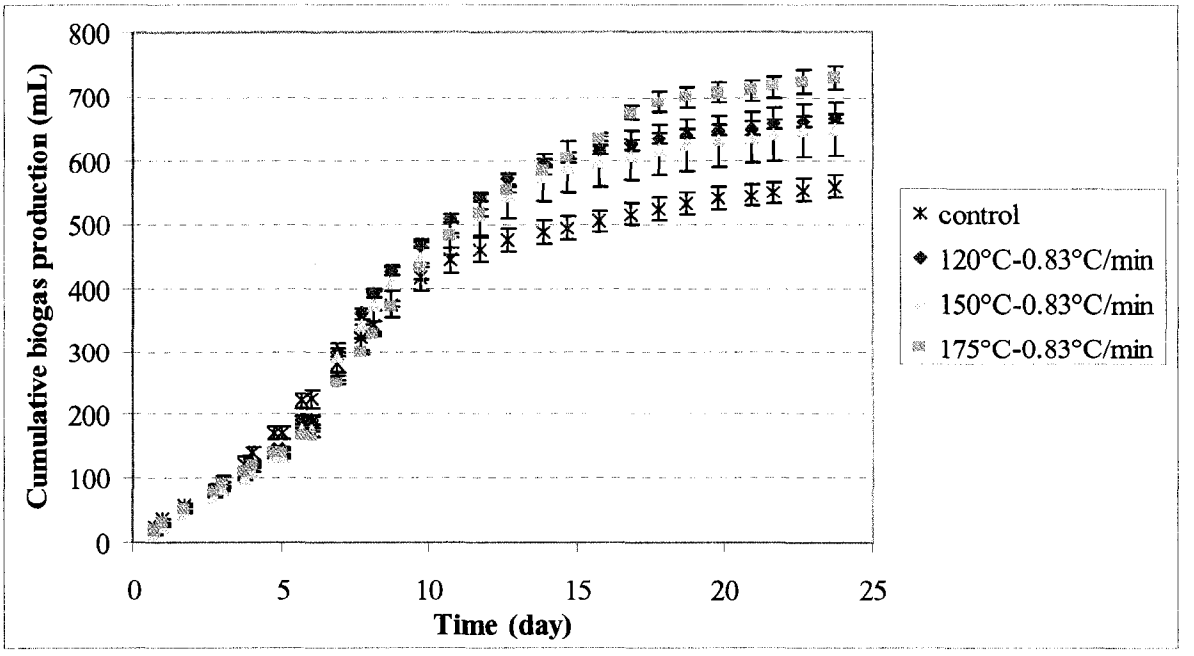

Figure 4.9: Cumulative biogas production for control and MW pretreated sludge obtained from the 2nd set of BMP test

The greatest improvement in CBP and TWAS stabilization was observed with TWAS pretreated to 175°C which at the 18th day was 31 ± 6% more than that of the control (raw TWAS) (Figure 4.9). The sCOD/tCOD ratio of TWAS (4.6% TS) after MW pretreatment to 175°C was 3.74 fold more than the control which is in the same range found for MW pretreatment at higher MW intensity (Test 1). It was observed previously that lower sludge concentration as well as lower MW intensity had the greatest impact on solubilization. Although initial sludge concentration (4.6%) was lower than the concentration used in the first set of experiments, lowering the MW intensity did not improve sCOD concentration of the sludge. In the first set of experiments BMP assays containing TWAS pretreated at 175°C and 7.5°C/min MW intensity had 12.6 g/L sCOD whereas in the second set of BMP tests TWAS pretreated at 175°C using 0.83°C/min MW intensity had approximately 10.8 g/L

sCOD. Despite slightly lower sCOD concentration TWAS pretreated at 175°C in the second set of BMP tests had greater improvement in CBP in a shorter time than observed in the first set of experiments. The improvement in biogas production compared to the control clearly shows that combining appropriate MAD acclimation with lower intensity MW pretreatment to high temperatures can have a significant positive impact on the digestion of TWAS.

Table 4.5 shows the duration and rate of exponential phase during Tests 1 and 2 for each condition. Exponential phase duration for TWAS pretreated at 110°C for both 3.75 and 7.5°C/min intensities was very similar to that of control at both TS concentrations studied. However as the pretreatment temperature increased exponential phase duration increased regardless of MW intensity and sludge concentration. In the first test, the rate of the exponential phase for all pretreated TWAS was observed to be lower than their controls. This was ascribed as the contribution of inhibition observed in the early stage of BMP assay. Decrease in the rate of biogas production was more pronounceable when the MW intensity decreased. TWAS pretreated at 175°C with low MW intensity at both TS concentrations showed much lower biogas production rates due to the secondary inhibition observed during BMP assay. On the other hand, in the second test, the acute inhibition decreased and the rate of biogas formation in the exponential phase became very similar to that of control for the pretreated TWAS.

Table 4.5: Duration and rate of exponential phase for Tests 1 and 2

	Duration of exponential phase (d)	Rate of exponential phase (L/L/day)	Rate relative to control
1ST TEST			
Control	8	0.37 ± 0.01	
110°C-7.5°C/min	8	0.30 ± 0.01	0.82 ± 0.03
150°C-7.5°C/min	11	0.24 ± 0.01	0.67 ± 0.03
175°C-7.5°C/min	11	0.23 ± 0.00	0.64 ± 0.02
110°C-3.75°C/min	10	0.28 ± 0.00	0.76 ± 0.02
150°C-3.75°C/min	12	0.22 ± 0.01	0.60 ± 0.04
175°C-3.75°C/min	23	0.14 ± 0.01	0.39 ± 0.02
Control-c	9	0.30 ± 0.01	
110°C-7.5°C/min-c	10	0.24 ± 0.00	0.80 ± 0.03
150°C-7.5°C/min-c	13	0.20 ± 0.01	0.66 ± 0.05
175°C-7.5°C/min-c	14	0.19 ± 0.04	0.64 ± 0.17
110°C-3.75°C/min-c	9	0.25 ± 0.06	0.81 ± 0.21
150°C-3.75°C/min-c	12	0.21 ± 0.01	0.67 ± 0.03
175°C-3.75°C/min-c	22	0.14 ± 0.01	0.45 ± 0.06
2ND TEST			
Control	7	0.57 ± 0.07	
120°C-0.83°C/min	8	0.63 ± 0.02	1.10 ± 0.17
150°C-0.83°C/min	8	0.59 ± 0.08	1.04 ± 0.23
175°C-0.83°C/min	12	0.52 ± 0.03	0.91 ± 0.15

Figures 4.10 and 4.11 show incremental biogas production of TWAS treated by MW to 150 and 175°C relative to the untreated TWAS control for BMP assay Test 1 and BMP assay Test 2), respectively. (Control sludge incremental biogas production was subtracted from pretreated sludge biogas production.) Table 4.6 shows the duration of inhibition as well as

the severity of inhibition. Severity of inhibition was defined as the area under the zero incremental biogas line in mL/g TS. Trapezoidal rule was used for area calculations since each data point is not equally spaced. For MW pretreatment to 175°C the duration of inhibition that occurred in the early stages of the BMP test was shortened to 7 days and was finished by day 9 for the longer acclimated inoculum compared with about 23 days of inhibition for BMP Test 1 (Figure 4.11). Additionally, the severity of the inhibition was less for better acclimated inoculum as realized by determining the smaller area under the zero incremental biogas line compared with Test 1 results which was decreased 16.7 times.

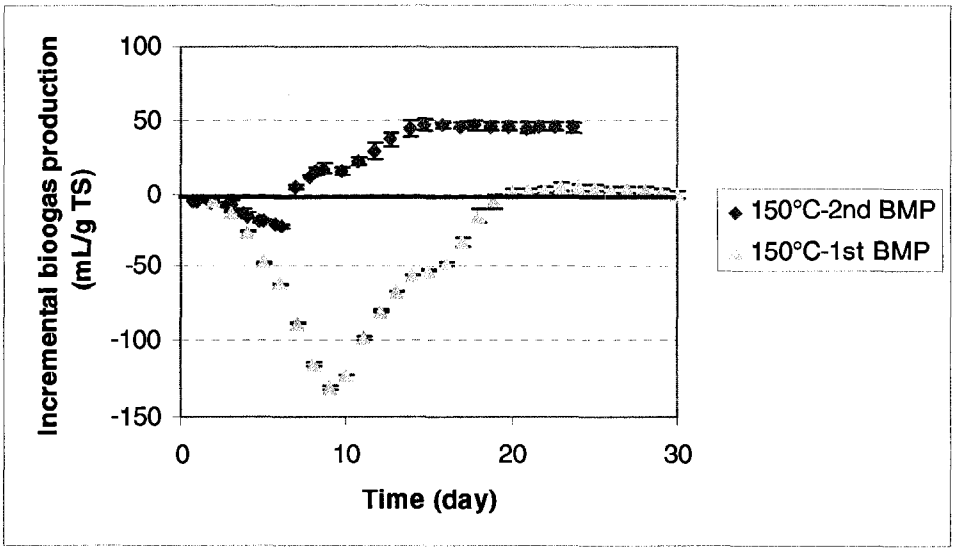

Figure 4.10: Differences between incremental biogas productions of TWAS pretreated at 150°C relative to the control for the first and second sets of BMP tests

Similarly, TWAS treated to 150°C and digested with better acclimatized MAD inoculum produced similar improvement in CBP compared to that found with shorter acclimatized inoculum both in terms of the length and severity of methanogenic inhibition. TWAS pretreated to 150°C produced a 19 ± 1% improvement in CBP over the control at day 14

(Figure 4.9). Duration of inhibition decreased from 19 to 7 days and severity of inhibition was improved by 13.4 times (Table 4.6).

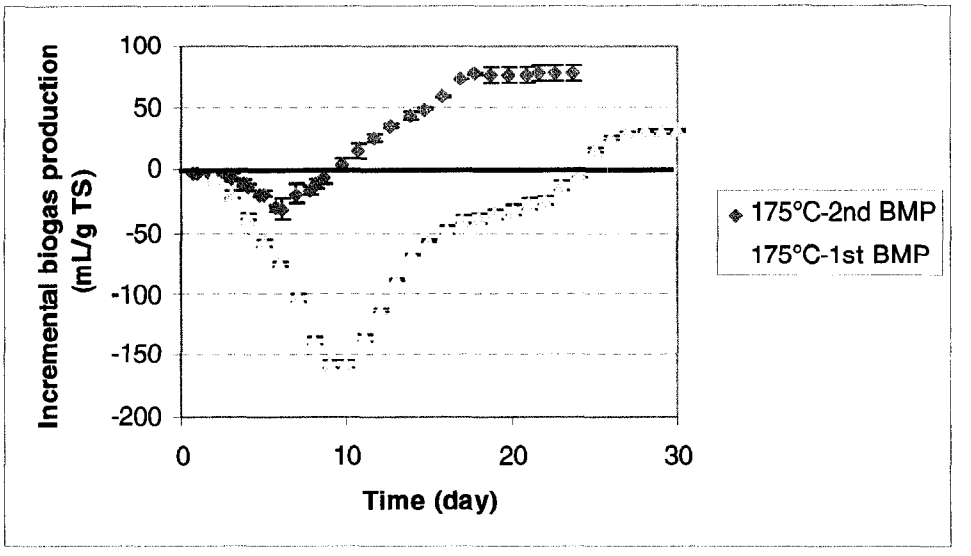

Figure 4.11: Differences between incremental biogas productions of TWAS pretreated at 175°C relative to the control for the first and second set of BMP tests

Table 4.6: Duration and severity of inhibition

	Duration of inhibition (day)	Severity of inhibition (mL biogas/g TS)
150°C – 1st BMP	19	1066.3
150°C – 2nd BMP	7	64.0
175°C – 1st BMP	24	1462.2
175°C – 2nd BMP	9	109.1

Following conclusion of the second BMP test CST/TS of the digestates were evaluated to observe whether there was an improvement in release of bound water by lowering the MW intensity. It was observed that the CST/TS values compared to controls were very similar to those obtained from the first BMP tests with temperature ramp rate of 3.75°C/min (Figure

4.12). It is concluded that intensity of MW pretreatment had little impact on dewaterability of MAD digestate for up to MW induced temperature ramp rates of 0.83 and 3.75°C/min.

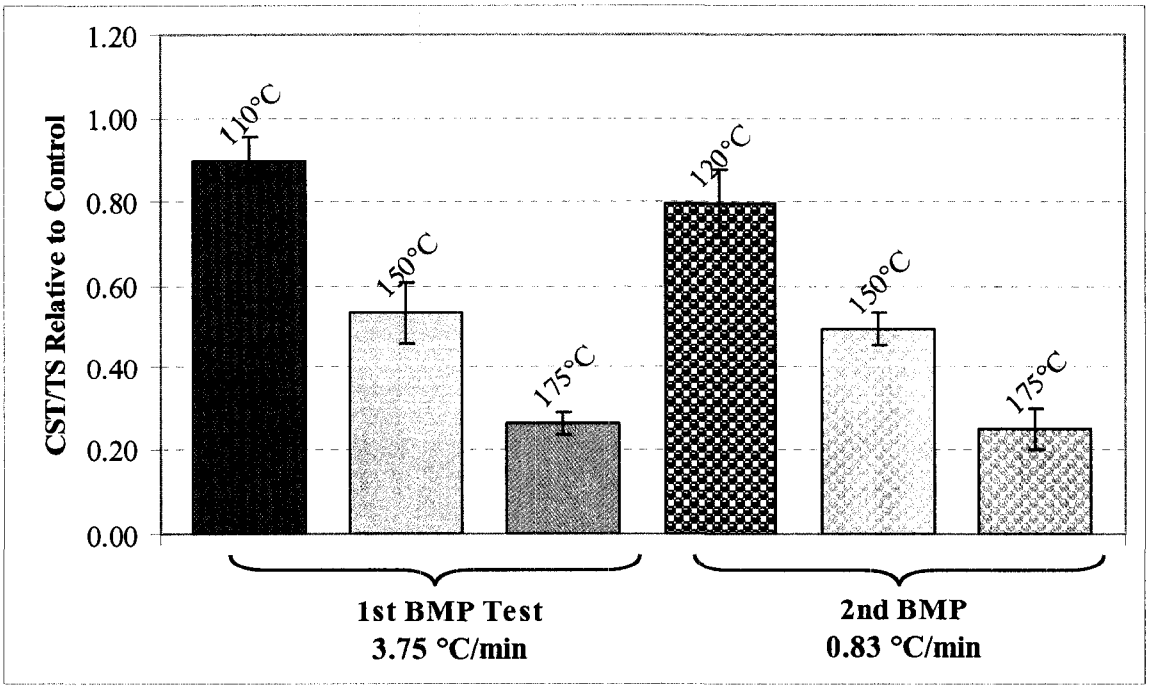

Figure 4.12: Dewaterability of sludge pretreated at different MW pretreatment temperatures after 1st and 2nd set of BMP tests in terms of CST/TS relative to control

4.5 CONCLUSIONS

In the first set of experiments, all BMP reactors containing MW pretreated sludge showed acute methanogenic inhibition causing a slight reduction in the rate of digestion; however, the exponential phase lasted longer for pretreated samples indicating that if inhibition could be overcome, there was potential for improving biogas production by high temperature MW pretreatment. Additionally, lower MW intensity extended the duration of the exponential phase of gas production suggesting that lower MW intensity could produce improvements in TWAS MAD. Despite inhibition, 6% TWAS pretreated at 175°C at MW intensity of

7.5°C/min resulted in the highest improvement of 13% in gas production over the control at day 21 of the BMP test.

A secondary methanogenic inhibition was observed with low MW intensity TWAS pretreatment to 175°C. While the secondary inhibition suppressed increased CBP at exponential phase it supports the results that lower intensity MW pretreatment to high temperatures improves pretreatment over higher MW intensity. The secondary inhibition suggests that a second inhibitory compound was produced at lower MW intensity that was not produced at higher intensity.

Methane yield was calculated from BMP reactors at 0.57 and 0.52 L CH_4/g VS removed for 6 and 11.85% TWAS, respectively. Similarly biogas yields for 6 and 11.85% TWAS were found to be 0.91 and 0.84 L biogas/g VS removed, respectively. Lower methane and biogas yields for higher concentrated TWAS pretreated to the same temperature at the same temperature ramp rate were not the result of release of more solubilized material from liquefaction of high concentrated TWAS by MW pretreatment. CST experiments showed that as pretreatment temperature increased and MW intensity decreased, potential dewaterability of digested sludge improved.

The second set of BMP tests, demonstrated that further acclimation of the MAD inoculum minimized methanogenic inhibition that resulted from compounds produced during high temperature MW pretreatment. Lowering the MW intensity and increasing the thermal and athermal treatment exposure of the TWAS enhanced MAD and for TWAS pretreated to 175°C produced 31 ± 6% more biogas than the control (raw TWAS) at the 18^{th} day of the BMP test.

4.6 ACKNOWLEDGMENTS

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CHAPTER 5:

Evaluation of Continuous Mesophilic Anaerobic Sludge Digestion after High Temperature Microwave Pretreatment

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5.1 INTRODUCTION

Sludge management has become an important issue in wastewater treatment plants in the last decade due to environmental and economical concerns. Sludge disposal activities are controlled by strict regulations due to the possibility of spreading pathogens as well as polluting agricultural lands, watersheds and ground waters. Moreover, sludge treatment and disposal presently accounts for about half of the total operational cost of wastewater treatment plants which is in addition to future issues such as decrease in availability of landfills and increased fuel transportation expenses (Weemaes, M. P. J and Verstraete, W. H., 1998). Anaerobic digestion (AD) is the most economic and commonly method used for sludge management. AD reduces the sludge volume by about half; consequently it reduces the handling and transportation costs to landfills as well as decreases the required area for land disposal. During AD energy is produced in the form of biogas. Despite the fact that

anaerobic digestion is a practical, environmental and cost effective way for sludge stabilization, its efficiency is limited to 30-45% volatile solids (VS) reduction for waste activated sludge (WAS) (Gosset and Belser, 1982). The reason for this is WAS is mainly composed of microbial cells within an extra-cellular polymeric floc matrix and their cell walls are physical barriers that do not permit intracellular organics to be easily biodegraded through digestion (Baier and Schmidheiny, 1997). Cell wall disruption or destruction is one of the main steps to increase digestion efficiency. The extra-cellular polymeric substances (EPSs) are another important part of WAS that keep the floc structure together (Bura *et al.,* 1998). Removing substances from this floc matrix also enhances AD. Therefore hydrolysis of WAS cells and EPS is the rate limiting step in anaerobic digestion of this material.

To enhance hydrolysis many pretreatment methods have been studied. These pretreatment methods can be classified under mechanical, chemical, thermal and their combinations. All these pretreatment methods show some degree of improvement in VS destruction and biogas production. However improvement in biogas production can be tempered with negative effects in other sludge management areas. Mechanical disintegration which is an energy intensive method has been evaluated at lab and pilot scale has resulted in negative effects on dewaterability characteristics of digested sludge (Kopp *et al.,* 1997; Muller *et al.,* 1998 and Weemaes and Verstraete, 1998). On the other hand ultrasound WAS pretreatment shows improvement in dewaterability and it is an energy effective pretreatment method (Thiem *et al.,* 2001 and Barber, 2005). However this method does not have any effect on pathogen destruction. Chemical pretreatment is usually performed by adding strong acid or bases (Knezevic *et al.,* 1995 and Navia *et al.,* 2002). Combining chemical with thermal

pretreatments showed better improvement in WAS solubilization as well as biogas production (Heo *et al.,* 2003 and Vlyssides and Karlis 2004). However, addition of chemicals makes this treatment less economically attractive. Ozonation is another costly chemical WAS pretreatment which improves digestion efficiency and biogas production but results in deterioration in digested sludge dewateribility characteristics (Goel *et al.,* 2003 and Scheminski *et al.,* 2000). Thermal WAS pretreatment is one of the earliest pretreatment methods that have been implemented. For temperatures below 100°C it was reported that biogas production can be increased 30% by pretreating sludge to 60 to 80°C when volumetric organic loading rate (OLR) was maintained at 3 kg VS/m^3.d (Hiraoka *et al.,* 1985). At high temperatures in the range of 120 and 180°C it was found that although methane production improved the percent increase over milder thermal pretreatment was relatively small. It was speculated that either inhibitory compounds were being formed that inhibited digestion or that a majority of the readily biodegradable solids had already been digested. Beyond 180°C a sharp decrease in methane production was observed. This phenomenon was described as a Maillard reaction which occurred between amino acids and low molecular weight sugars in the sludge producing inhibitory and difficult to degrade end products (Pinnekamp, 1989). Stuckey and McCarty (1984) also reported inhibition of AD following pretreatment of thickened WAS (TWAS) at elevated temperatures. They attributed the decrease in VS destruction to caramelization of sugars in the waste. Haug *et al.* (1978) reported that optimum pretreatment temperature for activated sludges in terms of the greatest increase in biodegradability for mesophilic digestion was near 175°C. It was reported that increase in biogas production with thermal pretreatment at 175°C was 61% greater than for untreated sludge at 15 day sludge retention time (SRT).

Among all these pretreatments, thermal disintegration at high temperatures (160-175°C) and pressures (6-8 bar) was found to be superior in terms of VS destruction, biogas production as well as pathogen reduction (Barnard *et al.*, 2002; Abraham and Kepp, 2003).

Microwave (MW) pretreatment is an alternative method to conventional thermal pretreatment to conserve energy, to destroy pathogens and to increase VS destruction (Decarau, 1985). MW irradiation can produce focused direct heat rapidly which lowers the energy losses while transmitting energy (conventional heating). Additionally, the changing dipole orientation of polar molecules occurring during microwave irradiation causes athermal (non- thermal) effects which collectively with thermal effects are hypothesized to cause the breakage of hydrogen bonds and unfolding and denaturing of complex biological molecules. The existence of the MW athermal effect on WAS solubilization and concomitant improvements in VS destruction and biogas production has recently been reported (Eskicoglu *et al.,* 2007c and Coelho *et al.,* 2008). TWAS solubilization in terms of soluble chemical oxygen (sCOD) to total COD (tCOD) ratio increased from 0.06 (untreated) to 0.18 after MW pretreatment at 96°C (Eskicioglu *et al.,* 2007a). Additionally, it is possible to produce Class A sludge when WAS is pretreated with MW at temperatures higher than 85°C prior to mesophilic anaerobic digestion (MAD) (Hong *et al.,* 2006).

Park *et al.* (2004) studied the effect of MW pretreatment on semi continuous MAD efficiency at different SRTs. It was reported that the improvement in biogas production rate of sludge MW pretreated at 91°C compare to the control (untreated sludge) increased from 24 to 36% when SRT decreased from 15 to 10 days. The methane production and to tCOD reduction for sludge MW pretreated were 315 ± 41 L CH_4/kg VS removed and 19.8 ± 1.3%

while that of control were 245 ± 22 L CH_4/kg VS removed and 13.8 ± 0.5%, respectively at 10 day SRT. It was concluded that SRT of MAD can be reduced from 15 days to10 days without any significant decrease in process efficiency.

In contrast to this study, Eskicioglu *et al.* (2007b) reported less than 5% improvement in biogas production at 10 day SRT from digestion of sludge MW pretreated at 96°C. However more significant improvements in biogas production were observed when the SRT was decreased to 5 day and was reported to be 15% and 28% for sludge MW pretreated at 50 and 96°C, respectively. Capillary suction time (CST) results indicated that digested sludge dewaterability improves by 39% with MW pretreatment at 96°C.

These results imply that there is a potential to increase biodegradability in full scale continuous digesters at shorter SRTs as well as produce Class A sludge with improved dewatering characteristics. Up to now, research on the effect of MW irradiation of WAS as a pretreatment method for continuous MAD has been conducted at temperatures lower than boiling point. However the literature indicates that conventional thermal pretreatment is most effective at temperatures between 160 and 170°C (Barnard *et al.*, 2002; Abraham and Kepp, 2003).

A preliminary study by Toreci *et al.* (2008) focused on the effect of MW pretreatment temperature, MW intensity and sludge concentration on WAS solubilization at temperatures between 110 and 175°C. It was observed that solubilization improves as MW pretreatment temperature increases, MW intensity decreases and sludge concentration increases. With increasing MW temperature, the difference between sCOD/tCOD ratios of sludge pretreated

at high and low MW intensity decreases which indicates that the temperature effect on solubilization is a more significant parameter than the effect of MW intensity at higher temperatures. The sCOD/tCOD ratio improved from 0.1 ± 0.02 to 0.46 ± 0.06 for 6% TS concentration and for 11.85% TS concentration it improved from 0.07 ± 0.01 to 0.57 ± 0.04 when TWAS was irradiated with MW to 175°C with 3.75°C/min MW intensity. These solubilization results are significantly higher than what was reported for low temperature MW pretreatment (Park *et al.*, 2004 and Eskicioglu *et al.*, 2007a).

Mesophilic batch test experiments done with high temperature MW pretreatment showed mild inhibition in the early stage of experiments despite the fact that inoculum was acclimatized with sludge pretreated at 175°C for 4 months (Toreci *et al.*, 2007). Further acclimation of another 3 months decreased the initial acute inhibition observed in biochemical methane potential (BMP) assays and made it easier to observe the positive effect of high temperature MW pretreatment on biogas production. The greatest improvement was observed for sludge pretreated to 175°C which produced 31% more biogas than untreated control by the 18^{th} day of then BMP test. Dewaterability of digested sludge was evaluated with the CST method and it was concluded that high temperature MW pretreatment had a positive effect on dewaterability characteristics. Decreasing MW intensity from 7.5 to 3.75°C/min decreased the CST whereas decreasing MW intensity further to 0.83°C/min did not show significant improvement of dewaterability of sludge over that of sludge pretreated at 3.75°C/min MW intensity.

It is known that dual phase digestion improves the digestion efficiency (Massey and Pohland, 1978, Cohen *et al.*, 1980 and Speece *et al.*, 1997) as well as provides better

stability at higher loading rates (Cohen *et al.,* 1982) by providing ideal conditions for enrichment of different type of bacteria for each phase. Azar and Speece (2001) concluded that two-phase dual sludge digestion lowers effluent COD significantly compared to a single stage control digester at total SRT of 30 days at a variety of operational conditions such as pH (4.5, 5.5 and 6.5), floc load (3, 9 and 27 g COD/gVSS) and first stage hydraulic retention time (HRT; 3, 8 and 24 h). They also reported that having a recycle line between the two phases lowered the efficiency of the process.

Research done by Park et al. (2005) combined two phase digestion with two pretreatment methods, thermochemical and biological hydrolysis. For thermochemical pretreatment WAS was heated to 121°C for 30 minutes (autoclave) and 7 g NaOH/ L WAS then added cooled for 2 hours prior to the pH being adjusted to 6.7 with HCl. For biological hydrolysis, sludge was stirred with aerobic bacteria at 150 rpm at 30°C. Retention time for pretreatment, acidogenic phase and methanogenic phase was set at 3, 6 and 12 days, respectively. Park reported that thermochemical pretreatment with dual phase digestion improved digestion efficiency more than biological hydrolysis pretreatment combined with dual phase digestion. It was also concluded that both of these pretreatment methods combined with two phase digestion gave better results when compare to other pretreatment methods (ultrasonic and mechanical pretreatment methods) and single stage MAD in terms of tCOD reduction, VS reduction and methane yield.

In light of these positive results, semi-continuous MAD experiment were undertaken to evaluate the effect of high temperature MW pretreatment and MW intensity on single stage MAD as well staged MAD performance.

5.2 EXPERIMENTAL PROCEDURE

TWAS (~4-5% TS) used in this experiment was obtained from the centrifuge thickener at the local municipal wastewater treatment plant (MWWTP) Robert O. Pickard Environmental Center (ROPEC) located at Gloucester, ON Canada. ROPEC is a conventional activated sludge plant operated at a SRT of approximately 5 days and incorporates FeCl addition prior to secondary clarification for P removal. Sludge pretreatment was carried out with a Mars 5© (MW Accelerated Reaction System; CEM Corporation) MW oven. Mars 5© can supply 1200 W ± 15% MW energy at 2450 MHz frequency and has a controllable operating range of up to 250°C and 3.45 kPa. MW intensity was controlled by adjusting the temperature ramping time to achieve the set temperature. TWAS concentration was maintained constant for all tests and was diluted to a standardized concentration of 3% TS using distilled water prior to use (Table 5.2).

MW pretreatment temperature of 175°C was selected for the semi-continuous digestion study as the greatest improvement in TWAS solubilization and biogas production was observed at this temperature using BMP assays (Toreci *et al.,* 2007). For a similar reason temperature ramps of 3.75 and 1.25°C/min were chosen as high and low MW intensities. The time required for TWAS to be heated by MW from room temperature to 175°C for high and low MW intensities were 40 and 120 minutes, respectively. Temperature holding time was set at one minute.

To have better comparison of reactor performance, the total SRT (SRT=HRT) of the dual stage digestion was the same as for the single stage MAD. Three SRTs were tested: 20, 10

and 5 days. For the dual stage configuration, the first reactor's SRT was maintained at 2 day to promote the acid fermentation phase. Decrease in TFVA concentration of mesophilic acidogenic digestion when SRT was increased from 2 to 2.7 days by Bhattacharya *et al.* (1996). Due to this reason SRT of first stage acidogenic digestion was kept at 2 days to minimize the acetate conversion to methane. To keep the SRT of both process configurations the same, the secondary dual stage digester was operated at SRT's of 18, 8 and 3 days. The volumetric flow rates and the digester volumes used in this experiment for the single and two phase configurations at different SRT are shown in Figure 5.1.

Inoculum was taken from effluent line of the anaerobic digester at ROPEC where primary and secondary sludge are treated together in a ratio of 48:52 by volume respectively. Inoculum was acclimatized with MW pretreated TWAS at 175°C for more than a year prior for this experiment. The SRT of the MAD inoculum reactor was set to 20 days. The properties of acclimatized inoculum are given in Table 5.1 (Data represent arithmetic mean of duplicates ± absolute difference between mean and duplicates).

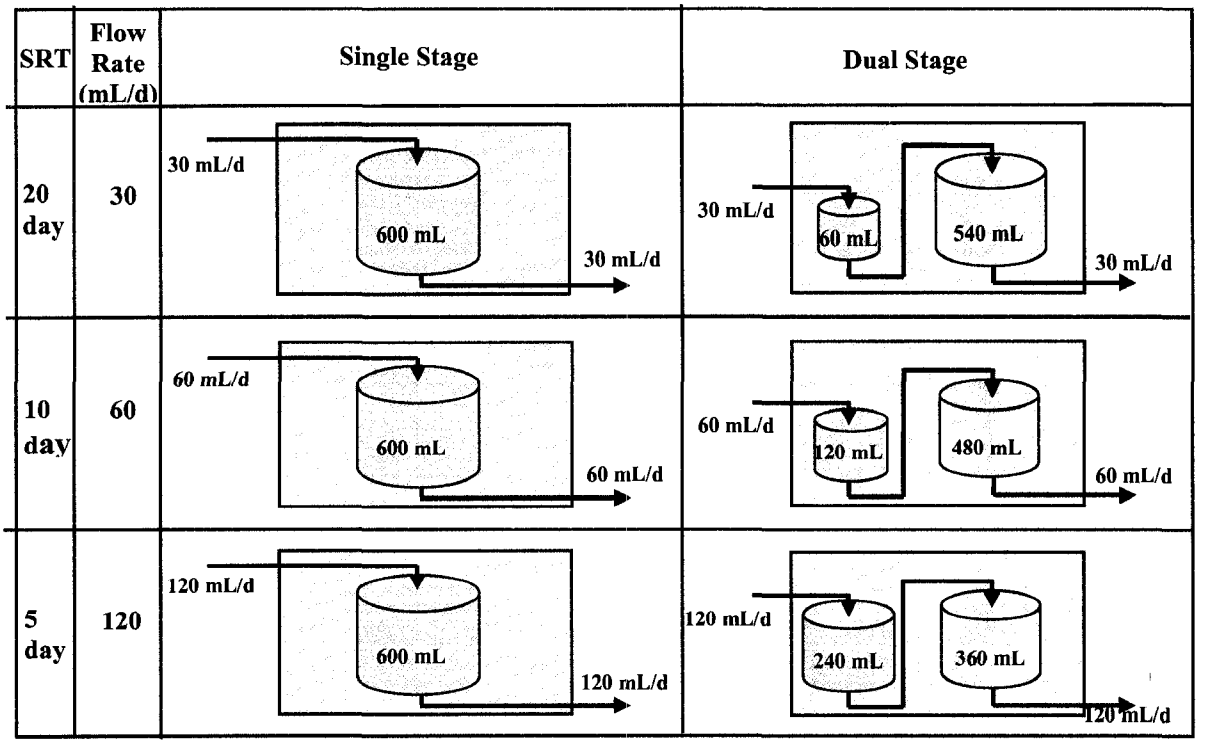

Figure 5.1: Schematic diagram of single stage and dual phase MAD at different SRTs.

Table 5.1: Properties of acclimatized inoculum

Properties	Acclimatised Inoculum
tCOD (mg/L)	13915±4345
VS (% w/w)	1.58±0.04
TS (% w/w)	3.33±0.24
VS/TS	0.47±0.02
TVFA (mg/L)*	81±10

*TVFA is the sum of acetic, propionic and butyric acids

Side-armed Erlenmeyer flasks which were sealed with two-hole rubber stoppers were used as digesters. The volume of the flasks used for single stage and secondary dual stage digesters were 1 L and the acid phase digesters of the dual stage were 0.5 L flasks. Ports in the rubber stopper were used to collect biogas and to withdraw sludge. Digesters were fed semi-continuously (i.e., one feeding each day) by using the side arm of the flask. 1 L tedlar bags were used for biogas collection and biogas production was measured daily by using a manometer. All digesters were started with acclimatized inoculum and TWAS was diluted to 3% total solids (TS) prior to feeding. All reactors were kept at 35°C in a New Brunswick incubator at a rotational speed of 95 rpm. Single stage reactors were started at typical 20 day SRT. In the two phase digesters the primary acid phase digester was maintained at a 2 day SRT and its effluent was transferred to the secondary dual stage digester which was initially operated at an 18 day SRT. Digesters were operated at the same SRT until steady state (SS) was reached which was defined as when daily effluent properties and biogas production fluctuated in a narrow range (10%) which was achieved usually in three SRTs (Ekama *et al.*, 1986). Total SRTs were decreased to 10 days when SS was reached. After the 10 day SRT data were collected total SRTs were decreased first to 7 days for a week and then it was decreased to 5 days to eliminate or lessen problems in the transient period that can be caused by the combination of shortened SRTs and high organic loading rates (OLR).

Twice weekly tCOD, sCOD, pH, total volatile fatty acids (TVFA) and biogas composition were determined while volatile solids (VS), TS, alkalinity, ammonia and dewaterability were analyzed once. For sCOD and tCOD analyses Standard Methods (SM) Colorimetric Method SM-5520C was used with a Coleman Perkin-Elmer model 295 spectrophotometer,

for alkalinity SM-2320B titration, ammonia SM-4500D with an ORION model 95-12 ammonia gas sensing electrode, VS/TS were done using SM-2540D while pH and dewaterability used a Fisher Accumet pH meter 7, and SM-2710G the Capillary Suction Time (CST) methods respectively (APHA, 1995). A Hewlett Packard (HP 5840A) packed Column GC with flame ionization detector was used for TVFA (acetic acid, propionic acid, and butyric acid) determinations. Biogas composition was determined by using HP GC model no 5710 equipped with a thermal conductivity detector.

5.3 RESULTS

Previous experiments (Toreci *et al.*, 2007) showed that high temperature MW pretreatment of TWAS increases solubilization. The increase in solubilization is more pronounced when pretreatment temperature increases and MW intensity decreases. Similar effects in terms of sCOD/tCOD ratios were again seen in this study, with feed TWAS MW pretreated to 175°C at high (3.75 °C/min) and low (1.25°C/min) MW intensity and are shown in Figure 5.2 for each of the SRTs evaluated. TWAS obtained from ROPEC showed variations in terms of solids concentrations due to seasonal differences in wastewater properties and operations at the WWTP. These variations are the source of the deviation in the properties of feed sludge (Table 5.2). In spite of this, solubilization almost doubled as MW pretreatment was applied to 175°C. In addition, the degree of solubilization further improved as MW intensity decreased (i.e., exposure time increased) from 3.75 to 1.25°C/min.

Table 5.2: Properties of feed at different SRTs

	20 day SRT			10 day SRT			5 day SRT		
Properties	**C**	**MW @ 175°C High MW int.**	**MW @ 175°C Low MW int.**	**C**	**MW @ 175°C High MW int.**	**MW @ 175°C Low MW int.**	**C**	**MW @ 175°C High MW int.**	**MW @ 175°C Low MW int.**
VS %	2.00±0.06	2.04±0.05	2.03±0.04	2.01±0.04	2.01±0.06	2.02±0.03	1.98±0.01	1.94±0.02	1.94±0.02
TS %	3.03±0.03	3.00±0.03	3.00±0.03	3.00±0.03	3.00±0.03	3.00±0.03	3.00±0.03	3.00±0.03	3.00±0.03
VS/TS	0.66±0.02	0.68±0.02	0.68±0.01	0.67±0.01	0.67±0.02	0.67±0.01	0.66±0.00	0.65±0.01	0.65±0.01
sCOD g/L	4.39±0.34	8.11±0.17	9.69±0.40	2.52±0.90	7.70±0.05	9.15±0.17	4.26±0.16	7.37±0.15	7.98±0.16
tCOD g/L	30.80±0.88	31.06±1.78	30.22±1.07	27.20±0.90	31.47±1.14	31.90±1.19	29.34±0.69	29.59±0.96	28.65±0.63
sCOD/tCOD	0.14±0.01	0.26±0.02	0.32±0.03	0.09±0.01	0.24±0.01	0.29±0.01	0.14±0.01	0.25±0.01	0.28±0.01
NH_3-N mg/L	777±112	1040±104	1077±150	465±258	787±82	1335±126	681±37	1068±32	968±82
Alkalinity mg $CaCO_3$/L	1789±296	1706±493	2177±619	1532±490	1684±291	2878±125	1688±22	2157±18	2062±17
TVFA[1] mg/L	1989±102	2447±325	2683±562	1048±205	3635±119	3962±119	1904±81	3063±198	2838±119

[1] TVFA = acetic acid + propionic acid + butyric acid

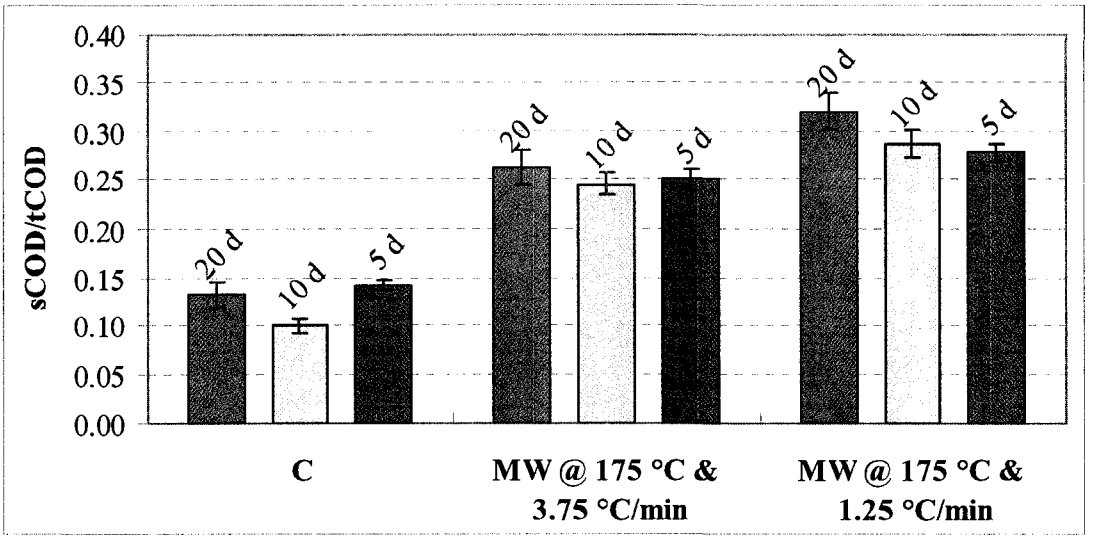

Figure 5.2: the effect of MW pretreatment on solubilization of feed sludge

To ensure confidence in the long term stability and quality of the results the experiment started with the longest SRT which was 20 days using acclimated biomass. Additionally, once SS conditions were achieved reactors were operated for another 3 SRTs before decreasing the SRT. It was observed that all digesters showed no adaptation problems when OLR was increased (SRT shortened). Daily biogas production data obtained from the single stage MAD fed with high intensity MW pretreated sludge through the duration of the experiment is shown as an example in Figure 5.3. Table 5.3 summarizes the steady state properties of the digesters at different SRTs. Data shown in Table 5.2 are the arithmetic means of measured values and standard deviations are indicated in the parenthesis below each data.

Results show that single stage digesters perform slightly better in terms of VS removal and biogas production at 20 day SRT than dual stage digesters. However, decreasing SRT

improves efficiency of dual digesters. In terms of VS removal, at 20 day SRT, MW pretreatment did not show any improvement indicating that 20 days was sufficient time to degrade the TWAS with or without pretreatment. The VS and biogas results would also tend to indicate that MW pretreatment to 175 C did not increase the amount of material available for biodegradation. This may be the result of a limitation of MW pretreatment or be due to the fact that ROPEC sludge is a relatively young sludge (5 d SRT) in which there is little accumulation of difficult to degrade biodegradable material. The fact that VS removal efficiency was about 48-49% at 20 d SRT for the control and pretreatment digesters tends to support the latter argument. The aspect of sludge age is being researched in another study. Decreasing the SRT clearly showed the improved performance of MAD for MW pretreatment over control single stage digesters. Figure 5.4 shows the VS removal percentages of digesters relative to single stage control at different SRTs. Based on previous BMP assays it was somewhat unexpected to see that the digester fed with sludge treated at high MW intensity showed greater improvement in terms of VS removal at both 10 and 5 day SRTs compared to low MW intensity. Improvements in VS removal and biogas production at lower SRTs compared to the control is a strong indication that increased solubilization via MW pretreatment has converted a portion of the more difficult to biodegrade material (degraded at 20 day SRT) and increased the amount of more readily biodegradable material. In dual stage digesters it was observed that MW pretreatment had a negative effect on VS removal for 20 day SRT. On the other hand at lower SRTs dual stage digesters fed with raw sludge showed improved VS removal. The highest improvements in VS removal were observed with dual stage digesters fed with raw TWAS and single stage digester fed with sludge pretreated at 175°C with high MW intensity which gave 38.3 and

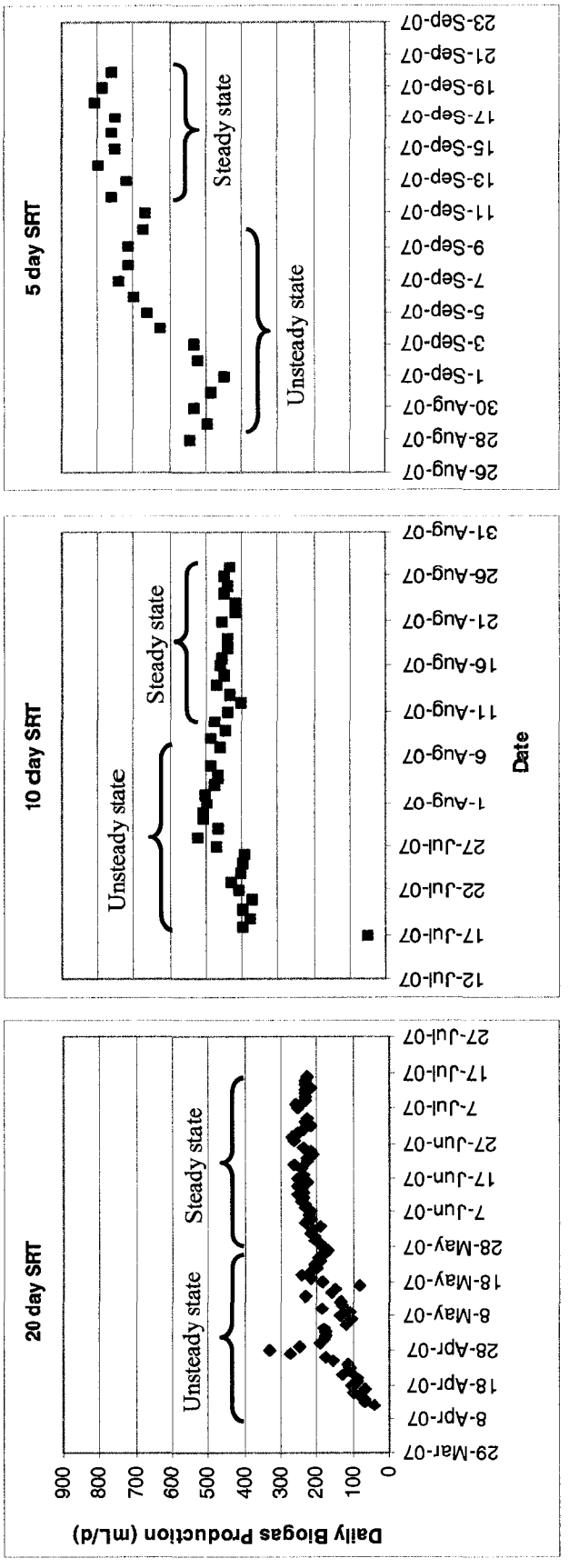

Figure 5.3: Daily biogas production of single stage mesophilic digester fed with sludge pretreated to 175°C with high MW intensity

Table 5.3: Steady state semi continuous digester properties

	20 day SRT						10 day SRT						5 day SRT					
		MW @ 175°C			MW @ 175°C			MW @ 175°C			MW @ 175°C			MW @ 175°C			MW @ 175°C	
Properties	**C***	**High MW int.**	**Low MW int**	**C* dual**	**High MW int. dual**	**Low MW int dual**	**C**	**High MW int.**	**Low MW int**	**C dual**	**High MW int. dual**	**Low MW int dual**	**C**	**High MW int.**	**Low MW int**	**C dual**	**High MW int. dual**	**Low MW int dual**
OLR gVS/L/d	1.00 (0.03)	1.02 (0.03)	1.02 (0.02)	1.00 (0.03)	1.02 (0.03)	1.02 (0.02)	2.01 (0.04)	2.01 (0.06)	2.02 (0.03)	2.01 (0.04)	2.01 (0.06)	2.02 (0.03)	3.96 (0.01)	3.87 (0.04)	3.88 (0.04)	3.96 (0.01)	3.87 (0.04)	3.88 (0.04)
OLR g tCOD/L/d	1.54 (0.04)	1.55 (0.09)	1.51 (0.05)	1.54 (0.04)	1.55 (0.09)	1.51 (0.05)	2.72 (0.09)	3.15 (0.11)	3.19 (0.12)	2.72 (0.09)	3.15 (0.11)	3.19 (0.12)	5.87 (0.14)	5.97 (0.19)	5.73 (0.13)	5.87 (0.14)	5.97 (0.19)	5.73 (0.13)
VS removal %	49.9 (4.6)	48.9 (1.5)	49.2 (2.0)	46.2 (4.3)	41.5 (1.9)	45.2 (4.3)	39.5 (1.6)	43.4 (1.6)	41.8 (1.5)	42.8 (1.3)	41.1 (1.1)	36.8 (1.1)	24.6 (2.2)	33.6 (3.6)	31.2 (2.1)	34.0 (0.5)	29.5 (1.7)	27.7 (1.8)
TS removal %	34.6 (2.5)	33.1 (1.6)	35.5 (1.5)	32.8 (2.6)	25.9 (3.1)	32.6 (2.3)	29.2 (1.0)	32.3 (2.5)	29.1 (1.3)	32.2 (0.7)	29.7 (1.0)	33.4 (2.1)	15.6 (1.6)	20.1 (2.1)	20.2 (1.7)	22.6 (1.5)	19.0 (1.6)	18.5 (1.6)
sCOD removal %	88.7 (3.9)	92.1 (1.5)	92.4 (3.6)	80.9 (2.3)	87.2 (0.5)	90.0 (1.5)	76.5 (4.6)	89.5 (1.1)	91.7 (0.7)	63.5 (2.9)	89.5 (1.1)	91.7 (0.7)	48.5 (3.7)	82.9 (0.9)	77.2 (0.9)	61.4 (3.6)	68.2 (4.4)	70.8 (2.3)
tCOD removal %	41.6 (5.7)	48.7 (6.4)	49.2 (3.6)	49.5 (4.3)	46.6 (5.6)	48.3 (3.3)	20.2 (3.8)	29.2 (3.3)	34.8 (3.4)	27.1 (1.4)	30.2 (2.6)	33.9 (3.0)	16.7 (1.8)	29.3 (2.3)	23.9 (2.7)	29.9 (0.7)	22.8 (2.1)	16.6 (2.8)
Biogas prod. L/d	0.22 (0.01)	0.24 (0.01)	0.22 (0.01)	0.23 (0.02)	0.22 (0.02)	0.24 (0.03)	0.32 (0.02)	0.44 (0.02)	0.44 (0.02)	0.36 (0.02)	0.43 (0.03)	0.44 (0.03)	0.42 (0.03)	0.77 (0.02)	0.62 (0.02)	0.54 (0.03)	0.60 (0.03)	0.42 (0.04)
Biogas prod. L/kgVS added	359.2 (24.5)	385.1 (26.0)	365.8 (16.6)	382.0 (43.8)	367.3 (43.2)	394.8 (58.2)	269.5 (18.1)	367.0 (22.5)	366.3 (18.0)	296.1 (25.0)	359.3 (27.2)	360.7 (28.9)	177.7 (12.6)	333.1 (11.9)	266.0 (12.6)	228.0 (15.6)	257.5 (14.7)	179.8 (18.9)
Biogas prod L/kg tCOD added	233.4 (15.5)	253.1 (22.7)	246.1 (14.0)	248.2 (28.2)	241.4 (31.8)	265.6 (40.2)	198.9 (14.6)	234.4 (15.4)	232.2 (14.7)	218.5 (19.5)	229.5 (18.2)	228.7 (20.5)	119.9 (9.1)	218.1 (11.0)	180.1 (9.5)	153.9 (11.3)	168.6 (11.3)	121.7 (13.1)
[1]CH_4 %	66.8 (0.6)	67.0 (0.6)	67.5 (0.8)	68.5 (0.7)	71.5 (0.9)	71.2 (0.6)	65.4 (0.9)	66.2 (0.4)	66.6 (0.5)	67.3 (0.3)	71.1 (0.5)	71.2 (0.6)	61.2 (0.5)	66.5 (0.3)	65.5 (0.0)	66.5 (0.2)	69.6 (1.0)	68.8 (0.3)
[1]pH	7.49 (0.03)	7.54 (0.04)	7.53 (0.05)	7.52 (0.03)	7.62 (0.03)	7.61 (0.03)	7.33 (0.07)	7.48 (0.02)	7.45 (0.04)	7.41 (0.06)	7.54 (0.03)	7.51 (0.04)	7.05 (0.03)	7.39 (0.03)	7.35 (0.04)	7.23 (0.03)	7.37 (0.06)	7.30 (0.07)
Biogas yield L/kg VS destroyed	675.6 (42.8)	769.1 (49.2)	734.5 (41.9)	859.0 (97.0)	889.2 (83.6)	843.9 (89.1)	679.0 (59.9)	839.6 (51.1)	875.2 (65.0)	688.6 (65.5)	877.2 (63.1)	928.9 (98.1)	701.5 (75.9)	1066.8 (86.3)	856.9 (79.3)	671.1 (47.8)	879.0 (74.3)	665.9 (83.9)
CH_4 yield L/kg VS destroyed	451.6 (33.4)	515.0 (38.3)	495.9 (33.4)	554.4 (73.8)	596.1 (65.7)	564.0 (69.3)	444.2 (45.7)	555.6 (39.2)	582.6 (50.2)	432.8 (51.0)	565.9 (57.7)	608.8 (75.7)	429.4 (53.8)	698.4 (65.3)	561.3 (60.0)	385.2 (82.6)	522.4 (91.3)	392.9 (74.1)

[1]Data represents single stage and the second digester of the dual configuration * Control no pretreatment

36.6% more VS removal over single stage control digester at 5 day SRT, statistically it is not possible to declare the superiority of one over the other one. Overall VS removal obtained from these two digesters were only 67-68% of VS removal obtained from single stage control digester operated at 20 day SRT.

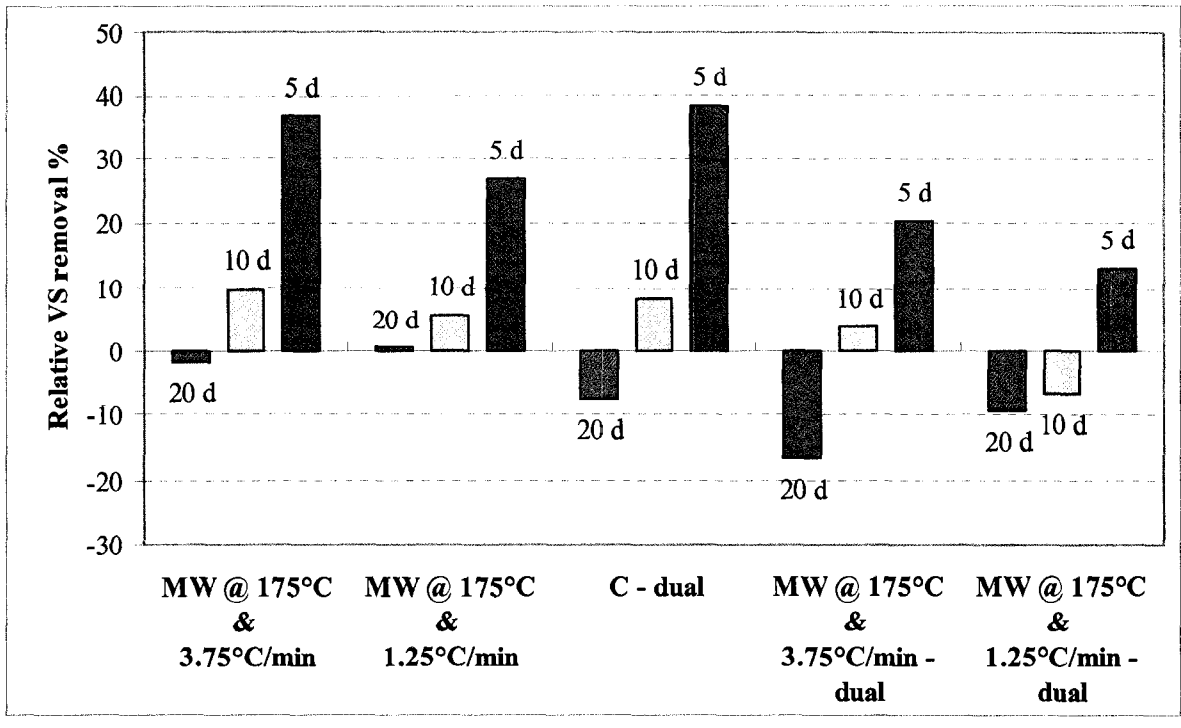

Figure 5.4: VS removal % relative to single stage mesophilic control digester

Very similar trends were observed for TS removal providing further confidence in the results. Highest improvement in TS removal over the single stage mesophilic control was observed at 5 day SRT (Figure 5.5). High MW intensity pretreatment showed more positive impact on TS removal in comparison to the low MW intensity. At 20 day SRT single stage digesters removed more TS than dual stage digesters. At 20 day SRT, TS removal from all digesters were very similar except TS data obtained from the dual digesters fed with sludge

pretreated at high MW intensity which was in the range of 32.6 to 35.5% removal. At 10 day SRT, similar TS removal percentages were obtained from single stage and dual stage digesters fed with sludge pretreated at 175°C with high MW intensity and the dual stage control which were 32.3 ± 2.5, 33.4 ± 2.1 and 32.2 ± 0.7, respectively. Greatest improvement in TS removal over the control was observed with dual stage control digester at 5 day SRT. Although the dual stage control showed 45% more TS removal than the single stage control at the same 5d SRT, it only reached 65% relative TS removal efficiency compared to of the single stage control digester performed at 20 day SRT.

All digesters fed with sludge pretreated with MW to 175°C had more than 87% sCOD removal at 20 and 10 days SRT. Control digesters in both single and dual stage configurations did not remove sCOD as efficiently as other pretreatment digesters. Highest improvement in sCOD removal relative to the single stage control was 71% and was achieved by the single stage digester fed with sludge pretreated at high MW intensity and operated at a 5 day SRT (Figure 5.6). This digester removed 83% of sCOD added which was 93% more than what the single stage control digester removed.

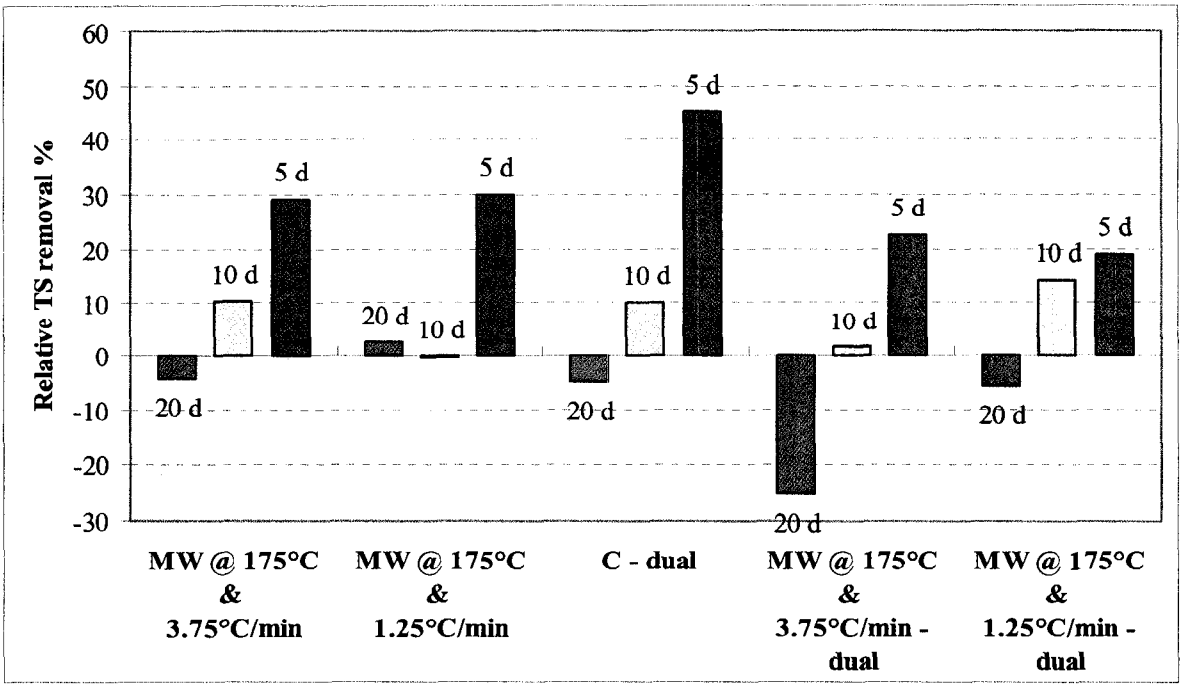

Figure 5.5: TS removal % relative to single stage control digester

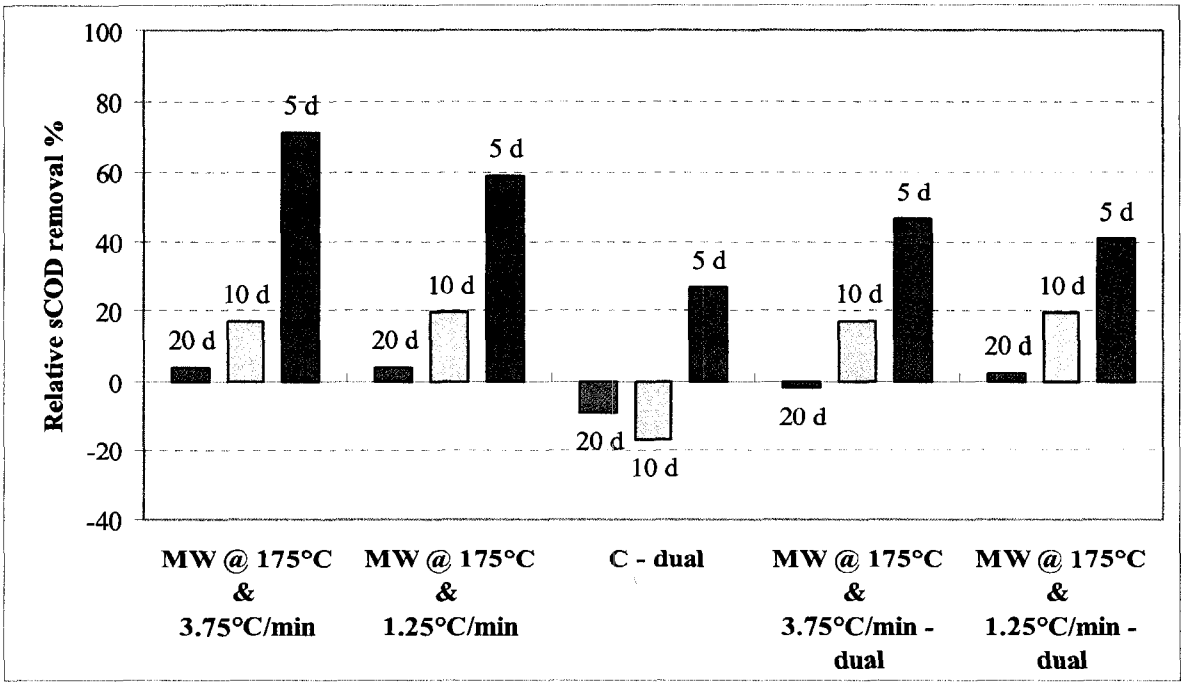

Figure 5.6: sCOD removal % relative to single stage control digester

Increase in tCOD removal over single stage control digester at 20 day SRT for all digesters was in the range of 12 to 19% (Figure 5.7). As SRT decreased the improvement on tCOD removal percentages varied. Decreasing SRT from 20 to 10 days improved removal efficiency of VS, TS, sCOD and tCOD however further decrease of SRT to 5 days showed opposite effect on removal efficiencies of these parameters.

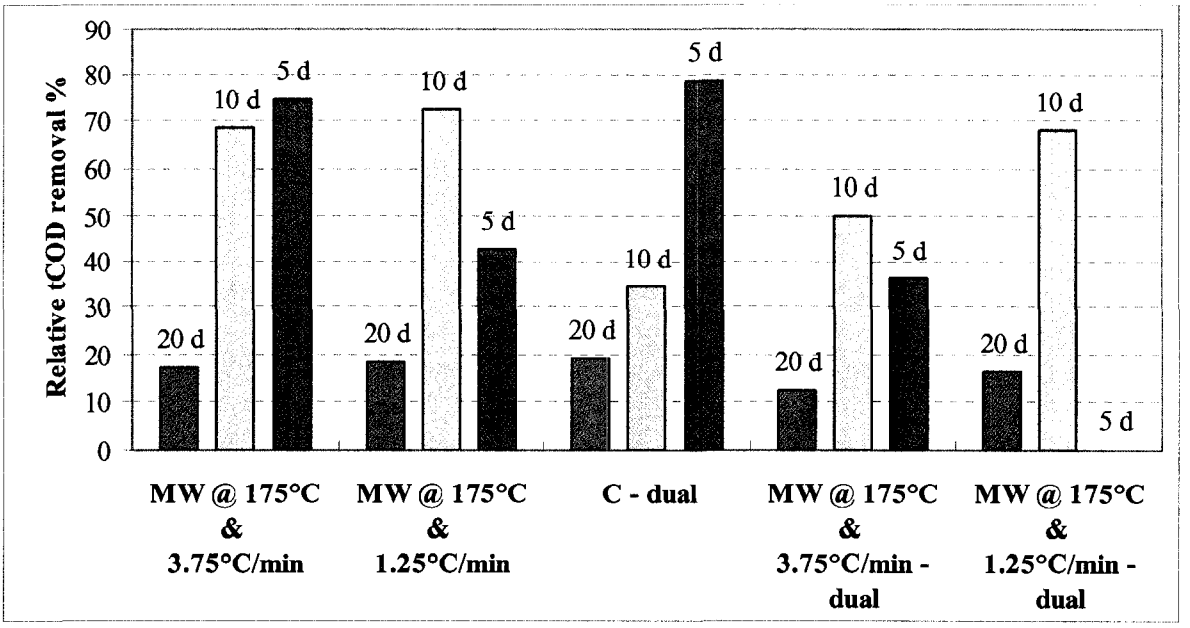

Figure 5.7: tCOD removal % relative to single stage control digester

The effect of MW intensity on TWAS solubilization showed that decreasing the MW intensity tended to increase the degree of solubilization. With greater solubilization more or faster biogas production from digesters might be expected. On the contrary, digesters fed with sludge treated at low MW intensity produced same or less biogas than ones fed with sludge treated at high MW intensity (Figure 5.8). From the batch BMP experiments sludge pretreated at 175°C with 0.83°C/min MW intensity produced 31% more biogas than

untreated sludge by the 18th day of the BMP test. Whereas from semi continuous digesters it was observed that at 20 day SRT daily biogas production was very similar for all digesters. When SRT was decreased to 10 days all digesters (both single stage and dual stage) except dual stage control digester fed with MW pretreated sludge had better VS removal and produced in the range of 34 to 37% more biogas over the single stage control. With further increase in OLR by reducing SRT to 5 days all digesters except dual stage digester fed with low MW intensity pretreated sludge showed further improvement. In general the secondary dual configuration digester treating low MW intensity sludge produced the same amount of biogas and had similar VS removal when compared to the single stage control digester. Similar trends can also be seen from daily biogas production per kg tCOD added or daily biogas production per kg VS added (Table 5.3).

Dual stage digestion with low MW intensity pretreated sludge was observed to have less ability to adapt to the highest OLRs when compared to single digesters. It is likely that the short SRT of 3 days in the secondary digester was insufficient to maintain good performance since the overall and primary digester SRTs were fixed at 5 and 2 days, respectively. However, results for the dual stage system were very good at 10 day SRT. Methane concentration of biogas produced was in the range of 65 to 67% for all single digesters except for the control digester which produced 61% when SRT decreased to 5 days. Secondary dual stage digesters produced higher methane concentration which was in the range of 69 to 71%.

The primary digesters produced very little biogas which was recorded as 1.54 ± 0.2, 1.52 ± 0.2 and 1.40 ± 0.2 mL biogas/mL sludge fed for the control, pretreated at high MW intensity

and at high MW intensity, respectively. The methane content was determined to be only 45 ± 2 % for all the primary digesters throughout experiment.

Final effluent characteristics for all conditions tested are given in Table 5.4. At 20 and 10 day SRTs, TVFA concentration of effluent stayed below 225 mg/L with high removal efficiency. Similar data was obtained for sCOD concentration and VS % with effluent less than 1000 mg/L and 1.22%, respectively. At 5 day SRT the single stage digester with sludge pretreated at high MW intensity still managed to convert organics into biogas more efficiently than other digesters and maintained low sCOD, TVFA and VS effluent concentrations.

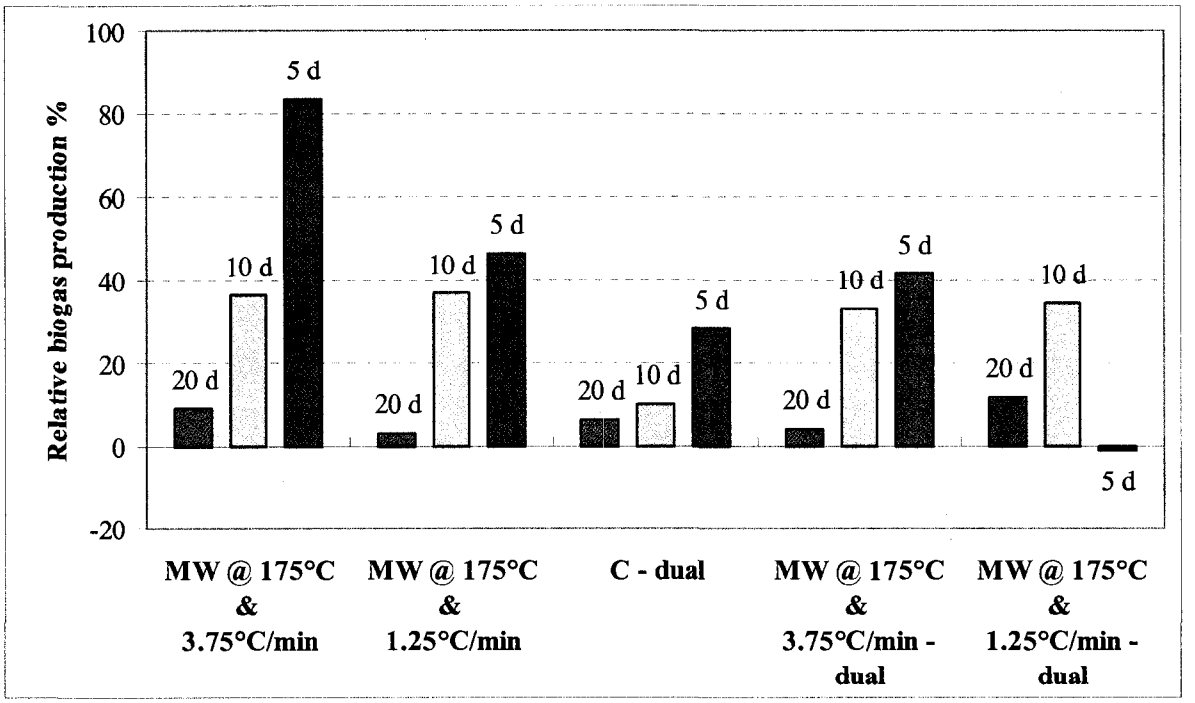

Figure 5.8: Biogas production % relative to single stage control digester

Table 5.4: Steady state properties of effluent after mesophilic anaerobic digestion

	20 day SRT						10 day SRT						5 day SRT					
		MW @ 175°C			MW @ 175°C			MW @ 175°C			MW @ 175°C			MW @ 175°C			MW @ 175°C	
Effluent	**C***	**High MW int.**	**Low MW int**	**C dual**	**High MW int. dual**	**Low MW int dual**	**C**	**High MW int.**	**Low MW int**	**C dual**	**High MW int. dual**	**Low MW int dual**	**C**	**High MW int.**	**Low MW int**	**C dual**	**High MW int. dual**	**Low MW int dual**
sCOD mg/L	389 (7)	668 (28)	593 (31)	801 (42)	1066 (38)	954 (62)	586 (77)	772 (81)	730 (27)	967 (49)	772 (81)	734 (27)	2225 (216)	1281 (36)	1906 (107)	1958 (369)	2226 (96)	2836 (439)
tCOD mg/L	17582 (684)	14560 (1050)	15808 (867)	15231 (610)	18007 (1303)	15791 (800)	21389 (1225)	20420 (737)	20641 (682)	19626 (601)	20156 (257)	20931 (523)	24093 (443)	20905 (859)	21491 (281)	20759 (206)	22318 (416)	24477 (961)
pH	7.5 (0.0)	7.5 (0.0)	7.5 (0.1)	7.5 (0.0)	7.6 (0.0)	7.6 (0.0)	7.3 (0.1)	7.5 (0.0)	7.5 (0.0)	7.4 (0.1)	7.5 (0.0)	7.5 (0.0)	7.1 (0.0)	7.4 (0.0)	7.4 (0.0)	7.2 (0.0)	7.4 (0.1)	7.3 (0.1)
NH_4-N mg/L	1750 (225)	1645 (70)	1630 (164)	1453 (114)	1607 (130)	1579 (132)	1186 (144)	1691 (182)	1467 (196)	1258 (47)	1605 (157)	1486 (93)	1874 (543)	1945 (173)	1561 (123)	1158 (59)	1390 (57)	1318 (283)
TVFA[1] mg/L	225 (72)	70 (20)	164 (14)	114 (34)	130 (21)	132 (20)	41 (1)	0 (0)	0 (0)	125 (93)	10 (13)	10 (7)	1190 (90)	85 (13)	730 (66)	856 (233)	1065 (173)	1393 (78)
Alkalinity[2]	4965 (132)	5185 (187)	5311 (330)	4632 (132)	5188 (363)	5108 (343)	3804 (322)	5298 (86)	4943 (138)	4275 (281)	5169 (213)	5046 (127)	3035 (204)	4467 (304)	3892 (369)	3373 (68)	3968 (139)	3522 (209)
VS %	1.04 (0.09)	1.05 (0.04)	0.99 (0.03)	1.08 (0.05)	1.16 (0.04)	1.08 (0.06)	1.22 (0.02)	1.12 (0.04)	1.22 (0.07)	1.16 (0.02)	1.17 (0.03)	1.22 (0.08)	1.49 (0.04)	1.28 (0.06)	1.33 (0.04)	1.61 (0.06)	1.36 (0.04)	1.40 (0.03)
TS %	1.94 (0.16)	2.04 (0.09)	1.99 (0.13)	1.99 (0.09)	2.25 (0.10)	2.10 (0.13)	2.13 (0.02)	2.03 (0.07)	2.18 (0.10)	2.04 (0.02)	2.11 (0.03)	2.16 (0.11)	2.53 (0.05)	2.43 (0.03)	2.42 (0.01)	2.69 (0.08)	2.43 (0.05	2.45 (0.04)

C* = Control digester

[1] TVFA = acetic acid + propionic acid + butyric acid

[2] Units for alkalinity is mg $CaCO_3$/L

Dewateribility characteristics of the digestates were determined by CST, where a decrease in suction time indicates potential improvement in the dewaterability of the sludge. Figure 5.9 shows the results before (TWAS feed) and after digestion at different conditions. It was observed that CST decreased for all the digestates compared to the raw feed sludge. For untreated control digestates, dewaterability improved when it was digested using either digester configuration with SRTs of 20 or 10 day. However when SRT decreased to 5 days single stage digester digestate dewaterability became poorer. However, for all pretreated sludge reactor digestates dewaterability was further improved over the raw feed and control reactors. Single stage digesters with MW pretreatment showed the best improvement on dewaterability in terms of reduced CST at all SRTs evaluated.

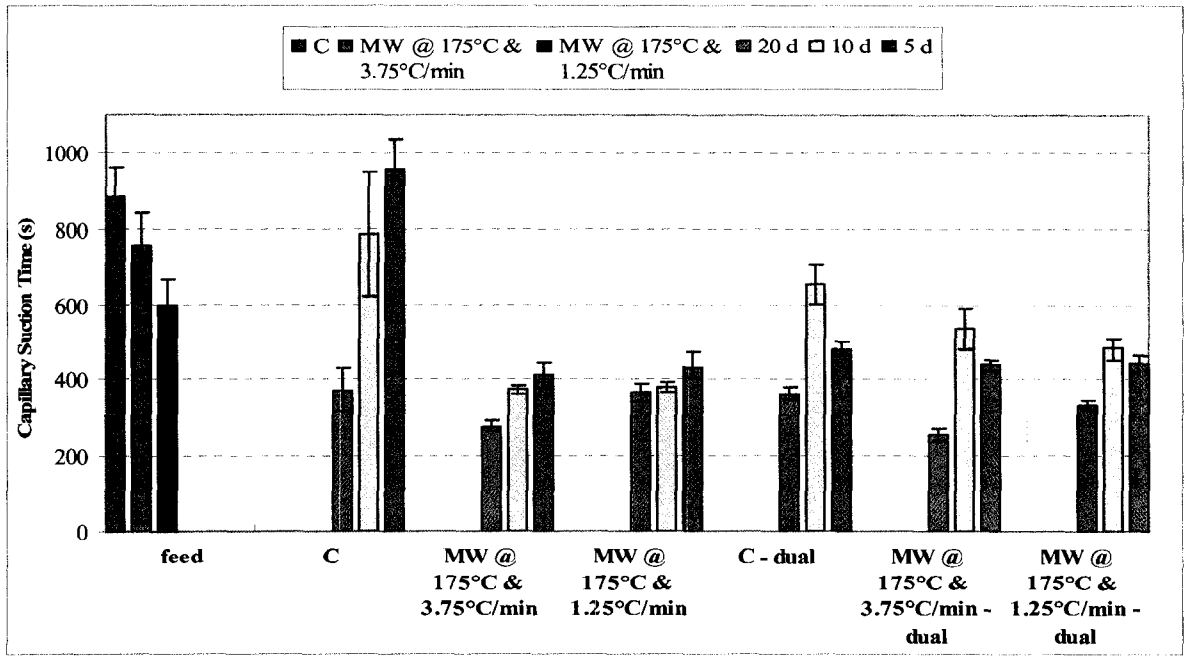

Figure 5.9: Dewaterability data for raw TWAS feed and reactor digestates for various conditions

5.4 DISCUSSION

5.4.1 Effect of MW Pretreatment Temperature

Only 2 studies can be found that evaluate the effect of MW pretreatment of TWAS on semi continuous MAD performance. Both studies are conducted at MW pretreatment temperatures less than boiling point (Park *et al.*, 2004 and Eskicioglu *et al.,* 2007b) and give conflicting results. Eskicioglu *et al.* (2007) pretreated sludge at 50 and 96°C by MW and water bath to compare conventional heating to MW heating. The results of Eskicioglu *et al.* (2007) showed that there was only a small improvement with MW pretreatment, on daily biogas production when digesters ran at 20 and 10 day SRT. At 5 day SRT digestion of sludge pretreated at 50°C by MW produced 13% more daily biogas than the control and there was a decrease in daily biogas production for the digester fed with sludge pretreated to 96°C with MW. They found that MW pretreatment at 50°C gives better results in terms of biodegradability with semi continuous digesters than that at 96°C. At 10 day SRT, the biogas yield observed for control, digesters fed with sludge pretreated at 50°C and 96°C were calculated as 737.3 ± 43, 815.2 ± 33 and 652.3 ± 23 L biogas/kg VS destroyed, respectively. Conventional thermal pretreatment at this temperature range gave similar results and did not show marked improvement in biogas production.

On the other hand, Park *et al.* (2004) reported more promising results. Biogas yield was improved from 323 ± 28 to 417 ± 46 L biogas/kg VS destroyed at 10 day SRT when

sludge was pretreated with MW to 91°C. Subsequently methane yield also improved from 245 ± 22 to 315 ± 41 L methane/kg VS destroyed. Although these values are very low compared to yields observed in other studies (Eskicioglu *et al.*, 2007; Park *et al.*, 2005 and Nah *et al.*, 2000) their data indicates that with MW pretreatment SRT can be decreased to 8 days without significant decrease in VS removal efficiency. The discrepancy between the two studies may be related to the interaction between MW pretreatment, sludge age and MAD. Eskicioglu *et al.*, (2007) used a young TWAS (5 d SRT) that would have a low accumulation of difficult to biodegrade substances compared to older sludge. Pretreatment is more likely to increase the rate of digestion rather than the extent of VS destruction. The high biogas yields and improvements with shorter SRT support this hypothesis. Unfortunately, Park *et al.* (2004) does not report the sludge age to support this but it might be speculated that this is an older sludge.

In this study biogas yield per kg VS destroyed was found to increase as the SRT decreased even down to 5 days for single stage digestion of MW pretreated sludge. The single stage control digester also produced a slightly higher biogas yield as SRT decreased to 5 days (3.8% improvement). Greatest improvement in biogas yield was observed with digestion of sludge pretreated at high MW intensity and 5 day SRT which showed 52% greater biogas yield than its single stage control digester and its biogas yield was 58% more than what was observed with single stage digester operated at 20 day SRT. Methane yield for the single stage control digester decreased slightly as SRT decreased from 20 to 10 and 5 d as 451.6 ± 33.4, 444.2 ± 45.7 and 429.4 ± 53.8 L methane/kg VS destroyed, respectively. For sludge pretreated at high MW intensity as

SRT time decreased methane yield increased however for sludge pretreated at low MW intensity methane yield increased by 17% when SRT decreased from 20 to 10 days but it decreased by 4% when SRT further decreased from 10 to 5 days.

5.4.2 Effect of MW Intensity

From batch studies (Toreci *et al.,* 2007) it was observed that lowering MW intensity from 7.5 to 3.75°C/min improved TWAS solubility however it increased the acute inhibition observed in the early stages of BMP assays. A similar trend was observed during semi continuous digestion. Although sCOD/tCOD ratios increased as MW intensity decreased from 3.75 to 1.25°C/min, less biogas production was observed for digesters fed with sludge pretreated with low MW intensity. Very similar trends were observed for VS, TS, sCOD and tCOD removal efficiency for these two MW intensities. It is possible that with young sludge extended exposure to MW irradiation and high temperatures with low MW intensities produces more refractory or uncommon compounds that microbes have difficulty degrading or are slightly inhibitory. The exact reasons and compounds involved are likely complicated and are presently unknown, respectively.

The greatest improvement in biogas production was observed for single stage MAD with MW pretreatment at high MW intensity and 5 day SRT. This configuration and operational condition produced 83% more biogas than the single stage control digester whereas digestion with MW pretreatment at low MW intensity only produced 47% improvement over the control.

5.4.3 Comparison of Single and Dual Stage Digestion

Dual stage digester with untreated TWAS produced more biogas than single stages at all SRTs. Biogas yield as well as methane composition were also slightly higher for dual stage compare to single stage for untreated sludge. However, for MW pretreated sludge digestion the dual stage configuration did not perform as well as the single stage reactors treating the MW pretreated TWAS at low SRTs. At 5 day SRT, the secondary reactor of the dual stage system had a 3 day HRT which caused problems at the high OLR and was especially evident for low MW intensity pretreated TWAS. At a 5 day SRT, improvement in daily biogas production over the single stage control digester for the dual stage control (untreated sludge) and the one with pretreated sludge at high MW intensity was 28 and 42% respectively, which were both lower than what was recorded for the single sludge digester with MW pretreatment (both for high and low MW intensities). It is apparent that the overall 5 day SRT (2 d + 3d) was too short for dual stage digestion. When dual stage 10 day SRT results are compared to single stage digesters it was seen that both process configurations performed very similar to each other. Therefore it can be concluded that dual stage mesophilic digesters as operated in this study do not offer any advantages over single stage digestion when TWAS is pretreated with MW irradiation.

5.5 CONCLUSIONS

High temperature (T=175°C) MW pretreatment of TWAS with different MW intensities (3.75 and 1.25°C/min) prior to semi-continuous MAD and performance of single and

dual stage digesters were compared to control (untreated sludge) systems. The following conclusions can be drawn:

High temperature MW pretreatment with 3.75°C/min MW intensity improved TWAS solubilization but did not enhance the extent of digestion with 20 day SRT. However application of high temperature MW pretreatment has potential benefits for decreasing SRT. It was possible to decrease SRT to 10 days with moderate decrease in VS removal from 49.9 to 43.4% while improving biogas yield from 676 to 839.6 L biogas/ kg VS destroyed. Further decreasing SRT to 5 days improved daily biogas production 83% compared to control digester and increased biogas production per amount of VS added from 177.7 to 333.1 L biogas/ kg VS added which was 93% of what was observed with control digester when it was operated at 20 day SRT (359.2 L biogas/ kg VS added). The effluent VS and sCOD concentrations for the control at 20 day SRT were 1.04 ± 0.16 mg/L and 389 ± 7 mg/L, respectively. The VS concentrations in the effluent from digesters with MW pretreatment for 10 and 5 day SRT were 1.12 ± 0.04 and 1.28 ± 0.06 mg/L, and sCOD concentrations of those were 772 ± 81 and 1281 ± 36 mg/L, respectively.

Low MW intensity increased the solubilization of TWAS; however, it had a negative effect on mesophilic anaerobic digestion.

Dual stage digestion showed slight improvement over single stage mesophilic digestion when no MW pretreatment was applied. On the other hand, with MW pretreatment single stage digesters preformed better than dual stage digesters.

MW pretreatment decreased capillary suction time of digestate considerably in all digester configurations and more improvement in digestates from MW pretreated digesters compared to untreated sludge control systems at all SRTs.

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CHAPTER 6:

Effect of High Temperature Microwave TWAS Pretreatment on Distribution and Digestion of Soluble Organic Matter

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6.1 INTRODUCTION

Limitations of waste activated sludge (WAS) stabilization are due to large macromolecules associated with bacterial cells present in WAS. It is known that extracellular polymeric substances (EPS) which are macromolecular organic compounds give structure and functional integrity to sludge (Flemming and Wingender, 2001). The main components of EPS are proteins and sugars. Exocellular protein concentration is reported to be greater than exocellular sugar concentration (Higgins and Novak, 1997). It is reported that 70 to 80% of EPS is composed of proteins and sugars and the remaining components attributed to humic compounds, uronic and nucleic acids and lipids (Dignac *et al.,* 1998). Main types of monosaccharides in EPS are found to be hexoses (found in pure bacterial cultures), pentoses (due to cell lysis) and glucose (can originate from wastewater glucose polymers such as cellulose) (Dignac *et al.,* 1998). Proteins can originate from several sources: exoenzymes

excreted into the floc in large quantities (Frolund *et al.,* 1995) and/or from wastewater compounds and/or due to cell lysis (Dignac *et al.,* 1998). Lectin was found to be a typical protein type extracted from several activated sludge systems (Higgins and Novak, 1997). The physical model for bioflocculation proposed by Higgins and Novak (1997) suggests that lectins play an important role in binding polysaccharides through their multiple binding sites. Lectins have the ability to bind to each other by divalent cations and polysaccharides act as bridges between adjacent lectins to form a stable biopolymer network.

EPS in activated sludge are highly hydrated and are a main obstruction to sludge dewaterability. Two main mechanisms were suggested by Flemming (1996) for water binding; electrostatic interactions and hydrogen bonds (Neyens *et al.,* 2004). Electrostatic interactions occur between permanent dipoles of water molecules and permanent dipoles of functional groups such as hydroxyl and carboxylate groups. Water molecules also can bind by hydrogen bonds to hydroxyl groups particularly in polysaccharides. The tertiary structure of proteins is supported by hydrogen bonds.

Disruption or destabilizaton of polymers as well as EPS is an important step for degradation (Park *et al.,* 2006). Dewaterability can also be enhanced by disrupting EPS and the divalent cation network (Ormeci and Vesilind, 2000). Many pretreatment methods have been studied to solubilize materials from intracellular and/or extracellular matrix. Some of these methods are; thermal (Jolis *et al.,* 2004 and Skiadas *et al.,* 2005); mechanical (Kopp *et al.,* 1997 and Muller *et al.,* 1998); ultrasonic (Thiem *et al.,* 2001 and Barber, 2005); chemical (Knezevic *et al.,* 1995 and Navia *et al.,* 2002) and ozonation (Goel *et al.,* 2003 and Scheminski *et al.,* 2000).

Microwave (MW) pretreatment is a recent method used in sludge solubilization as a pretreatment to digestion. Due to the dipole orientation that occurs during MW treatment MWs have an additional athermal effect in addition to the thermal effect, which results in an increase in medium temperature (Coelho *et al.,* 2008). This athermal effect causes possible breakage of hydrogen bonds that are supporting the tertiary structure of proteins and as a result leads to disintegration of floc matrix (Loupy 2002). Studies done on MW pretreatment at temperatures above the boiling point showed that solubilization can be increased significantly as pretreatment temperature increased (Toreci *et al.,* 2008). Increasing exposure time by decreasing MW intensity (from 7.5 to 3.75°C/min) also showed positive impact on solubilization and anaerobic digestion (AD) stabilization. However, from semi-continuous AD experiments it was found that further lowering MW intensity (from 3.75 to 1.25°C/min) improved solubilization slightly but AD efficiency decreased with low MW intensity (Toreci *et al.,* 2009). This suggests that the athermal effect plays role that affects the characteristics of organics that are solubilized due to MW pretreatment and there must be an optimum intensity to achieve the highest solubility with the highest biodegradability.

Molecular weights (Mws) of soluble compounds originated from intermediate or end products of substrate degradation and cell lysis vary over a wide range between 1 to 100,00 kDa (sizes smaller than 0.45μm) (Boero *et al.,* 1996). Information on molecular weight distributions of organics in wastes and effect of treatments on Mw distribution are limited. Also, results obtained by different researchers are difficult to compare, as no standardized procedures were followed for determination of Mw distribution. There are two commonly used methods for size distribution which are; continuous distributions by gel permeation

chromatography (GPC) and discrete distributions using ultrafiltration (UF) membranes. Both methods have some disadvantages (Logan and Jiang, 1990). For GPC analysis, there should be no chemical interactions between column packing and solvent to prevent changes in travel time through the column. It was observed that some compounds move more rapidly than their calibration standards which causes overestimation of component Mws (Knuutinen *et al.,* 1988 and Logan and Jiang, 1990). Inversely, other compounds may be delayed in the column due to adsorption or electrostatic interaction with the packing material (Miles and Brezonik, 1983 and Logan and Jiang, 1990). Another disadvantage of GPC is that it requires evaporation or freeze-drying to concentrate samples which may alter their size distribution.

In UF, several controllable factors affect transportation of organics through membranes such as, membrane pore size distribution, cell pressure, solution pH, water temperature, ionic strength, size, shape and affinity of molecules. The most important advantage of UF over GPC is that the size distributions can be obtained by using a larger sample volume which enables further characterization with recovered samples. UF can be operated in parallel or in series. Parallel processing requires less time since they can be run simultaneously and it was observed that size distribution would have smaller errors than serial processing (Logan and Jiang, 1990). On the other hand, membrane clogging would be less problematic for smaller Mw cutoffs when UF is performed in series.

It was concluded by Urano *et al.* (1980) that GPC is a better technique for separation of organic pollutants; however, it cannot be used for fractioning organics in water solely by Mw (Barber and Stuckey, 1999).

This paper focuses on biodegradability and rate of degradation of soluble organics in pretreated TWAS for different Mw intervals. The Mw distribution of soluble organics was determined by using the in series UF method. The effect of MW pretreatment temperature and MW intensity was compared to an untreated sample.

6.2 EXPERIMENTAL SETUP

TWAS was obtained from the local municipal wastewater treatment center, ROPEC (Robert O. Pickard Environmental Center) located in Gloucester, ON, Canada. Average sludge retention time (SRT) of conventional aerobic activated sludge in this facility is 5 days and average TWAS concentration was 5.6% with 68% volatile solids (VS). Inoculum for AD was also obtained from ROPEC where primary sludge and TWAS are blended in a 42:58 (v/v) ratio prior to mesophilic AD. Inoculum was taken from the effluent line of the anaerobic digester which has an average SRT of 15-20 days. Inoculum was acclimatized to TWAS prior to biochemical methane potential (BMP) assay by feeding 10 L of anaerobic semi-continuous reactor with TWAS MW pretreated at 175°C. The seed reactor was run more than a year at approximately 20 d SRT (Ekama *et al.*, 1986).

MW pretreatment was performed using a Mars 5© (MW Accelerated Reaction System; CEM Corporation) MW oven with 2450 MHz frequency and variable power supply up to 1200 W ± 15% MW energy at full capacity. The Mars 5© is designed to ensure complete MW penetration of sample vessels which can be operated up to 250°C and 3.45 kPa. MW intensity is controlled by adjusting the ramp time to reach the set temperature.

Previously, it was observed that increasing pretreatment temperature (PTT) improved the solubilization and 175°C PTT showed the best results in terms of enhancing TWAS solubilization and biogas production (Toreci *et al.,* 2007). It was also observed that a low (3.75°C/min) MW intensity had more impact on TWAS solubilization than high (7.5°C/min) MW intensity. However, additional semi-continuous AD experiments showed that lowering MW intensity from 3.75 to 1.25°C/min had a negative effect on AD performance at low SRTs (Toreci *et al.,* 2009). These results indicate that the end product of MW solubilization resulting in break down of TWAS organics into smaller molecules is affected by MW intensity and the combination of thermal and athermal effects. Concomitantly, the following operating conditions were selected to examine the organics distribution in the soluble fractionation (Table 6.1) of MW pretreated TWAS (5.6% TS)

Table 6.1: Variables and their levels used for soluble fractioning

Variables → / **Levels ↓**	**Temperature (°C)**	**Temperature Change Rate (°C/min)**
1	110	3.75
2	175	7.5

The time required for samples to be heated from room temperature to 110 and 175°C with 3.75°C/min MW intensity and to 175°C with 1.25°C/min MW intensity were 23, 40 and 120 minutes, respectively. The MW temperature hold time was one minute and samples were cooled back to room temperature by placing in an ice bath.

Untreated control samples and pretreated samples were centrifuged at 5856 relative centrifugal force (RCF) for 20 minutes to recover the supernatant. Supernatant were then initially filtered through Durapore membrane filters with 5 μm pore size (Millipore, SVLP04700) to discard any biomass residual remaining in the soluble phase. Due to clogging problems supernatant filtered through 5 μm were diluted with Milli-Q water with a ratio of 4.19:1. Initially filtered supernatants (5 μm pore size) were then subjected to a secondary filtration through 0.45 μm pore size disc filters (GN-6 Metricel S-Pack membrane). Prior to UF soluble chemical oxygen demand (sCOD), soluble sugar, soluble protein and total volatile fatty acid (TVFA) characterization of untreated and pretreated samples were determined for Mw materials that were smaller than 5 and 0.45μm.

sCOD measurements were conducted according to Standard Method's colorimetric method 5220C using a Coleman Perkin-Elmer model 295 spectrophotometer (APHA, 1995). The method of Bradford (Bradford, 1976) was used for the determination of soluble protein concentration while for soluble sugar concentration; the colorimetric method described by Dubois et al. (1956) was used. HP 5840A gas chromatograph with glass Chromosorb 101 column (Chromatographic Specialties Inc., Brockville, ON, Canada, mesh size: 80/100, column length × ID: 304.8 cm × 2.1 mm) and a flame ionization detector were used for TVFA determination according to van Huyssteen (1967).

For UF of material less than 0.45 μm, Amicon model 8400 stirred cells (Amicon Corp., MA, USA) with a 400 mL reservoir using high recovery, low organic adsorption hydrophobic membranes (Millipore, MA, USA) were used. Supernatants filtered through 0.45 μm were

ultra-filtered from higher Mw cutoff to lower. Mw cutoffs used for UF were 300 kDa (PES300), 100 kDa (YM100), 10 kDa (YM10) and 1 kDa (YM1) (Figure 6.1).

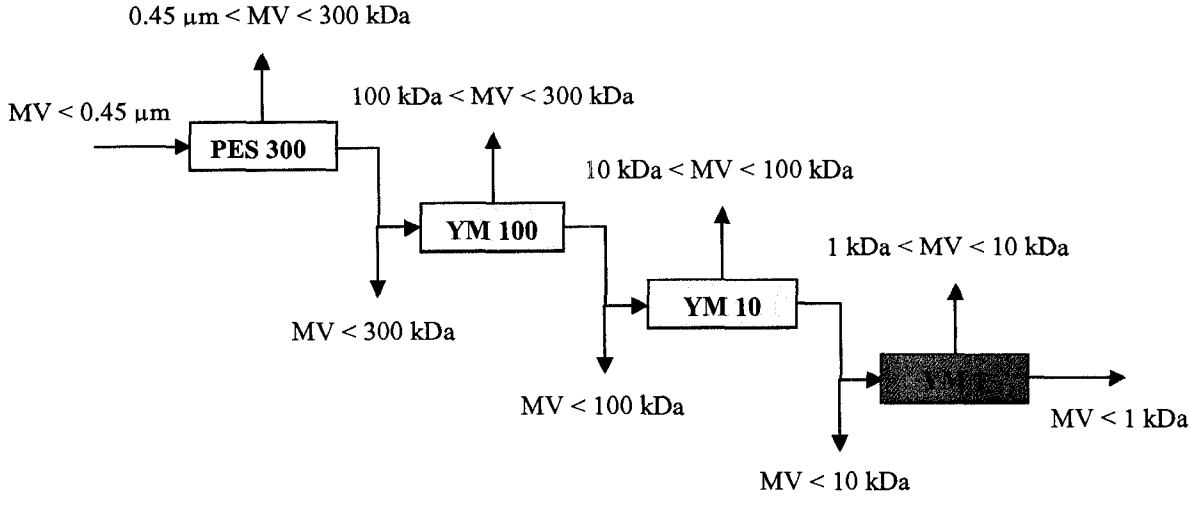


Figure 6.1: Schematic diagram of UF in series for AMW determination.

Prior to UF, membranes were soaked with room temperature Milli-Q water for an hour by changing the water three times. Rinsed membranes were mounted in the UF cell and rinsed further by filtering Milli-Q water for at least 5 minutes. The cells were pressured with nitrogen gas to 10 psi for PES300 and YM100 and 30 psi for YM10 and YM1. After rinsing, 300 mL of supernatant was loaded to a cell for UF where 270 mL of effluent was allowed to pass through the filter and remaining 30 mL was collected as retentate after depressurizing the cell. This procedure was repeated until sufficient amounts of permeates and retentates were collected for each sample and for each Mw cutoffs. Soluble organics in terms of sCOD, soluble protein, soluble sugar and TVFA concentrations of each permeates and retentates of untreated and MW pretreated samples were measured.

Biochemical methane potential (BMP) assays were performed for biodegradability analysis of each of the fractions including UF permeates and retentates. For the BMP assay, 125 mL serum bottles with butyl rubber stoppers were used as reactors. In each reactor 70 mL of sample (UF permeates and retentates) and 15 mL acclimatized inoculum were added. An equal volume mixture of potassium and sodium bicarbonate was added to provide 4000 mg/L of bicarbonate alkalinity. Nitrogen gas was bubbled into the reactors to prevent air exposure before sealing the reactors. BMP tests were performed in duplicate at 35 ± 1°C on a New Brunswick rotary shaker at a speed of 95 rpm (total of 80 reactors). Biogas composition was determined with a HP 5710A GC with Porapak T packed column (Chromatographic Specialties Inc., Brockville, ON, Canada, mesh size: 50/80, column length × OD: 304.8 cm × 6.35 mm) and thermal conductivity detector according to Ackman, (1972).

6.3 RESULTS

6.3.1 Characterisation of colloidal and soluble matter

Prior to the BMP assay, SCOD, soluble protein, soluble sugar and TVFA concentration profiles for the different Mw intervals were conducted to observe the effect of MW temperature as well as MW intensity on the extent of solubilization. Soluble organics were grouped in to two categories: the first is defined as the colloidal organics that are filterable through 5 μm but are larger than 0.45 μm. The second group is truly soluble organics which are smaller than 0.45 μm. Samples filtered through 5 μm filter includes the colloidal and true soluble organics. By difference, samples filtered through 5 μm and 0.45 μm pores allow

determination of the colloidal matter. Samples filtered through 5 μm and 0.45 μm pores showed very similar characteristics (Figures 6.2 and 6.3). In terms of sCOD concentration, all MW pretreated TWAS filtered through 0.45 μm were slightly less than the concentrations that filtered through 5 μm (Figure 6.2). This indicates that in the original untreated TWAS the majority of the soluble organic matter was truly soluble. With MW pretreatment solubilization increases the colloidal matter in the soluble phase (by difference). However this difference effect was not observed for soluble sugar concentration which indicates that their contribution to sCOD was all true soluble material (Figure 6.3). Soluble protein is the other main contributor to sCOD. At high MW temperature, soluble protein is composed of both colloidal and true soluble protein especially evident with high MW intensity at 175°C. It can be concluded although high temperature MW pretreatment at 175°C with high MW intensity improves both sugar and protein solubilization, the protein contribution to colloidal sCOD is greater than that of the sugars.

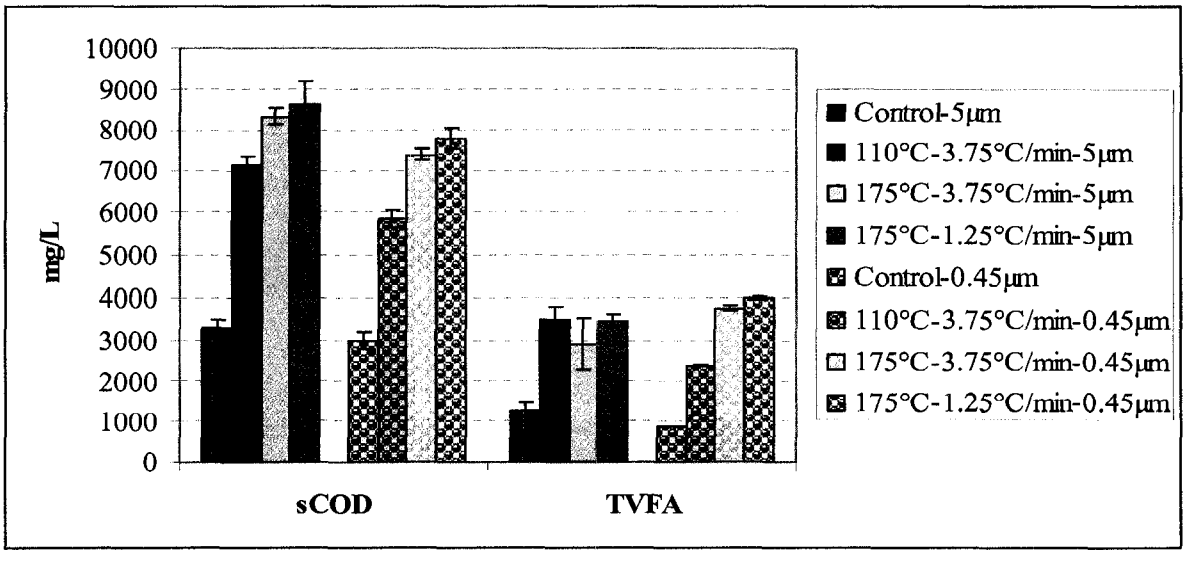


Figure 6.2: sCOD and TVFA concentrations of untreated control and pretreated TWAS filtered from 5 and 0.45 μm

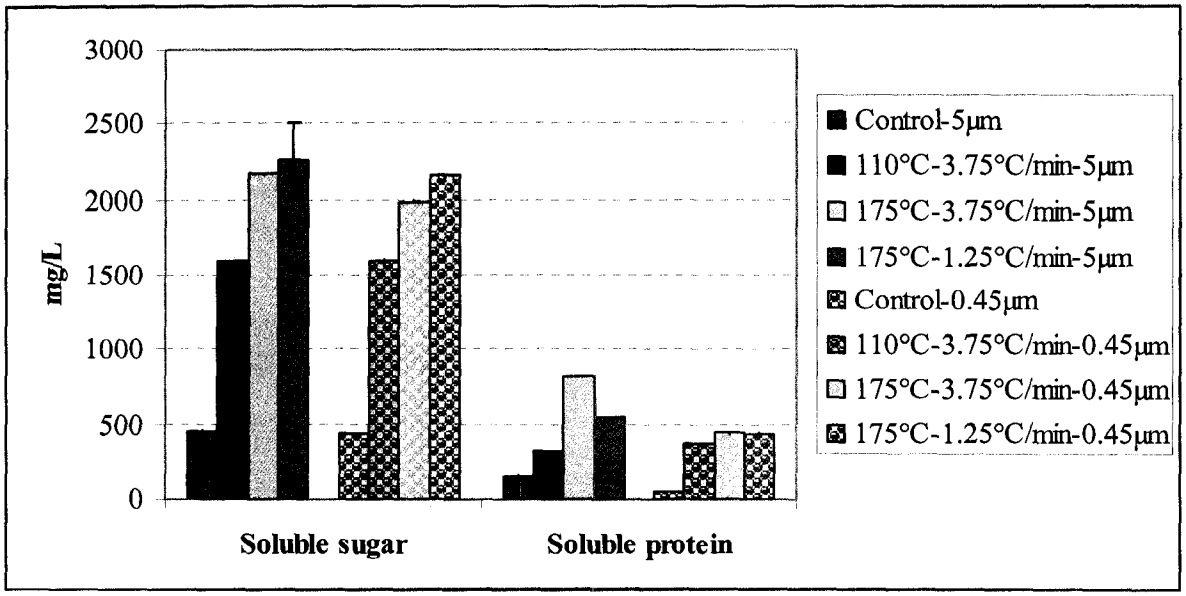


Figure 6.3: Soluble sugar and protein concentrations of untreated control and pretreated TWAS filtered from 5 and 0.45 µm

The changes in the soluble part of TWAS after MW treatments at different conditions compared to untreated control as well as the percent distribution of soluble components based on Mw are shown in Table 6.2. Initial sCOD concentration determinations show that an increase in MW temperature to 110 and 175°C increases the organic matter concentration in the soluble phase by 95 and 146% relative to the control respectively (Figure 6.4). However, TWAS exposed to the same pretreatment temperature (175°C) but lower MW intensity (3.75 to 1.25°C/min) showed only a marginal increase in sCOD relative to the control (146 vs. 161% respectively). These results confirm previously reported MW intensity experimental data in terms of sCOD, TVFA and sugar concentrations (Toreci *et al,* 2008). It was reported that decreasing MW intensity from 7.5 to 3.75°C/min dramatically improved sCOD, TVFA, sugar concentrations and soluble protein concentration however further decreases in MW intensity to 1.25°C/min did not show significant improvement in

solubilization of TWAS suspended solids. These results indicate that solubilization is related both to temperature of pretreatment and MW exposure time which is related to MW intensity.

The extent and degree of MW solubilization in terms of Mw distribution is important if we wish to optimize MW pretreatment and understand any relationships that may exist between TWAS solubilization and TWAS stabilization via AD. Characterization of the TWAS supernatant and Mw distribution of soluble components less than 0.45μm shows that MW pretreatment disrupts the floc matrix and enables extracellular polymeric substances (EPS) and/or intracellular polymers to breakdown and release in to the soluble phase. Fractioning and comparing the supernatants of the untreated control and MW pretreated TWAS provides a much better understanding of the effects of MW pretreatment conditions (temperature and MW intensity) on the disruption of TWAS at the molecular level. Figure 6.5 shows the distribution of sCOD at 5 different Mw intervals. Initially, 55% of sCOD of the control was in the interval of Mw < 1 kDa and 18% of sCOD was in the interval of Mw > 300 kDa. Introducing MW pretreatment increased the concentration and mass of sCOD in all intervals however the Mw distribution profile showed variations for different MW treatment conditions. MW pretreatment at 110°C with 3.75 °C/min resulted in a greater proportion of larger sCOD in the Mw > 300 kDa. sCOD percentages for largest and smallest Mw intervals were 32.5 and 44%, compared with the initial values of 18 and 55%, respectively. Further increase in MW temperature to 175°C at the same MW intensity produced a greater amount sCOD in the system and the percentages for Mw > 300 kDa and Mw < 1 kDa became 37 and 21%, respectively. Decrease in MW intensity for the same temperature (175°C) resulted

in only a small increase in the mass of sCOD produced from the TWAS but the degree of solubilization was also increased as a larger portion of the organics were converted into smaller components since 59% of sCOD accumulated in the smallest Mw < 1 kDa interval with a more even distribution for the other interval fractions. The impact of solubilization fractions on BMP is not known but will also be accessed in this study.

In terms of TVFA distribution, control and sample pretreated at 110°C showed very similar trends; 68 and 76% for Mw < 1 kDa and 11 and 16% for Mw > 300 kDa, respectively (Figure 6.6). Increasing MW pretreatment temperature from 110 to 175°C at 3.75°C/min MW intensity produced more TVFA and the Mw distribution shifted towards the larger Mw intervals. However decreasing the MW intensity to 1.25°C/min moved the Mw distribution back closer to the control and sample pretreated at 110°C with 72 % for Mw < 1 and 18% for Mw > 300 kDa. These results are in line with the sCOD findings and tend to indicate that increasing MW temperature to 175°C at 3.75°C/min improves the release of VFAs from the floc matrix but is not sufficient to breakdown bonding interactions between TVFAs and other floc constituents into smaller individual components.

Table 6.1: Characteristics of untreated and MW treated TWAS at different apparent molecular weight intervals by using UF

		Before UF (mg./L)	After UF* (mg/L)	Mw<1 kDa (%)	1 kDa<Mw<10 kDa (%)	10 kDa<Mw<100 kDa (%)	100 kDa<Mw<300 kDa (%)	Mw>300 kDa (%)
sCOD	Control	576±39	391±10	55.1±1.5	5.9±0.1	9.7±0.0	11.4±0.2	17.9±1.8
	110°C	1125±39	1388±25	44.3±0.4	7.3±0.1	8.7±.01	7.2±0.4	32.5±0.6
	175°C-high intensity	1417±108	1314±29	20.9±0.3	18.4±0.0	11.5±0.3	12.1±0.2	37.1±0.2
	175°C- low intensity	1506±48	1485±36	59.4±0.7	9.7±0.3	9.6±0.3	13.8±0.1	7.6±0.1
Protein	Control	9.5±0.5	10.5±0.1	45.0±0.9	11.0±0.1	10.5±0.2	7.8±0.3	25.7±0.4
	110°C	70.5±0.4	64.5±1.1	9.7±0.3	17.2±0.2	17.1±0.1	9.6±0.1	46.3±0.0
	175°C-high intensity	84.9±1.9	85.8±2.8	18.1±1.7	20.5±0.4	9.1±0.1	13.3±0.4	39.0±1.0
	175°C- low intensity	82.9±2.7	75.6±1.2	10.5±0.4	13.9±0.3	14.5±0.1	31.0±0.3	30.1±0.5
Sugar	Control	83.9±0.7	33.3±0.6	2.9±0.9	12.1±0.1	23.3±0.2	7.1±0.4	54.7±1.3
	110°C	307.7±2.6	205±6.8	7.3±0.3	9.0±0.4	19.4±0.7	6.3±0.1	58.0±1.5
	175°C-high intensity	382.9±1.7	305.3±8.2	9.1±0.3	11.7±0.7	18.7±0.7	10.8±0.3	49.6±0.6
	175°C- low intensity	414.5±0.4	310.8±9.6	7.1±0.3	9.4±0.0	18.6±0.3	15.5±2.6	52.6±1.4
TVFA†	Control	166.4±0.0	170.7±3.7	10.8±0.1	9.7±0.0	7.2±0.0	4.4±0.0	67.8±0.1
	110°C	459.0±6.2	416.2±2.3	16.0±0.1	6.6±0.2	0.8±0.3	0.5±0.0	76.1±0.4
	175°C-high intensity	723.5±14.0	488.4±23.0	48.2±40.8	24.4±0.5	2.4±0.6	1.4±0.1	23.7±0.5
	175°C- low intensity	769.4±8.0	548.1±5.8	18.2±0.1	8.8±0.6	0.4±0.2	0.2±0.1	72.4±0.7

*Sum of 5 apparent molecular weight fractions after UF.

†Sum of acetic acid, propionic acid and butyric acid concentrations.

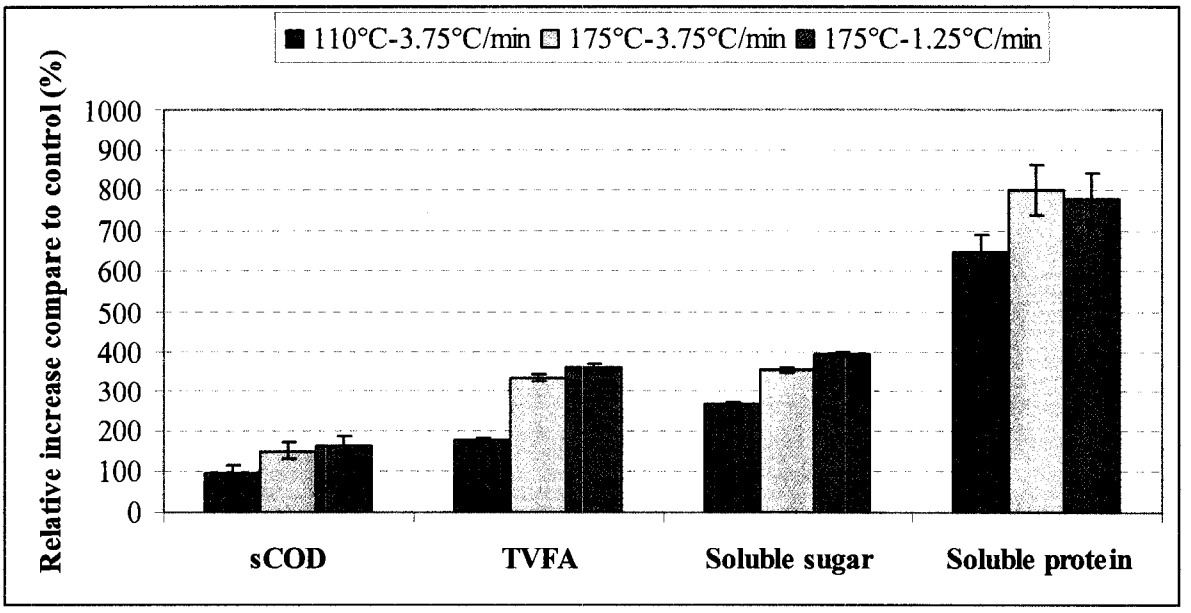


Figure 6.4: MW pretreatment effect on supernatant characterisation.

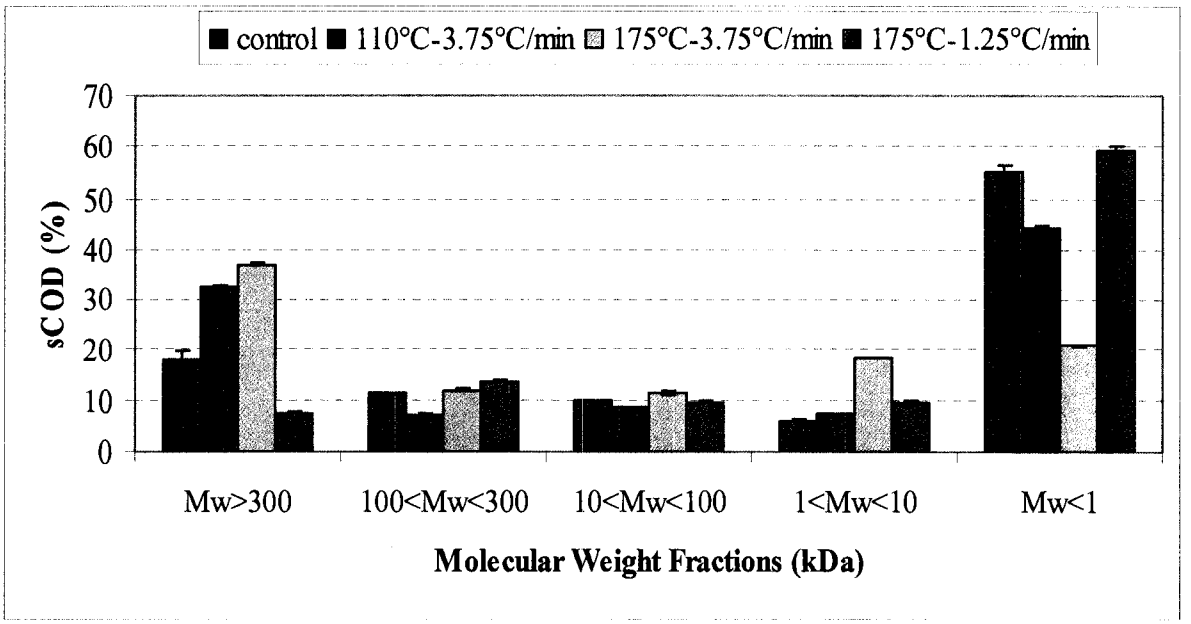


Figure 6.5: sCOD % (w/w) distribution for untreated control and MW pretreated samples

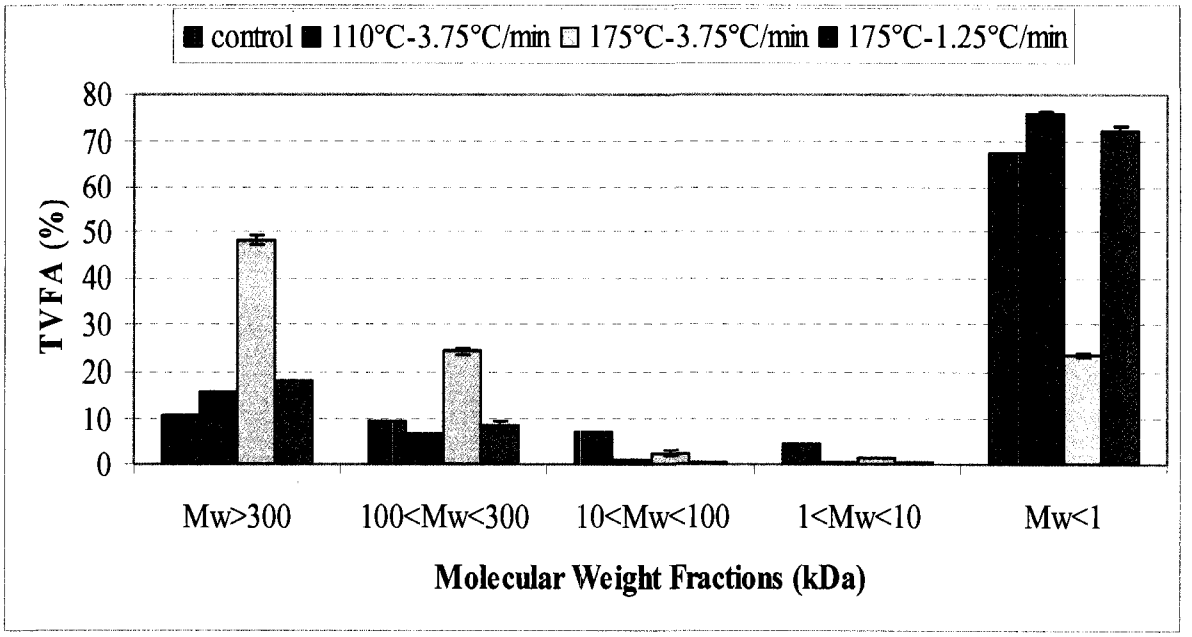


Figure 6.6: TVFA % (w/w) distribution for untreated control and MW pretreated samples

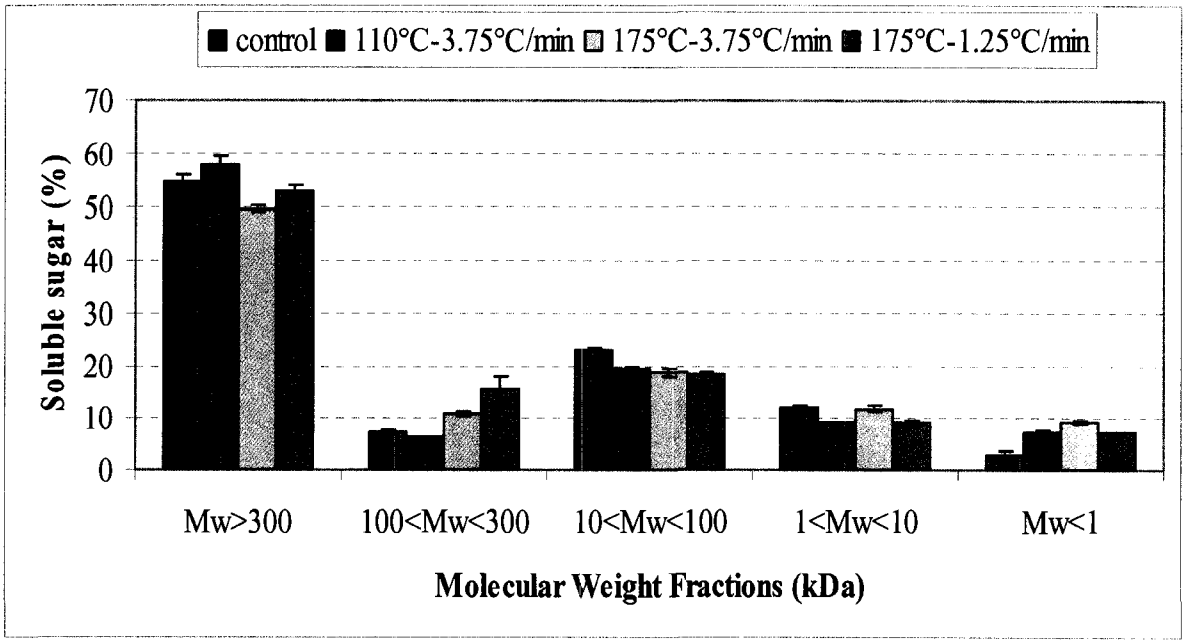


Figure 6.7: Soluble sugar % (w/w) distribution for untreated control and MW pretreated samples

For all MW pretreated samples the mass of sugar released into the soluble phase increased substantially with increases of between 267 and 394% compared to the control. As with sCOD, similar pretreatment temperature (175°C) but decreased MW intensity from 3.75 to 1.25°C/min showed only a marginal increase in sugar relative to the control (356 vs. 394% respectively) (Table 6.2, Figure 6.4). For all MW pretreated samples the Mw distribution profile of the sugar released into the soluble phase was very similar to that of untreated TWAS despite the increase in the amount of sugar solubilized through pretreatment (Figure 6.7). It was observed that more than 50% of soluble sugar is in the range of Mw > 300 kDa. The interval which contains the second most soluble sugar is Mw between 10 and 100 kDa. These results would tend to indicate that the sugars released in to solution were larger di-, tri- and polysaccharides resulting from insufficient pretreatment or from some type of re-polymerization reactions from MW over treatment.

Soluble protein concentration with MW pretreatment increased in the range of 642 and 794% compare to control (Figure 6.8). Soluble protein was determined to be 45% in the smallest and 26% in the largest Mw interval for untreated TWAS. Pretreating samples to 110 with 3.75°C/min increased the amount of soluble protein in all intervals and increased the percentage at Mw > 300 kDa to 46%. Further MW treatment to 175°C with the same MW intensity increased the amount of soluble protein in all intervals as well as hydrolysed larger molecules into smaller ones. Although the soluble protein concentration and mass difference between high and low MW intensity at 175°C was very similar, it was observed that low MW intensity distribute proteins more evenly between Mw > 300 kDa and 100 kDa

< Mw < 300 kDa than high MW intensity which may indicate further degradation of proteins or lysis of cell walls.

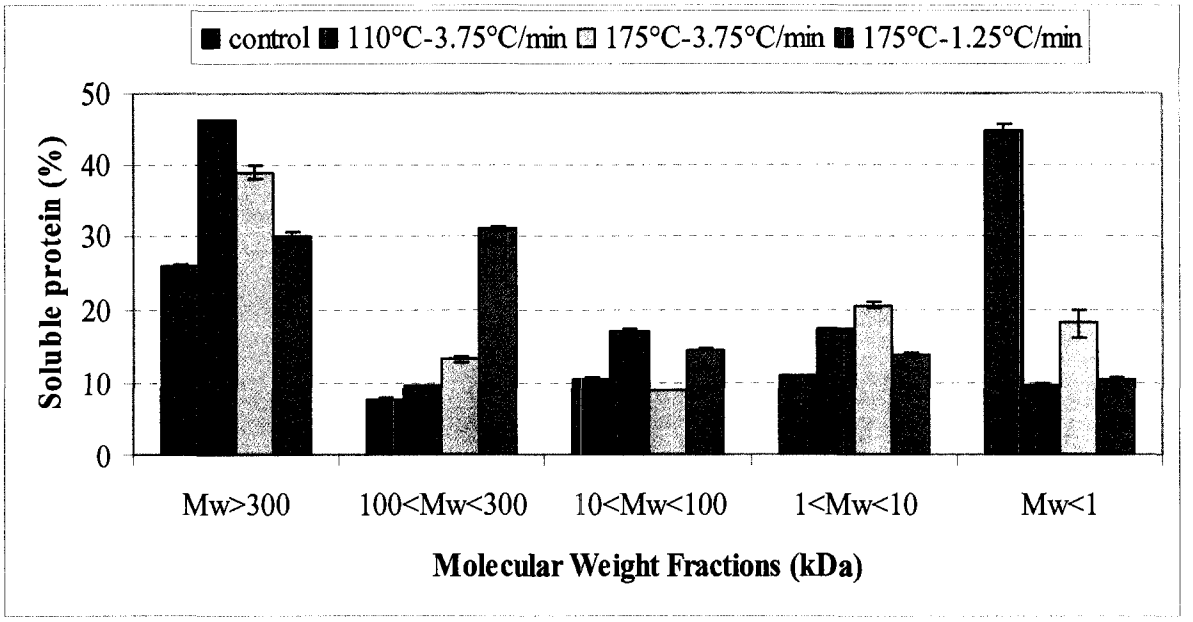


Figure 6.8: Soluble protein % (w/w) distribution for untreated control and MW pretreated samples

It can be concluded from the Mw distribution of soluble organics that both MW temperature and MW intensity impact on degree and extent of solubilization of organics and hydrolysing them into their smaller base molecules. Based on the Mw profiles alone it may be hypothesised that a MW pretreatment strategy may be tailored to produce the optimum solubilization conditions to enhance BMP from TWAS. This is discussed in the following sections.

6.3.2 Digestion and kinetics of soluble matter

Permeates and retentates from each apparent Mw cut off UF interval were digested in duplicate with acclimatized mesophilic inoculum. The observed temporal average cumulative biogas productions from each condition with the standard derivations are presented in Figure 6.9.

The anaerobic digestion kinetics of samples from different Mw intervals and MW pretreatment conditions were evaluated by using a first order reaction. The substrate utilization rate, r_s [mg/L] can be expressed by first order reaction as:

$$r_s = \frac{dS}{dt} = -kS \tag{1}$$

where S is the concentration of substrate [mg COD/L] and k is the anaerobic degradation rate constant [d^{-1}]. Integration of this equation generates:

$$S = S_o e^{-kt} \tag{2}$$

In terms of organics removed equation (2) can be rewritten as the following:

$$Y_t = L(1 - e^{-kt}) \tag{3}$$

where Y_t is the organics removed [mg COD/L] at time equal to t and L is the ultimate biodegradable organics [mg COD/L]. The ultimate biodegradability factor for organics (μ_b) in a sample can be found by evaluating the L/S_o value where S_o is the initial COD concentration of the sample. CBP data were used for the calculations of μ and k values. Chi

square (X^2) values were minimized for constant determination and the adequacy of fits were tested by the goodness of fit test in which chi square values found from model fit were compared to critical chi square values with 95% confidence interval. The definition of chi square value is expressed as:

$$X^2 = \sum_{\text{all data points}} \frac{(\text{observed} - \text{estimated expected})^2}{\text{estimated expected}} \tag{4}$$

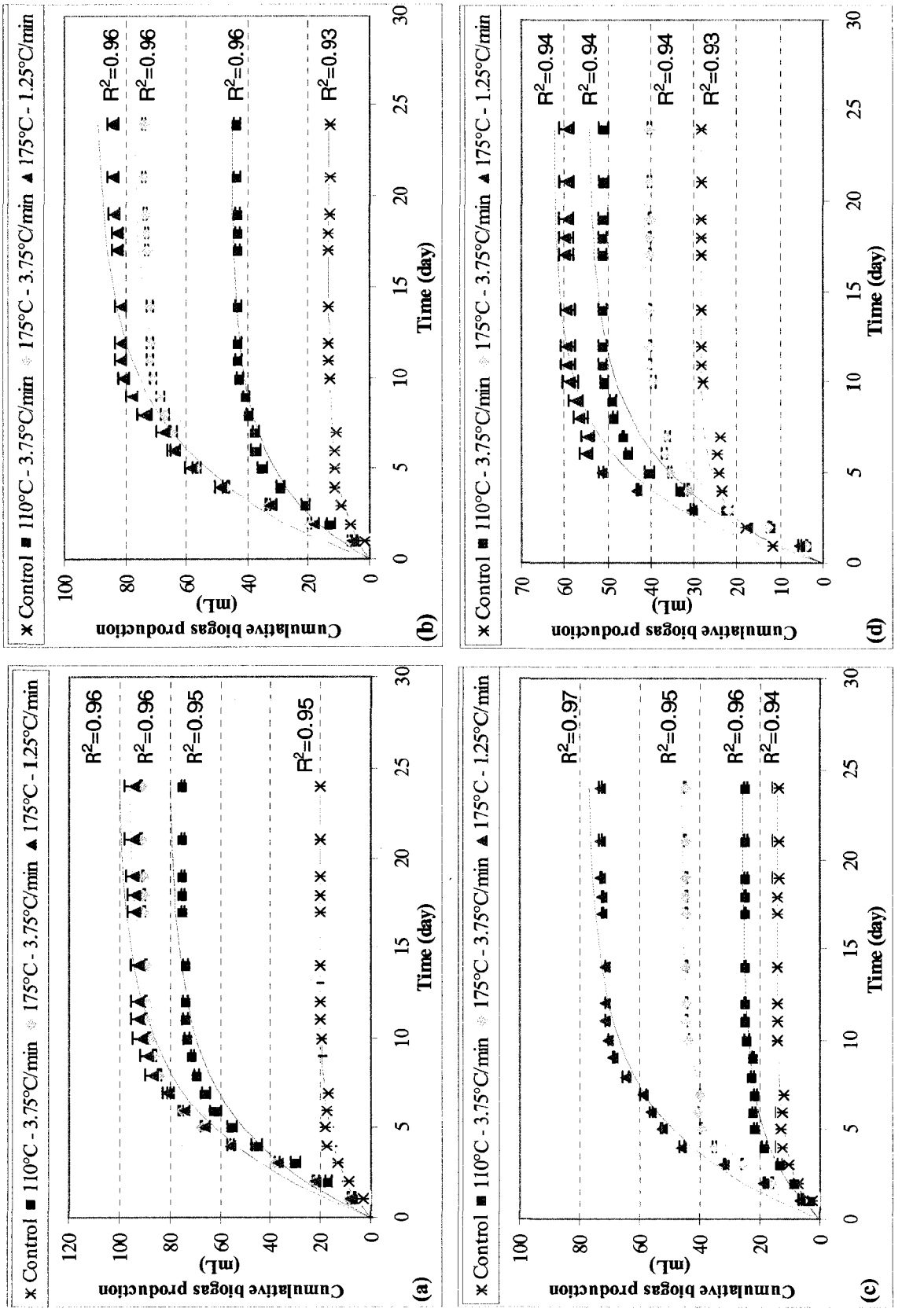
It is important to note that goodness of fit with chi square values only provides information that the general form of the model fits within the selected confidence interval, it does not uniquely determine data probabilities and expected data counts. Adequacy of fit can also be determined by R^2 values as well as visual judgement (Figure 6.9).

$$R^2 = \left(1 - \frac{\sum_{i=1}^{n} (\text{estimatedexpected} - \text{observed})^2}{\sum_{i=1}^{n} (\text{observed} - \text{mean})^2} \right) \tag{5}$$

Nonlinear model fit was computed by using the Microsoft Excel Solver and X^2 values and results of goodness of fit test for 95% confidence interval are tabulated in Table 6.3. 94% of the model parameters found by this method were able to pass the test with a 95% confidence interval, the remaining five batch test results were able to fit with a 99% confidence interval indicating that for these results the variation of values of the constants are larger. Visual comparison between model and observed data as well as R^2 values indicate that it is not possible to say that the fitted model is unsatisfactory (Figure 6.9). Table 6.4 shows the estimated μ and k values as well as experimental μ and cumulative biogas production for

untreated and pretreated samples for different Mw fractions. Data presented are the average values and in parentheses the absolute difference between the mean and duplicate measurements are given. It is important to note that estimated μ values are in the range of 0.91 to 1.0 indicating the goodness of fit for the tail end of the experimental data whereas observed μ shows the biodegradability of organics present in the sample.

The CBP data show that there was little or no lag phase (due to acclimation) and most of the digestion of organics was completed within the first 10 days of the BMP assay (Figure 6.9). It was also observed that the duration of the exponential phase decreased as the size of Mw fractions decreased. This would tend to suggest that as the Mw got smaller there was less biodegradable matter and the material digested was readily biodegradable and was consumed in a shorter period of time


Control 110°C - 3.75°C/min 175°C - 3.75°C/min 175°C - 1.25°C/min
Cumulative biogas production (mL)
Time (day)
(a)
R²=0.96
R²=0.96
R²=0.95
R²=0.95
(b)
R²=0.96
R²=0.96
R²=0.96
R²=0.93
(c)
R²=0.97
R²=0.95
R²=0.96
R²=0.94
(d)
R²=0.94
R²=0.94
R²=0.94
R²=0.93

Control ■ 110°C - 3.75°C/min ● 175°C - 3.75°C/min ▲ 175°C - 1.25°C/min
(e)
Cumulative biogas production (mL)
Time (day)
R²=0.94
R²=0.94
R²=0.94
R²=0.93
(f)
Cumulative biogas production (mL)
Time (day)
R²=0.93
R²=0.90
R²=0.93
R²=0.92
Control ■ 110°C - 3.75°C/min ● 175°C - 3.75°C/min ▲ 175°C - 1.25°C/min
(g)
Cumulative biogas production (mL)
Time (day)
R²=0.97
R²=0.96
R²=0.96
R²=0.98
Control ■ 110°C - 3.75°C/min ● 175°C - 3.75°C/min ▲ 175°C - 1.25°C/min
(h)
Cumulative biogas production (mL)
Time (day)
R²=0.95
R²=0.96
R²=0.95
R²=0.92

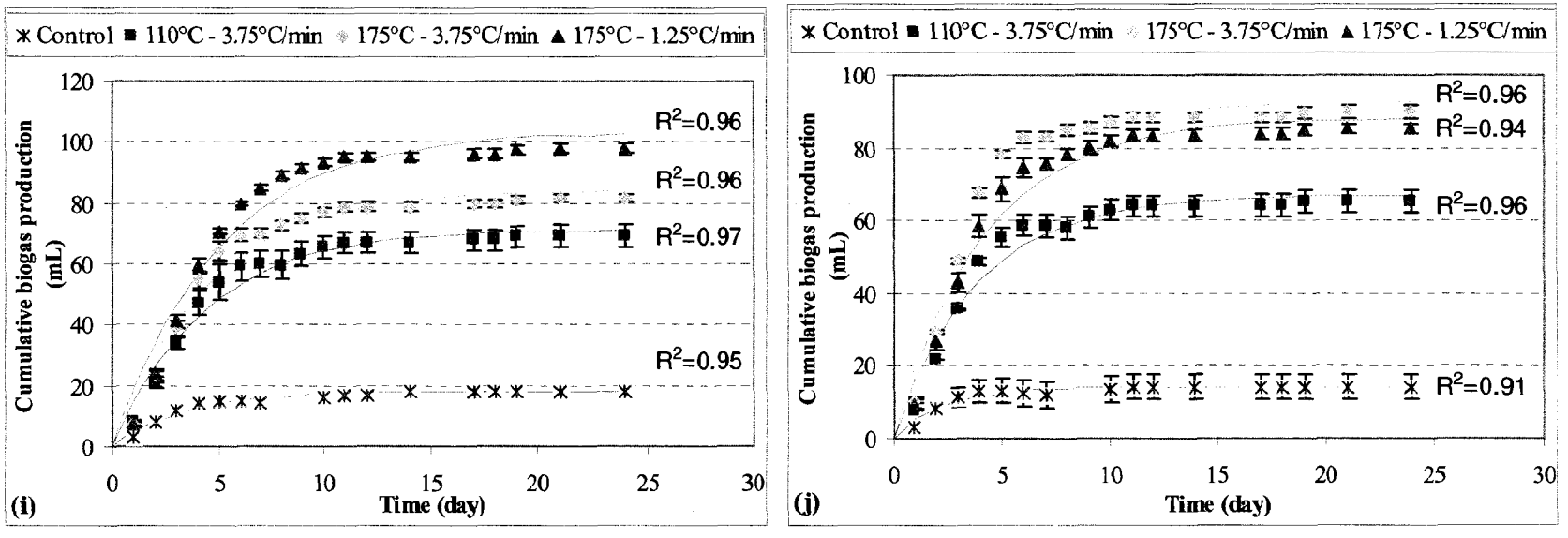


Figure 6.9: Observed (markers) and predicted (lines) cumulative biogas production of control and MW pretreated TWAS supernatant from Mw fractions of (a) Mw < 5 μm; (b) Mw < 0.45μm; (c) Mw < 300 kDa; (d) Mw < 100 kDa; (e) Mw < 10 kDa; (f) Mw < 10 kDa; (g) 300 kDa < Mw < 0.45 μm; (h) 100 kDa < Mw < 300 kDa; (i) 10 kDa < Mw < 100 kDa; (j) 1 kDa < Mw < 10 kDa

Table 6.3: Chi square values (X^2), degree of freedom (DF) and goodness of fit results for 95% confidence interval of each condition

Condition	X^2	DF	Goodness of fit	Condition	X^2	DF	Goodness of fit
C-P5	2.08	13	Accepted	C-P5-d	1.66	13	accepted
110-3.75-P5	11.85	15	Accepted	110-3.75-P5-d	12.34	15	accepted
175-3.75-P5	11.66	15	Accepted	175-3.75-P5-d	12.23	15	accepted
175-1.25-P5	10.84	15	Accepted	175-1.25-P5-d	15.92	15	accepted
C-P0.45	2.52	13	Accepted	C-P0.45-d	1.39	13	accepted
110-3.75-P0.45	4.44	15	Accepted	110-3.75-P0.45-d	5.52	15	accepted
175-3.75-P0.45	10.16	15	Accepted	175-3.75-P0.45-d	10.00	15	accepted
175-1.25-P0.45	11.52	15	Accepted	175-1.25-P0.45-d	14.18	15	accepted
C-P300	1.74	13	Accepted	C-P300-d	1.04	13	accepted
110-3.75-P300	2.70	15	Accepted	110-3.75-P300-d	2.72	15	accepted
175-3.75-P300	5.10	13	Accepted	175-3.75-P300-d	5.11	13	accepted
175-1.25-P300	7.16	15	Accepted	175-1.25-P300-d	8.34	15	accepted
C-P100	0.91	13	Accepted	C-P100-d	-	-	-
110-3.75-P100	9.90	15	Accepted	110-3.75-P100-d	10.83	15	accepted
175-3.75-P100	6.97	13	Accepted	175-3.75-P100-d	6.43	13	accepted
175-1.25-P100	9.48	15	Accepted	175-1.25-P100-d	11.04	15	accepted
C-P10	1.52	13	Accepted	C-P10-d	1.21	13	accepted
110-3.75-P10	5.89	13	Accepted	110-3.75-P10-d	6.27	13	accepted
175-3.75-P10	5.95	13	Accepted	175-3.75-P10-d	5.69	13	accepted
175-1.25-P10	7.01	15	Accepted	175-1.25-P10-d	8.51	15	accepted
C-P1	0.89	13	Accepted	C-P1-d	1.13	13	accepted
110-3.75P1	4.84	13	Accepted	110-3.75P1-d	5.50	13	accepted
175-3.75-P1	1.85	13	Accepted	175-3.75-P1-d	1.76	13	accepted
175-1.25-P1	8.10	13	Accepted	175-1.25-P1-d	9.21	13	accepted
C-R300	1.19	13	Accepted	C-R300-d	1.01	13	accepted
110-3.75-R300	28.64	15	**Rejected**	110-3.75-R300-d	22.12	15	accepted
175-3.75-R300	27.63	16	**Rejected**	175-3.75-R300-d	30.27	16	**rejected**
175-1.25-R300	30.03	16	**Rejected**	175-1.25-R300-d	32.42	16	**rejected**
C-R100	1.42	13	Accepted	C-R100-d	1.29	13	accepted
110-3.75-R100	7.15	15	Accepted	110-3.75-R100-d	7.01	15	accepted
175-3.75-R100	8.16	15	Accepted	175-3.75-R100-d	10.80	15	accepted
175-1.25-R100	13.73	15	Accepted	175-1.25-R100-d	15.14	15	accepted
C-R10	1.31	13	Accepted	C-R10-d	1.89	13	accepted
110-3.75-R10	8.05	15	Accepted	110-3.75-R10-d	5.15	15	accepted
175-3.75-R10	10.76	15	Accepted	175-3.75-R10-d	9.47	15	accepted
175-1.25-R10	15.56	15	Accepted	175-1.25-R10-d	13.21	15	accepted
C-R1	1.69	13	Accepted	C-R1-d	1.23	13	accepted
110-3.75-R1	7.99	15	Accepted	110-3.75-R1-d	6.55	15	accepted
175-3.75-R1	12.46	15	Accepted	175-3.75-R1-d	12.06	15	accepted
175-1.25-R1	8.12	15	Accepted	175-1.25-R1-d	9.90	15	accepted

Table 6.4: Anaerobic biodegradability for different Mw fractions

	CBP (mL)	μ [% (w/w)]	μ* [% (w/w)]	k (d^{-1})		CBP (mL)	μ [% (w/w)]	μ* [% (w/w)]	k (d^{-1})
PERMEATES									
Mw < 1 kDa					**Mw < 10 kDa**				
Control	11.8 (0.5)	0.60 (0.18)	0.98 (0.00)	0.48 (0.01)	Control	12.8 (0.9)	0.86 (0.01)	0.98 (0.00)	0.41 (0.04)
110°C-3.75°C/min	32.5 (1.7)	0.92 (0.01)	0.96 (0.00)	0.30 (0.02)	110°C-3.75°C/min	41.5 (0.2)	0.90 (0.01)	0.96 (0.00)	0.28 (0.01)
175°C-3.75°C/min	15.9 (0.6)	0.75 (0.07)	0.99 (0.00)	0.48 (0.04)	175°C-3.75°C/min	40.6 (1.7)	0.88 (0.00)	0.97 (0.00)	0.27 (0.00)
175°C-1.25°C/min	44.1 (2.1)	0.92 (0.03)	0.96 (0.00)	0.26 (0.01)	175°C-1.25°C/min	50.5 (1.6)	0.87 (0.00)	0.96 (0.00)	0.27 (0.01)
Mw < 100 kDa					**Mw < 300 kDa**				
Control	28.3	0.64 (0.02)	1.00	0.48	Control	13.9 (1.6)	0.70 (0.02)	0.98 (0.01)	0.39 (0.04)
110°C-3.75°C/min	50.9 (0.9)	0.90 (0.01)	0.93 (0.00)	0.21 (0.01)	110°C-3.75°C/min	24.9 (0.4)	0.81 (0.04)	0.96 (0.00)	0.26 (0.01)
175°C-3.75°C/min	40.3 (0.3)	0.77 (0.02)	0.96 (0.00)	0.26 (0.00)	175°C-3.75°C/min	44.8 (0.27)	0.82 (0.01)	0.97 (0.00)	0.28 (0.00)
175°C-1.25°C/min	59.5 (1.7)	0.87 (0.00)	0.95 (0.00)	0.25 (0.01)	175°C-1.25°C/min	73.3 (0.4)	0.93 (0.00)	0.95 (0.00)	0.20 (0.00)
Mw < 0.45μm					**Mw < 5 μm**				
Control	13.2 (1.1)	0.81 (0.03)	0.98 (0.01)	0.32 (0.04)	Control	20.0 (1.3)	0.85 (0.02)	0.98 (0.01)	0.33 (0.02)
110°C-3.75°C/min	24.9 (0.4)	0.87 (0.02)	0.96 (0.01)	0.23 (0.01)	110°C-3.75°C/min	75.0 (0.7)	0.89 (0.00)	0.96 (0.01)	0.20 (0.01)
175°C-3.75°C/min	44.8 (0.3)	0.85 (0.01)	0.95 (0.00)	0.21 (0.00)	175°C-3.75°C/min	91.2 (0.3)	0.85 (0.00)	0.95 (0.00)	0.20 (0.00)
175°C-1.25°C/min	73.3 (0.4)	0.85 (0.01)	0.93 (0.01)	0.18 (0.01)	175°C-1.25°C/min	94.6 (3.3)	0.92 (0.00)	0.93 (0.01)	0.19 (0.01)
RETENTATES									
1 kDa < Mw < 10 kDa					**10 kDa < Mw < 100 kDa**				
Control	14.1 (3.5)	0.72 (0.02)	1.00 (0.01)	0.43 (0.01)	Control	18.1 (0.9)	0.82 (0.01)	1.00 (0.01)	0.30 (0.02)
110°C-3.75°C/min	65.4 (3.0)	0.87 (0.00)	0.98 (0.00)	0.26 (0.01)	110°C-3.75°C/min	69.3 (3.6)	0.87 (0.01)	0.97 (0.00)	0.23 (0.01)
175°C-3.75°C/min	89.9 (1.6)	0.91 (0.00)	0.97 (0.00)	0.27 (0.00)	175°C-3.75°C/min	81.7 (1.4)	0.87 (0.00)	0.97 (0.01)	0.23 (0.01)
175°C-1.25°C/min	85.3 (1.4)	0.82 (0.03)	0.97 (0.01)	0.24 (0.01)	175°C-1.25°C/min	98.0 (1.7)	0.84 (0.00)	0.95 (0.00)	0.20 (0.00)
100 kDa < Mw < 300 kDa					**300 kDa < Mw < 0.45μm**				
Control	18.1 (0.9)	0.86 (0.02)	1.00 (0.01)	0.30 (0.02)	Control	23.8 (1.5)	0.79 (0.03)	0.99 (0.00)	0.30 (0.00)
110°C-3.75°C/min	69.3 (3.6)	0.92 (0.01)	0.97 (0.00)	0.23 (0.01)	110°C-3.75°C/min	137.2 (7.5)	0.90 (0.02)	0.90 (0.00)	0.14 (0.00)
175°C-3.75°C/min	81.7 (1.4)	0.91 (0.00)	0.97 (0.01)	0.23 (0.01)	175°C-3.75°C/min	177.2 (6.6)	0.85 (0.02)	0.91 (0.01)	0.14 (0.01)
175°C-1.25°C/min	98.0 (1.7)	0.90 (0.00)	0.95 (0.00)	0.20 (0.00)	175°C-1.25°C/min	204.3 (1.8)	0.82 (0.01)	0.87 (0.01)	0.12 (0.01)

*predicted by the first order model.

Samples used for BMP assays were broken down into 2 major groups. Samples with size between 0.45 and 5 um which could be considered colloidal in nature and be significant in terms of biogas production when considering pretreatment. The second major group was the soluble material less than 0.45 um. Subsequently, this soluble material was further subdivided in to 4 different Mw fractions. The degree of biodegradability of permeates of 5 μm was observed to be higher than that of permeates of 0.45 μm except TWAS pretreated at 175°C with high MW intensity (Table 6.4). This shows that colloidal matter between 0.45 and 5 μm are more biodegradable that soluble organics less than 0.45 μm. From characterization of colloidal matter, soluble protein concentration of sample pretreated at 175°C with high MW intensity was observed to be higher in the colloidal fraction than other samples studied. This may show that the protein components may be less biodegradable than other organics in the colloidal fraction.

TWAS samples pretreated at 175°C with low MW intensity produced more biogas than samples pretreated at 175°C with high MW intensity for both the colloidal and soluble groups and each individual Mw fractions except for the interval of 1 kDa < Mw < 10 kDa. However, for this interval, the difference between the two samples was only about 5% which was not deemed to be a significant difference (Figure 6.9). Samples pretreated at 110°C produced more biogas than that pretreated at 175°C with the same intensity for permeates of 1, 10 and 100 kDa average Mw UF intervals. Although for these conditions samples pretreated at 175°C produced more sCOD, the biodegradable COD in the samples was less than that of sample pretreated at 110°C, possibly due to accumulation of refractory COD (Table 6.4). Biodegradability of organics for samples pretreated at 175°C with

3.75°C/min MW intensity was similar or less than that of samples pretreated at the same MW intensity but at 110°C except for Mw intervals between 1 kDa and 10 kDa. Samples pretreated at 175°C exhibited only 4% more organic biodegradability than samples pretreated at 110°C for this Mw interval. An interesting observation was made for all Mw intervals except the smallest one (Mw< 1 kDa), samples pretreated at 175°C with the lower MW intensity (1.25°C/min) demonstrated lower biodegradability than samples pretreated at high MW intensity (Table 6.5 and Figure 6.9). It can be speculated that the lowest AD biodegradability was observed with MW pretreatment at 175°C with 1.25°C/min intensity which tended to produce more solubilized organics that were not readily biologically degradable, especially in the interval between 300 kDa and 0.45 μm. While biodegradability was poor these organics did not cause any obvious acute methanogenic inhibition. On the other hand, overall biodegradability of the truly soluble fraction (Mw < 0.45μm) for TWAS pretreated at 175°C for both MW intensities were the same. For low MW intensity the biodegradability of colloidal matter was also observed to be higher than that for high MW intensity. This may indicate that although there are differences in biodegradability of each Mw fraction for different MW intensities, their combined positive and negative interactions do not affect overall biodegradability.

Generally it can be stated that MW pretreatment methods improve the overall as well as fractional biodegradability of TWAS as well as increase the degradation rate. The first order model fit to the data attempts to describe the overall substrate degradation behavior, however the model is strongly influenced by the ultimate biogas production and it tended to underestimate the rate constants resulting in lower biogas production estimates in the early

portion of the BMP assay when biogas production was increasing exponentially with time. The model suggests lower reaction rate constants with MW pretreatment compensated for by higher soluble substrate concentrations that result in overall greater biogas production rates. To better describe the rate of substrate degradation it was decided to use a zero-order model covering only exponential phase data and use this for estimating the zero-order rate constant (k') as more precise estimate of the effect of MW pretreatment on individual Mw fraction rate constants values for samples untreated and pretreated at different conditions. The results for zero order reaction model fit have been tabulated in Table 6.5 and shown in Figure 6.10 as well. From Figure 6.10 it can be seen that MW pretreatment improves the rate of biodegradation for all Mw fraction intervals by 2-4 fold compared to the control. At the same MW intensity increasing the MW pretreatment temperature improved the rate for all Mw fractions except permeates of 1 kDa for sample pretreated at 175°C with high MW intensity which showed an approximately 30% drop in the rate constant compared to that of sample pretreated at 110°C for the same MW intensity. Consecutively, for Mw < 10 kDa and Mw < 100 kDa the rate constant for sample pretreated at higher temperature was slightly lower than that of sample pretreated at 110°C. Samples pretreated at 175°C at different MW intensities give very similar degradation rate constant for all Mw intervals. The largest difference in rate constants between high and low MW intensities was observed for Mw < 1 kDa where lower MW intensity treated sample produced 72% faster biogas than a similar high MW intensity treated sample. For the remaining Mw intervals sample pretreated with low MW intensity showed 37 and 28% higher zero-order rate constants for Mw < 100 kDa and 100 kDa < Mw < 300 kDa intervals respectively. Looking at the general trend in each interval it can be concluded that MW pretreatment improves the degradation rate compared

to the control. On average, MW pretreatment at 175°C for both 1.25 and 3.75°C/min MW intensities increased the value of the zero order rate 3 fold compared to the rate of the control. It was observed that rate constants of permeates were smaller than that of retentates (Figure 6.10) but the reason for this is not known.

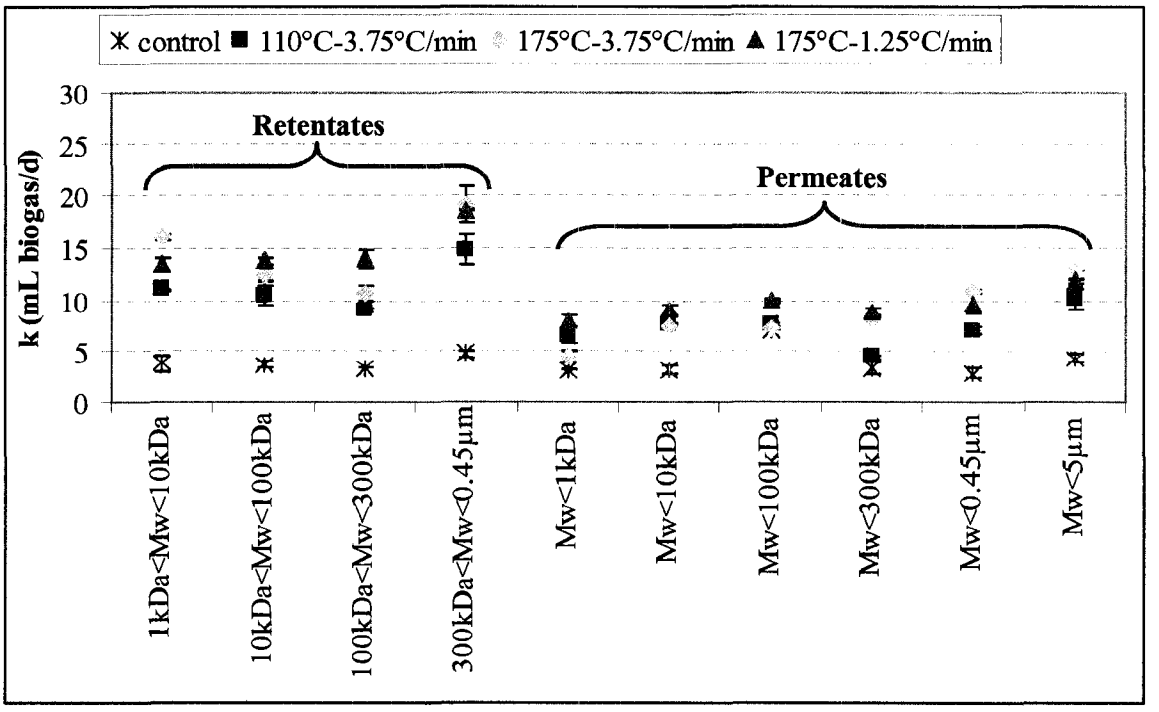


Figure 6.10: Degradation rate constants at for untreated and MW pretreated samples at different Mw intervals

It is also important to examine any change of refractory COD to better understand the effect of MW pretreatment conditions on solubilization. Table 6.6 shows the refractory COD concentration as well as the improvement in the biodegradable COD/refractory COD ratio compared to the control. Refractory COD concentrations of permeates of all Mw cut off levels for all MW pretreated samples were very similar to each other as well as to those of their controls. For retentates an increase in refractory COD concentrations was observed as MW temperature was increased and as MW intensity was decreased. Although refractory

COD concentrations increased for retentates, biodegradable COD/refractory COD ratios of each sample also increased indicating that a greater proportion of biodegradable CODs were solubilized as the result of MW pretreatment.

The improvement in biodegradable COD/refractory COD ratio of sample pretreated at 110°C was calculated to be higher than that of sample pretreated at 175°C at the same MW intensity except for the Mw interval between 1 and 10 kDa. Decreasing the MW intensity to 1.25°C/min showed a somewhat similar improvement on that ratio compared to the ratios of sample pretreated at 110°C with 3.75°C/min MW intensity. Overall (Mw < 5μm), biodegradable COD/refractory COD ratio of samples pretreated to higher temperature with lower MW intensity gave the most improvement compared to control and other pretreatment conditions studied. It may be conjectured that the athermal effect is more significant when samples are exposed to a lower MW intensity combined with the high temperature thermal effect. This combination may be better suited to cause breakage of hydrogen bonds of macromolecules, resulting in improved TWAS solubilization. However, the end product of this enhanced solubilization action results in production of more refractory organics in the higher molecular weight intervals compared with lower temperatures or higher MW intensity. However, a high refractory organic concentration is offset by greater improvement in the biodegradable COD/refractory COD ratio, which ultimately leads to higher biogas production.

Table 6.4: Zero-order biodegradability constant (k') for untreated and MW pretreated samples.

	Zero order rate constant (k') (mg biogas/d)				Fold increase in k' over control		
	Control	110°C-3.75°C/min	175°C-3.75°C/min	175°C-1.25°C/min	110°C-3.75°C/min	175°C-3.75°C/min	175°C-1.25°C/min
Retentates							
1 kDa<Mw<10 kDa	3.90 (0.85)	11.15 (0.12)	15.97 (0.25)	13.38 (0.65)	3.00 (0.75)	4.29 (1.08)	3.60 (0.93)
10 kDa<Mw<100 kDa	1.01 (0.00)	0.97 (0.00)	0.97 (0.01)	0.95 (0.00)	0.96 (0.00)	0.96 (0.00)	0.94 (0.00)
100 kDa<Mw<300 kDa	3.34 (0.02)	9.10 (0.21)	10.86 (0.77)	13.93 (0.80)	2.72 (0.07)	3.25 (0.27)	4.17 (0.28)
300 kDa<Mw<0.45μm	4.80 (0.25)	14.81 (1.46)	19.06 (1.76)	18.47 (0.08)	3.09 (0.40)	3.98 (0.49)	3.86 (0.23)
Permeates							
Mw<1 kDa	3.18 (0.06)	6.55 (0.74)	4.48 (0.62)	8.01 (0.54)	2.06 (0.27)	1.41 (0.23)	2.52 (0.20)
Mw<10 kDa	3.20 (0.38)	7.68 (0.14)	7.48 (0.04)	9.19 (0.56)	2.43 (0.34)	2.37 (0.32)	2.91 (0.45)
Mw<100 kDa	7.12	7.68 (0.17)	7.31 (0.08)	10.03 (0.23)	0.95 (0.02)	0.90 (0.01)	1.23 (0.03)
Mw<300 kDa	3.38 (0.55)	4.40 (0.17)	8.29 (0.06)	8.91 (0.36)	1.34 (0.26)	2.52 (0.47)	2.71 (0.52)
Mw<0.45μm	2.89 (0.42)	7.00 (0.37)	11.01 (0.24)	9.77 (0.95)	2.48 (0.44)	3.89 (0.66)	3.46 (0.70)
Mw<5μm	4.37 (0.42)	10.16 (0.97)	13.00 (0.09)	11.88 (0.22)	2.35 (0.37)	3.00 (0.33)	2.74 (0.31)

Table 6.5: The effect of MW pretreatment on refractory COD concentration

	Refractory COD (mg/L)				Increase in Biodegradable COD/ Refractory COD ratio over control		
	Control	**110°C-3.75°C/min**	**175°C-3.75°C/min**	**175°C-1.25°C/min**	**110°C-3.75°C/min**	**175°C-3.75°C/min**	**175°C-1.25°C/min**
Retentates							
1 kDa<Mw<10 kDa	221* (8)	300 (4)	390 (15)	440 (32)	2.5 (0.3)	4.0 (0.5)	1.9 (0.5)
10 kDa<Mw<100 kDa	217 (2)	305 (12)	349 (8)	386 (6)	1.5 (0.1)	1.4 (0.1)	1.1 (0.1)
100 kDa<Mw<300 kDa	204 (8)	217 (10)	274 (2)	341 (4)	2.0 (0.4)	1.7 (0.2)	1.4 (0.2)
300 kDa<Mw<0.45μm	266 (10)	531 (56)	735 (75)	763 (31)	2.4 (0.7)	1.5 (0.4)	1.2 (0.3)
Permeates							
Mw<1 kDa	255 (58)	213 (8)	234 (31)	238 (10)	6.4 (1.7)	1.9 (0.8)	6.6 (1.7)
Mw<10 kDa	195 (4)	219 (6)	245 (4)	274 (6)	1.5 (0.2)	1.2 (0.1)	1.2 (0.1)
Mw<100 kDa	272 (8)	232 (15)	294 (12)	268 (6)	5.1 (1.0)	1.9 (0.3)	5.7 (0.6)
Mw<300 kDa	222 (4)	265 (33)	275 (4)	271 (2)	2.0 (0.6)	2.0 (0.2)	5.5 (0.6)
Mw<0.45μm	237 (14)	269 (23)	324 (4)	335 (4)	1.6 (0.4)	1.3 (0.3)	1.3 (0.3)
Mw<5μm	228 (8)	304 (4)	353 (2)	326 (2)	1.4 (0.2)	1.0 (0.2)	2.1 (0.3)

*Arithmetic mean of duplicates and absolute difference between the mean and experimental data in parenthesis.

These results conflict with semi-continuous MAD data where high MW intensity produced more biogas than low MW intensity at low SRTs (5 and 10 days) (Toreci *et al.*, 2009). This discrepancy may be attributed to MW intensity driven microbial-substrate interactions between the suspended solids and/or colloidal matter >5 μm rather than soluble organics biodegradability.

6.4 CONCLUSIONS

High temperature MW pretreatment disrupts the TWAS floc matrix and as a result EPS and/or intracellular polymers break down into smaller components and are released to the colloidal and true soluble phase. Solubilization was improved as MW temperature was increased; however, decreasing MW intensity from 3.75 (high) to 1.25°C/min (low) did not yield significant improvement in sCOD concentrations.

Mw profile distributions of soluble organic concentrations (sCOD, soluble protein, soluble sugar and TVFA) differ for each MW pretreatment condition. High and low MW intensities at the same temperature produced similar sCOD concentrations; however, Mw distribution profiles were very different confirming that MW intensity has an impact on TWAS solubilization at the molecular level.

MW intensity did not affect overall biodegradability of truly soluble organics (Mw < 0.45μm) of TWAS pretreated at 175°C. Although there are differences in biodegradability of each Mw fraction for different MW intensities, their combined positive and negative interactions do not affect overall biodegradability.

A first-order batch BMP model fit the tail section of the biogas curve accurately but underestimates the rate constants and exponential phase biogas production. Zero-order kinetics better described the initial degradation phase and high temperature MW pretreatment improves degradation rate.

Athermal effect of low MW intensity combined with thermal effect of high pretreatment temperature increased the overall (Mw < 5μm) biodegradable COD/refractory COD ratio. Overall CBP was not affected by MW intensity, although for low MW intensity overall biodegradability (Mw < 5 μm) is higher and refractory organic concentration is slightly lower than that of high MW intensity.

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CHAPTER 7:

Feasibility Analysis of Mesophilic Anaerobic Digestion with Microwave Pretreatment

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7.1 INTRODUCTION

Sludge management is a growing issue in activated sludge wastewater treatment plants due to environmental and economical issues. It is a known fact that sludge handling accounts for approximately 50% of the total capital and operating cost of wastewater treatment plants. Pathogens in sludge are also a concern due to the danger of spreading diseases after final disposal. Additionally, the availability of landfill space for sludge disposal decreases each year with concomitant increased tipping costs both in North America and in Europe. Anaerobic digestion is still the most commonly used method to stabilize sludge. However, anaerobic stabilization is limited to 30-45% volatile solids (VS) destruction since more than 50% of sludge is not readily biodegradable or nonbiodegradable (Gosset and Belser, 1982).

Microbial cell walls and extracellular polymeric (EPS) substances in sludge are the main limitations to hydrolysis which is the rate limiting step in anaerobic digestion (Baier and Schmidheiny, 1997).

There are several pretreatment methods that enhance anaerobic digestion by disrupting the floc matrix and/or cell lysis such as chemical, mechanical, thermal, ultrasound and ozonation. Thermal pretreatment at high temperatures (160-175°C) and high pressures (6-8 bar) was found to be superior to other methods in terms of VS destruction, pathogen removal and biogas production (Barnard *et al.*, 2002; Abraham and Kepp, 2003). Recently, microwave (MW) heating has been proposed and studied as a sludge pretreatment method. It has two advantages over conventional heating. Firstly, direct and internal MW heating decreases the energy lost through convection and conduction. Secondly, the dipole orientation caused by the oscillating electromagnetic field during microwaving has an additional disrupting athermal effect on dipole molecules. It is hypothesized that the athermal effect may be responsible for hydrogen bond breakage which stabilizes the tertiary structure of proteins and as a result leads to disruption or denaturation of the EPS floc matrix (George *et al.,* 2008 and Loupy 2002).

Studies have also shown that, MW heating to above 85°C followed by mesophilic anaerobic digestion (MAD) can result in sufficient pathogen destruction to produce Class A sludge (Hong et al., 2004). MW pretreatment to temperatures around 90°C have also been shown to result in a 3-fold increase in sludge solubilization compared to untreated sludge (Eskicioglu *et al.,* 2007a, Park *et al.,* 2004) and that increasing sludge MW treatment temperature to 175°C further improved solubilization 4.5 ± 0.8 and 8.8 ± 0.9 fold greater than untreated

thickened waste activated sludge (TWAS) for 6.0 and 11.8% total solid (TS) concentrations, respectively (Toreci *et al.,* 2008). Park *et al.* (2004) observed that semi-continuous MAD sludge retention time (SRT) could be reduced from 15 to 10 days without any significant loss in process efficiency when sludge was MW pretreated to 91°C. However, Eskicioglu *et al.* (2007b) who worked with the same TWAS as Toreci *et al,* (2008) also reported biogas production improvement at 10 day SRT but the degree of improvement was reported at 36% over 15 d SRT biogas production. This was less than what was observed by Park *et al.* (2004). Further decrease in SRT to 5 days resulted in a 28% improvement in biogas production over the 15 d SRT results when sludge was MW pretreated at 96°C (Eskicioglu *et al.,* 2007b). The differences between the two studies may be related to the sludge age (Esckicioglu *et al.* 2007b, 5-7 d , Park *et al.* 2004, not reported) and differing characteristics of the TWAS. Semi-continuous MAD experiments with 5-7 d SRT TWAS, MW pretreatment at 175°C with 3.75°C/min MW intensity resulted in 83% more biogas production when SRT decreased from 20 to 5 days (Toreci *et al.,* 2009). Interestingly, pretreatment at 175°C with a lower MW intensity of 1.25°C/min increased the extent of TWAS solubilization; however, it did not result in any further improvement and in fact had a negative effect on MAD when SRT decreased. Dual-stage MAD was also examined combined with high temperature MW pretreatment. It was concluded that dual-stage digestion had a slight improvement over single-stage mesophilic digestion of untreated sludge. On the other hand, with MW pre-treatment, single stage digesters preformed better than dual-stage digesters. Dewateribility was improved for all cases when sludge was pretreated with MW.

So far MW pretreatment effects on MAD biodegradability have been examined when sludge has been digested with pretreatment [i.e., suspended solids (SS) + soluble matter combined]. Another approach to TWAS management may be the separation of supernatant and SS and digesting only the supernatant since most of the biodegradable components are in the supernatant of TWAS once solubilization with MW pretreatment has been conducted. In the literature there is only one example of this application. Sawayama *et al.* (1995) studied the efficiency of supernatant digestion of TWAS after pretreating TWAS thermally at 175°C with an electric furnace and holding it at 4 MPa for 1 hour in an autoclave. After the pretreatment, supernatant was separated from TWAS by centrifugation (1000g, 10 min). After 9 days of batch MAD it was found that biogas production of un-separated TWAS increased 35% from 3224 to 4370 mL following pretreatment. AD of the supernatant alone of pretreated sludge produced 3080 mL biogas which accounted for 96 and 70% of the biogas produced by untreated and pretreated TWAS, respectively. It was observed that biogas production per g of VS added of the supernatant was higher than that of the whole pretreated TWAS which indicates that a larger proportion of refractory material was left in the SS. Concomitantly, pretreating TWAS increases the solubility of sludge as well as its biodegradability, which would indicate that by digesting only the supernatant, digester volume may be decreased and more efficient and rapid digestion can be achieved with only a small decrease in overall efficiency and biogas production.

To be able to remove supernatant from SS it is important to know the characteristics of the floc matrix and its relationship with water. Sludge, in general, posses four types of water. Bulk or free water can easily be removed by mechanical methods and it is the water between

the flocs that does not associate with suspended particles. The second type is interstitial water which is trapped in the floc matrix. Some of the interstitial water can be found also inside the bacteria cells in the sludge. Although physical properties of interstitial water are similar to bulk water it behaves differently due to its close proximity to the suspended particles; moreover, the interaction between interstitial water and particles' surfaces is not clearly known. Vicinal or surface water is the third type of water and probably the most interesting type of water found in sludge. Hydrogen bonds keep water molecules close to the particle surfaces causing formation of several layers of water that are well structured. It has very different properties compared to other types of water. Finally the fourth type of water in sludge is water of hydration which is chemically attached to particles. It can be removed only by thermal energy exposure. Usually the combination of interstitial, vicinal and water of hydration is called bound water (Vesilind, 1994).

By applying mechanical methods for dewatering it was found that only bulk and a protion of interstitial water can be removed from the sludge. It is impossible to remove vicinal water and hydration water mechanically (Tsang *et al.,* 1990). It was seen that decreasing the floc size can improve the release of interstitial water in to the bulk water phase resulting in an increase in the degree of dewaterability of the sludge.

Another way of improving dewaterability can be achieved by breaking the cell walls of bacteria in the sludge matrix. However, the fact that the type of water a cell contains is unknown makes this argument uncertain. Generally, it has been reported that the interstitial space between cells varies between 50 to 150 nm. Since the layer of vicinal water usually has a thickness of 3 nm, water layers greater than this thickness should be interstitial water.

However it was claimed that the vicinal water can have surface effects up to 50 nm therefore leaving all or most of the water inside the cell wall characterized as vicinal water (Clegg, 1981). Therefore breaking cell walls would not improve dewaterability of sludge unless the cell surface is also destroyed.

The objective of this paper is to evaluate dewaterability of sludge with MW pretreatment and also the biodegradability of the soluble phase of MW pretreated sludge at different conditions. A preliminary feasibility analysis was also conducted for various supernatant MAD cases only, using different pretreatment conditions as well as digestion of different components of sludge.

7.2 EXPERIMENTAL SETUP

TWAS [approx. 5% w/v; 80% volatile SS (VSS)] was obtained from the local municipal wastewater treatment centre ROPEC in Gloucester, ON, Canada. Sludge is produced by a conventional activated sludge unit operated at 5 day SRT and is concentrated through a thickener centrifuge before MAD. Inoculum was taken from the effluent line of the mesophilic anaerobic digesters which operate at a 15-20 days SRT, stabilizing mixed primary and secondary sludge [42:58 (v/v)]. Inoculum was acclimatized for 4 months by feeding 3% TS TWAS, MW pretreated at 175°C to minimize any possible inhibition associated with pretreatment (Ekama *et al.*, 1986). A Mars 5© (MW Accelerated Reaction System; CEM Corporation) MW oven was used for MW pretreatment which has a frequency of 2450 MHz and can deliver 1200 W ± 15% of MW energy at full power. MW intensity was controlled by changing the time to reach the set temperature. The Mars 5

sample vessels are designed to ensure full MW penetration and operating conditions can be controlled and varied up to 250°C and 34.5 bar.

Pretreatment temperature, MW intensity (expressed as rate of sample temperature change) and sludge concentrations were selected as variables in a multilevel statistical design to investigate effects of these variables on supernatant separation as well as MAD. Table 7.1 shows the variables and their levels and Figure 7.1 shows the illustration of the multilevel statistical design employed.

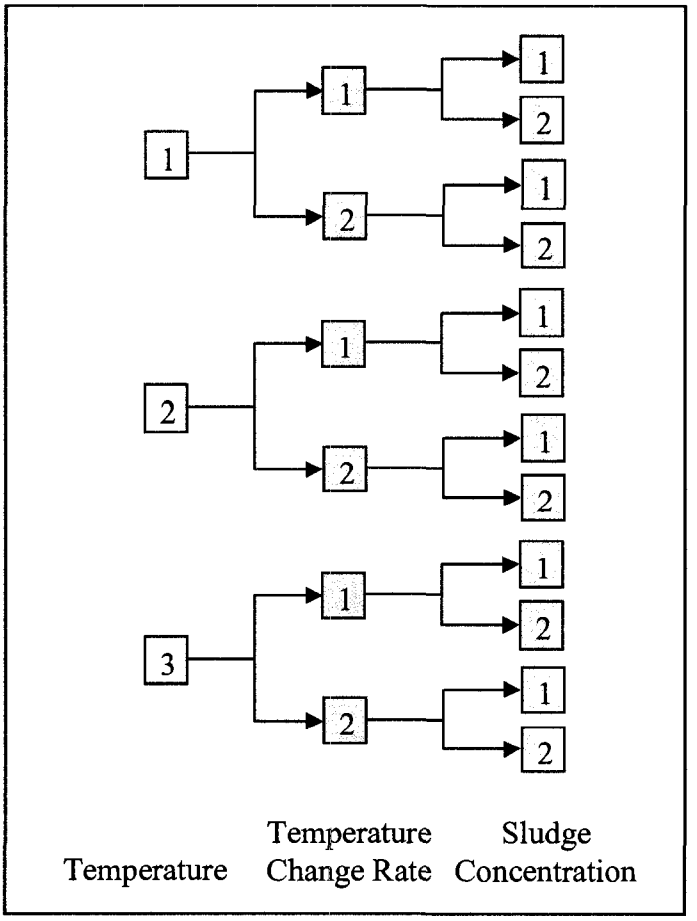

Figure 7.1: Illustration of multilevel factorial design used in this set of experiments

Table 7.1: Variables and their levels used in statistical design

Variables → / Levels ↓	Temperature °C	MW Intensity °C/min	Sludge Concentration %
1	110	3.75	6.0
2	150	7.5	11.8
3	175		

TWAS was centrifuged at 6513 relative centrifugal force (RCF) for 20 minutes to obtain a high TS concentration. To remove the supernatant from SS, untreated and MW treated sludge was centrifuged again at 6513 RCF for 30 minutes followed by filtration through 0.45 μm GF/C grade binder free glass microfibre filters. A volume of 140 mL of supernatant was mixed with 35 mL of acclimated inoculum in 250 mL glass bottles which were used as reactors with butyl rubber stoppers for mesophilic biological methane potential (BMP) assays. Nitrogen was bubbled through the mixture to prevent culture exposure to oxygen. After addition of potassium and sodium bicarbonate as a pH buffer to provide 4000 mg/L of bicarbonate alkalinity, the reactors were sealed. BMP tests were performed in duplicate at 35 ± 1°C using a New Brunswick rotary shaker at a speed of 95 rpm.

Daily biogas production was measured. Total volatile fatty acids (TVFA) and biogas composition were monitored once a week and pH of the reactors was measured biweekly. Before and after the BMP assay, soluble CODs (sCODs) were measured according to Standard Methods colorimetric method 5220C using a Coleman Perkin-Elmer spectrophotometer model 295 (APHA, 1995). TVFA (acetic acid, propionic acid and butyric

acid) concentrations were determined using a HP 5840A GC with glass Chromosorb 101 column (Chromatographic Specialties Inc., Brockville, ON, Canada, mesh size: 80/100, column length × ID: 304.8 cm × 2.1 mm) and a flame ionization detector according to van Huyssteen (1967). Biogas composition was determined with a HP 5710A GC with Porapak T packed column (Chromatographic Specialties Inc., Brockville, ON, Canada, mesh size: 50/80, column length × OD: 304.8 cm × 6.35 mm) and thermal conductivity detector according to Ackman (1972). pH measurements were determined using a Fisher Accumet pH meter 750 and a combination electrode.

7.3 RESULTS

7.3.1 The Effect of MW Treatment on Dewaterability

Centrifuging untreated and MW pretreated samples at an RCF of 6513 for 30 minutes indicated that microwaving increased the release of water from TWAS improving water separation from the sludge matrix (Figure 7.2). In Figure 7.2, black and white squares represent the SS and the water portions of raw whole TWAS, respectively. Squares with different striped colors represent the proportion of the water in the sample that could not be removed by centrifuging at 6513 RCF for 30 minutes based on the different MW conditions applied to the TWAS. As the coloured squares become smaller, a larger portion of the water associated with the TWAS could be removed. All the water could be removed from the TWAS sample if the striped coloured box approached the size of the black box which represents only the SS. From Figure 7.2 it can be observed that as the MW temperature

increases from 110 to 150 to 175°C, the size of the coloured boxes decreases indicating that temperature had a significant positive impact on TWAS dewaterability. As MW treatment temperature increased it was easier to concentrate TWAS by centrifuging.

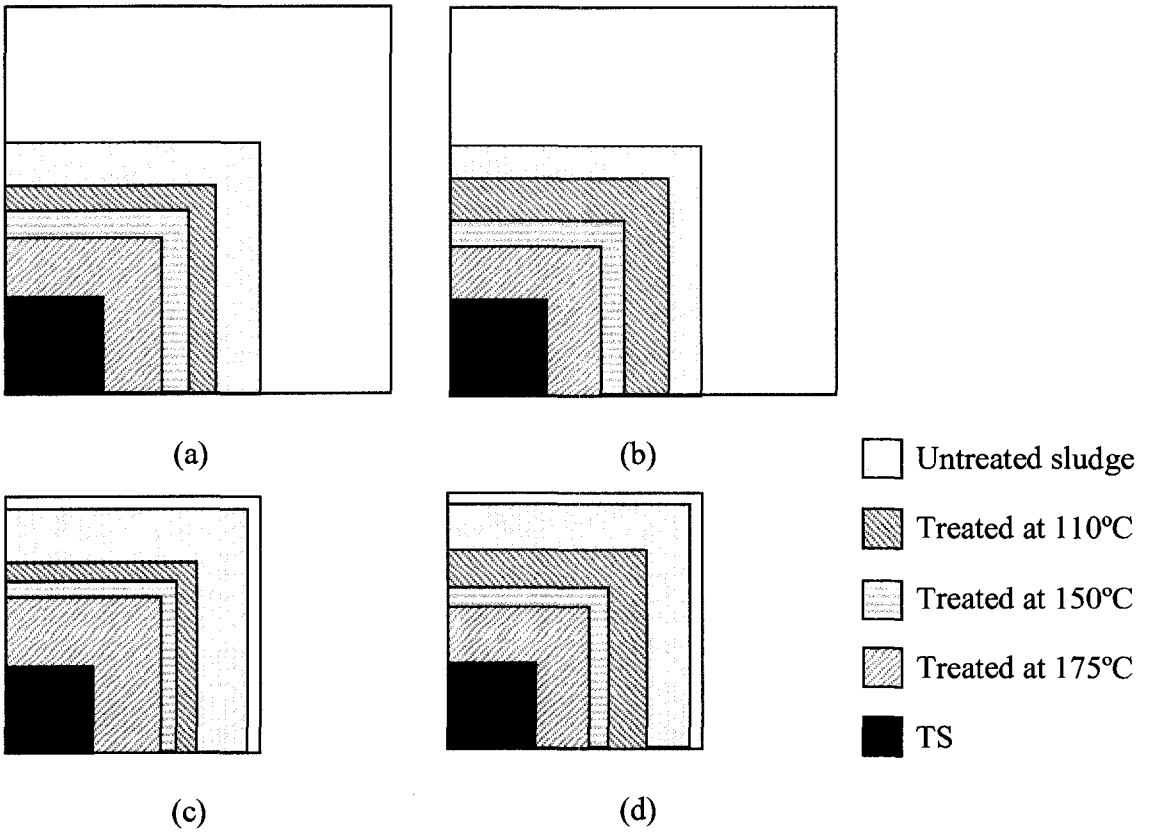

Figure 7.2: Illustration of solid and supernatant content of sludge at different conditions: (a) 6.0% TWAS treated with high MW intensity (b) 6.0% TWAS treated with low MW intensity (c) 11.8% TWAS treated with high MW intensity (d) 11.8% TWAS treated with low MW intensity [Area of boxes are to scale and represents fraction of sample in various fractions SS (black), free water (white), bound water (striped)]

The effect of concentrating sludge first and treating with MW after was also investigated. The overall improvement in dewaterability for 6.0% TWAS treated with MW compared with more concentrated 11.8% sludge is also shown in Figure 7.2.c,d and Table 7.2. As observed from the table, the difference in degree of dewaterability at two very different

concentrations was very small. At the lowest MW temperature (110°C) the difference in dewaterability was slightly more noticeable compared with higher temperatures which showed no difference. MW intensity also only had a very slight effect on water separation from TWAS. The fact that the similar coloured boxes remain about the same size in Figures 7.2a and 7.2b and similarly in 7.2c and 7.2d indicate that temperature had the greatest impact on dewatering compared to MW intensity and sludge concentration. Improvements in water release may be the result of smaller floc size or even by cell lysis caused mainly by higher temperatures resulting from MW treatment while being relatively independent of MW intensity and TWAS concentration in the region evaluated.

Table 7.2: Overall percentage of supernatant obtained from different treatments

Overall Supernatant Percentage (%)				
Pretreatment Temperature	**High MW Intensity (15°C/min)**		**Low MW Intensity (7.5°C/min)**	
	6.0% TWAS	**11.8% TWAS**	**6.0% TWAS**	**11.8% TWAS**
110°C	70	76	68	74
150°C	77	81	79	83
175°C	83	84	84	85

7.3.2 Anaerobic Digestion of Supernatant

Biogas productions of the supernatant portion of TWAS treated at different conditions and their controls and duplicates are shown in Figures 7.3-7.6. For 6.0% TWAS supernatant pretreated at 175°C, a very minor inhibition was seen for both MW intensities, but they quickly caught up with the rest of pretreated supernatants and controls. The same acute inhibition but with greater effect was also seen between days 10-20 for 11.8% TWAS supernatant. At day 19, pH dropped below 6, and extra alkalinity was supplied by addition of calcium and potassium carbonate. After addition of alkalinity, pH returned to around 7 and the biogas production increased. Supernatant of pretreated 11.8% TWAS showed secondary and/or tertiary lag phases during 130 days of BMP tests compared to the supernatant of the less concentrated MW treated TWAS. This may suggest that MW pretreatment of highly concentrated TWAS could produce larger more complex soluble components that are less easily biodegradable than those formed during MW pretreatment of less concentrated TWAS. This result is consistent with MAD biogas yields for TWAS at different TS concentrations previously reported by Toreci *et al.,* (2007). However, the very mild degree of inhibition with supernatant only MAD compared to whole sludge MAD tends to indicate that inhibition observed in the early phases of BMP assays with whole sludge is mainly caused by compounds resulting from MW pretreatment and associated with the SS phase of the sludge.

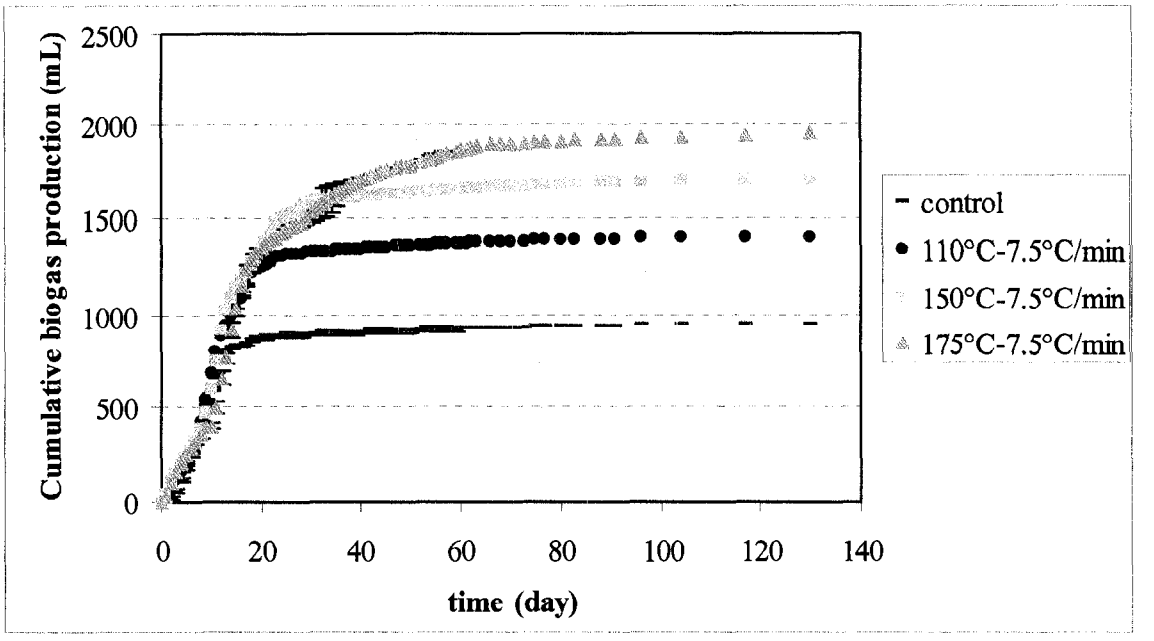

Figure 7.3: Biogas production of supernatant of 6% TWAS pretreated with high MW intensity at different temperatures and its control

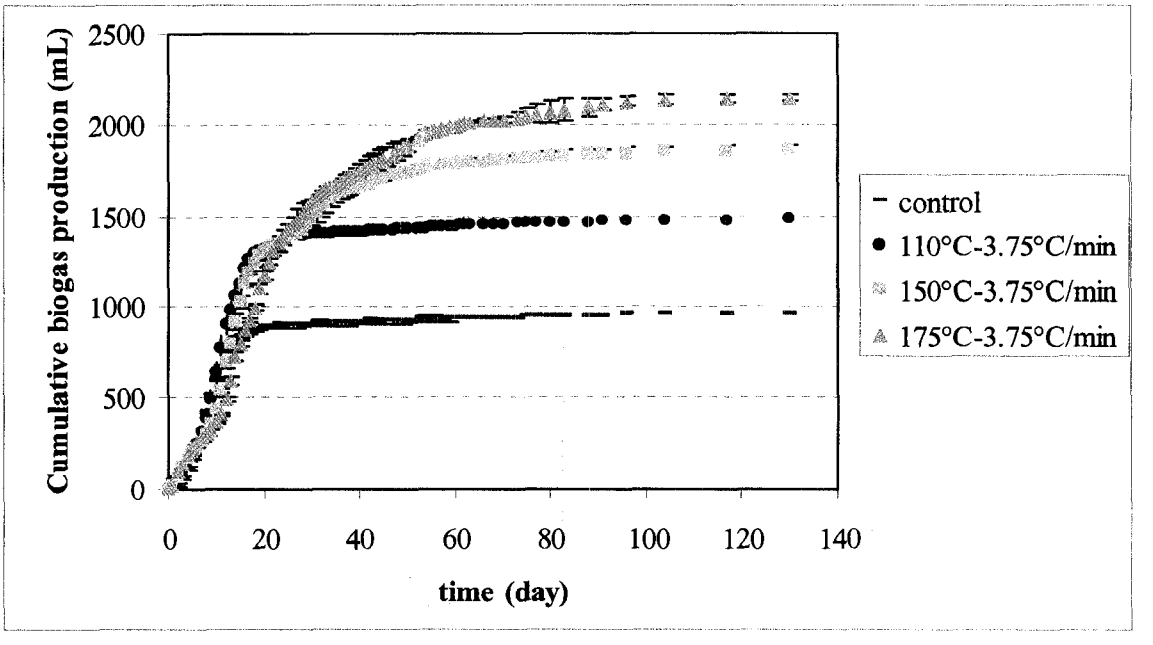

Figure 7.4: Biogas production of supernatant of 6% TWAS pretreated with low MW intensity at different temperatures and its control

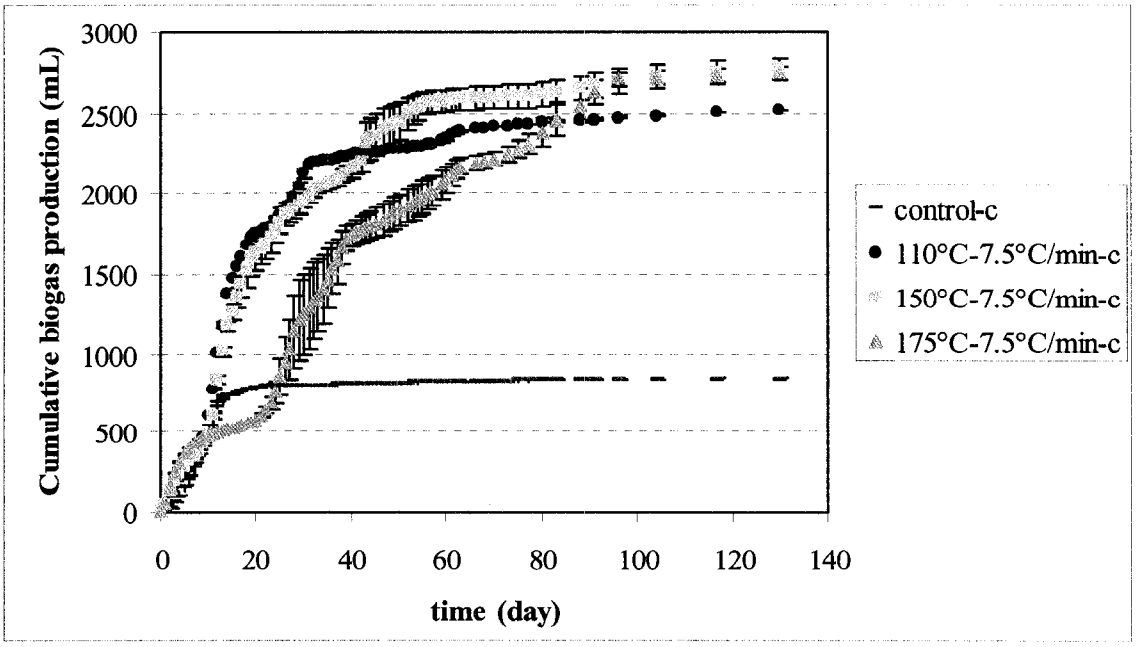

Figure 7.5: Biogas production of supernatant of 11.8% TWAS pretreated with high MW intensity at different temperatures and its control

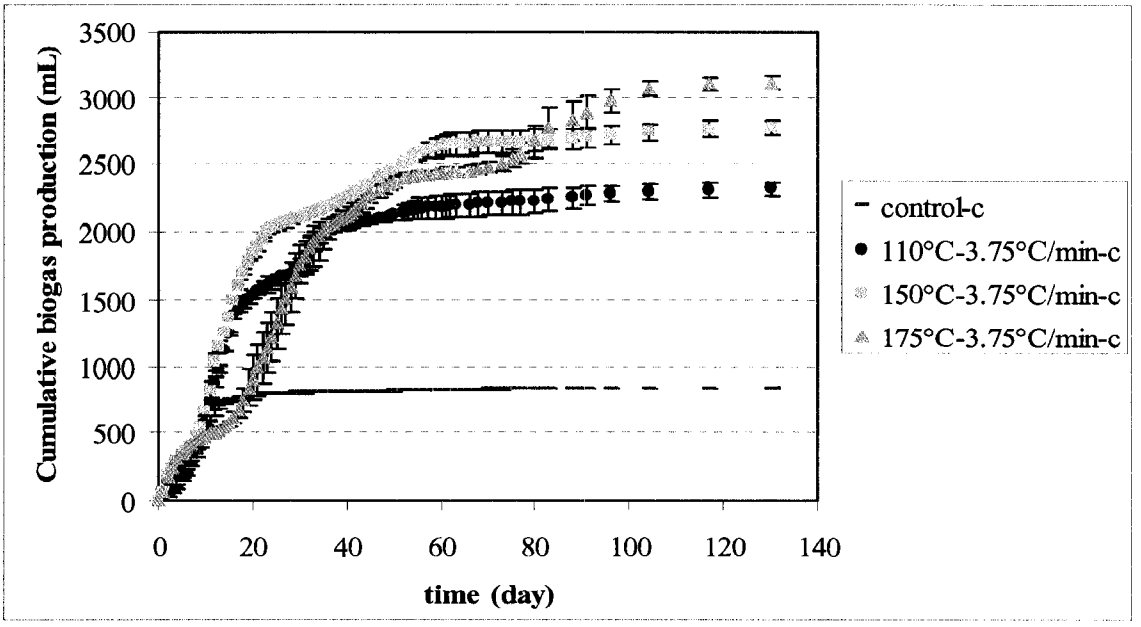

Figure 7.6: Biogas production of supernatant of 11.8% TWAS pretreated with low MW intensity at different temperatures and its control

In order to compare the biogas production from supernatant of TWAS pretreated at different MW operating conditions to whole MW pretreated TWAS, it is important to calculate methane yield at day 20 and 61 compared to the final COD removed or biogas production at the end of the BMP assay (130^{th} day). Table 7.3 (columns 4 and 5) shows methane production on days 20 and 61 per gram of ultimate COD removed (day 130). As the value approaches the theoretical value of 0.35 m^3 CH_4/kg COD removed we can ascertain the level of organic conversion at either day. This is then summarized in columns 6 and 7. Yields for day 20 were less than day 61 as less biogas had evolved compared to the ultimate COD removed (day 130).These days were selected because general SRTs for MAD in practical application are around 20 days and day 61 was selected as reasonable ultimate digestibility due to fact that BMP tests of whole sludge were terminated at day 61. Column 6 and 7 in Table 7.3 show biogas production percentages at days 20 and 61 compared to final biogas production obtained at 130^{th} day of the BMP assay. Biogas production percentages at day 20 were lower than that at day 61 which was expected as stabilization of organics was ongoing. At day 20, biogas production percentages were in the range of 54 to 93% except for concentrated sludge pretreated at 175°C with both MW intensities which were in the range of 21 to 29% (attributed to acute inhibition). The biogas production efficiency compared to the final values were very similar at the end of the 61^{st} day and biogas production percentages were higher than 93% of final biogas production except again supernatant of high TWAS concentration treated at 175°C with both MW intensities. It was observed that lowering the MW intensity mostly improves biogas production per ultimate (day 130) mass of COD removed at the highest MW pretreatment temperature. Although it may be seen that cumulative biogas produced (CBP) at the 20^{th} day relative to the ultimate CBP decreased as

the pretreatment temperature increased it must also be taken into consideration that in the early stage of the BMP, all pretreated sludge showed inhibition which masks any improvement that may have been seen around the 20th day of the BMP test.

Table 7.3: Biogas produced/COD removed values from supernatant BMP test

Pretreatment temperature (°C)	MW intensity (°C/min)	TWAS concentration (%)	Methane produced/ final COD removed (m^3/kg)		Percentage of biogas produced compared to final (%)	
			Day 20	Day 61	Day 20	Day 61
Controls		6	0.33±0.00	0.34±0.00	0.92	0.96
		11.85	0.27±0.00	0.28±0.00	0.93	0.97
110	3.75	6	0.24±0.00	0.27±0.00	0.89	0.97
		11.85	0.20±0.00	0.27±0.01	0.66	0.94
	7.5	6	0.23±0.00	0.26±0.00	0.89	0.97
		11.85	0.18±0.00	0.25±0.00	0.69	0.94
150	3.75	6	0.25±0.01	0.34±0.00	0.70	0.96
		11.85	0.20±0.01	0.32±0.02	0.66	0.95
	7.5	6	0.19±0.00	0.25±0.00	0.78	0.97
		11.85	0.22±0.03	0.31±0.02	0.59	0.93
175	3.75	6	0.19±0.01	0.27±0.00	0.54	0.93
		11.85	0.04±0.03	0.14±0.01	0.29	0.78
	7.5	6	0.16±0.01	0.27±0.00	0.69	0.95
		11.85	0.04±0.00	0.11±0.02	0.21	0.77

Due to fact that high temperature MW pretreatment solubilizes most of the organics presents in TWAS, it was hypothesized earlier that MAD, digesting only the soluble portion could be advantageous in minimizing reactor size and energy requirements. To evaluate this

hypothesis it is important to know the rate and ultimate biogas production from sludge and supernatant digestion. To be able to compare biogas production from sludge digestion and from supernatant digestion, the fraction of supernatant that can be separated from sludge has to be known. Table 7.4 shows supernatant fractions, biogas production from sludge itself and from the supernatant fraction as well as percentage of biogas produced by supernatant vs. whole sludge at days 20 and 61 when the BMP test for sludge terminated.

It was very difficult to remove supernatant from raw concentrated TWAS; however, conditions improved dramatically by introducing MW pretreatment. The MW intensity effect on supernatant fraction was not significant between 3.75 and 7.5°C/min intensities; however, the percentage of biogas produced from the supernatant was improved with lower MW intensity. At day 20 digesting supernatant pretreated at 150°C had better efficiency compared to that pretreated at 175°C due to higher biogas production from a smaller supernatant volume. At day 20, 72% of biogas produced by sludge pretreated at 150°C with low MW intensity can be recovered by digesting its supernatant only, which is 90% more biogas than can be produced by digesting the same volume of supernatant obtained from raw TWAS. It is important to acknowledge that inhibition in the early stage of the sludge BMP assay reduced the biogas production at the 20^{th} day of the assay. A reduction in supernatant biogas production ratio over biogas produced by digesting whole sludge is possible when inhibition is prevented or decreased by better acclimation of inoculum (Toreci *et al.*, 2007).

Table 7.4: Supernatant fractions and CBP of sludge and supernatant at day 20 and 61

Pretreatment Temperature (°C)	MW Intensity (°C/min)	TWAS Concentration (%)	Supernatant Fraction	Cumulative Biogas Production (mL)					
				20th day			61st day		
				Whole Sludge	Supernatant	Supernatant Biogas Fraction %	Whole Sludge	Supernatant	Supernatant Biogas Fraction %
Control		6	0.58	3315±59	1028±7	0.31±0.00	3826±66	1080±9	0.28±0.00
		11.85	0.09	3194±11	143±1	0.04±0.00	3767±3	149±0	0.04±0.00
110	3.75	6	0.68	3487±8	1805±26	0.52±0.01	3948±11	1977±19	0.50±0.00
		11.85	0.39	3205±60	1220±19	0.38±0.01	3685±79	1708±66	0.46±0.02
	7.5	6	0.70	3386±9	1780±16	0.53±0.00	3845±11	1928±4	0.50±0.00
		11.85	0.44	3200±0	1555±10	0.49±0.00	3646±9	2087±18	0.57±0.00
150	3.75	6	0.79	3674±3	2653±23	0.72±0.01	4014±0	3593±32	0.89±0.01
		11.85	0.60	3335±21	2264±71	0.68±0.02	3773±20	3169±72	0.84±0.04
	7.5	6	0.77	3607±39	2125±30	0.59±0.01	3959±50	2557±11	0.65±0.01
		11.85	0.55	3270±73	3186±338	0.57±0.09	3752±97	2892±223	0.77±0.05
175	3.75	6	0.84	3117±27	2113±29	0.68±0.01	4017±5	3395±3	0.85±0.00
		11.85	0.64	2910±38	1268±676	0.44±0.19	3719±72	3125±117	0.84±0.03
	7.5	6	0.83	3748±2	2247±36	0.61±0.01	4114±8	3107±21	0.76±0.00
		11.85	0.62	3412±85	755±48	0.22±0.01	3830±30	2632±271	0.69±0.06

It is important to have an energy balance for each condition and each step to have a better understanding of the efficiency of supernatant MAD vs. whole sludge MAD at the different MW pretreatment conditions.

7.4 ENERGY CALCULATIONS

It is very important to analyze the economic aspects of the addition of pretreatment. Ideally, enhancement of digestion should result in lower costs as well as improved treatment. The most common way to minimize the energy requirement is to use the methane produced during digestion as an energy source. Additional energy sinks can also be identified where there is accessible energy that can be used as a heat source for other parts of the treatment plant. The main energy losses are heat loss through external digester walls, reactor mixing, energy input for TWAS pretreatment, dewatering and a very important energy cost that is sometimes neglected is transportation for disposal of dewatered digestate to landfill.

Three major scenarios will be examined here: (1) MAD of TWAS + primary sludge (60:40) without any pretreatment, (2) MAD of TWAS + primary sludge (60:40) with MW pretreatment and (3) MAD of MW pretreated TWAS supernatant + primary sludge. Simplified general schematic diagrams of these scenarios are illustrated in Figure 7.7.

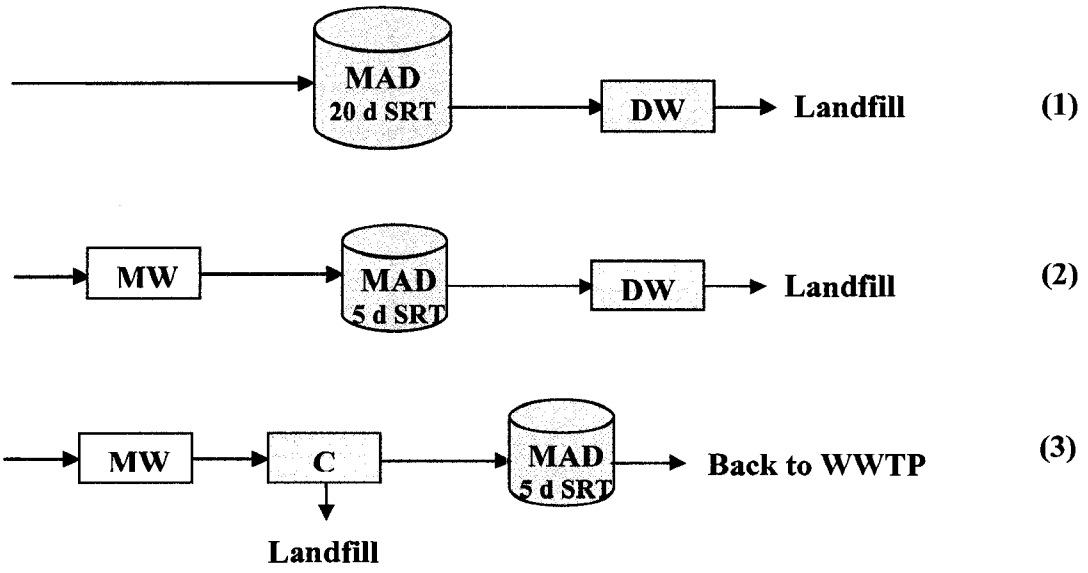

Figure 7.7: Schematic diagrams of three different sludge digestion scenarios

The net energy required (E_{net}) can be formulated as follows:

$$E_{net} = E_{pretreatment} + E_{heat} + E_{digester} + E_{mixing} + E_{dewatering} - E_{CH_4} - E_{sink} \quad (1)$$

where $E_{pretreatment}$ is the energy input for MW pretreatment; E_{heat} is the heat required to heat sludge to digester temperature, $E_{digester}$ is all heat loss from the digester; E_{mixing} and $E_{dewatering}$ are the energy required for mixing and dewatering, respectively; E_{CH_4} is the energy recovery by methane production and E_{sink} is the accessible energy that was not used by the process and was estimated as the energy potential to cool TWAS from 175 to 35°C. This energy could be used elsewhere in the process to offset energy requirements such as $E_{digester}$ or energy in the plant for other purposes. These energy inputs and outputs are formulated by the following equations:

$$E_{pretreatment} = k_e * k_{MW} * M_s * C_{p,s} * (T_p - T_i) \quad (2)$$

$$E_{heat} = M_s * C_{p,s} * (T_p - T_i) / k_h \quad (3)$$

$$E_{digester} = U * SA * (T_r - T_a) \quad (4)$$

$$E_{mixing} = k_m * V_s \quad (5)$$

$$E_{CH_4} = h_m * Q_s * (S_{VS,i} - S_{VS,e}) * M \quad (6)$$

$$E_{sink} = M_s * C_{p,s} * (T_p - T_r) * k_h \quad (7)$$

$$E_{dewatering} = k_d * Q_s \quad (8)$$

Where M_s and Q_s are the mass and volumetric flow rates of influent sludge (kg/d and m^3/d, respectively); T_p, T_i, T_r, T_a are pretreatment, influent sludge, reactor and ambient temperatures, respectively (°K); k_e (1/0.7), k_{MW} (1/0.95), k_h (0.70) are energy efficiency constants to convert electricity to MW energy, MW energy onto samples and heat exchanger efficiency, respectively; $C_{p,s}$ ($4.184*10^{-3}$ MJ/kg sludge/°K) is the specific heat capacity of sludge which was taken to be the same as water; k_m (1.138 MJ/d/m^3), h_m (37 MJ/m^3), k_d (11.48 MJ/m^3) are specific energy constants for mixing, methane and dewatering, respectively; M is the methane yield factor (m^3 CH_4 produced/g VS removed); $S_{VS,i}$ and $S_{VS,e}$ are VS of influent and effluent, respectively (g VS/m^3 sludge); U (0.216 MJ/d/m^3/°C) is overall heat coefficient for a well insulated digester and SRT of digester is in d (Owen,

1982, Droste, 1997, Barber, 2005 and Environmental Waste International). Sludge density was assumed to be 1000 kg/m^3. Energy of the centrifuging step for digesting of supernatant scenario was calculated by using the dewatering equation (Equation 8). For dewatering and centrifuging steps calculations are very rough estimations. For all scenarios the same amount of energy input for dewatering and centrifuging was used. However, previously reported capillary suction time CST experiments (Toreci *et al.*, 2007) demonstrated that dewatering properties of MW pretreated digested TWAS improved dramatically over the control. However there is no direct information on how to integrate CST results to actual energy input for dewatering. In pilot scale applications using other pretreatment methods, polymer addition for dewatering decreased or dewatered digestate sludge concentrations increased (Barber, 2005).

Previously, MW pretreatment at 175°C with 3.75°C/min MW intensity exhibited the best improvement in MAD biogas production at a 5 d SRT (Toreci *et al.*, 2009) in a complete mixed digester. Data from this condition were used for energy calculations. The primary sludge calculations were done by assuming the biogas yield is 1.00 L biogas/g VS destroyed and 35% methane in biogas from primary sludge. Initial VS concentration in WW was considered as 100 g/m^3 and VS removal efficiency from primary sludge was taken as 70% Parkin and Owen, 1986 and Malina and Pohland, 1992). For the supernatant digestion scenario the same MW pretreatment conditions were taken as the base. However no data was available for continuous reactor efficiencies for supernatant digestion. Therefore, batch reaction results at that 5th day of BMP assay was used for energy calculation purposes. Table

7.5 contains energy calculation results of these 3 scenarios for 20 m^3/d primary sludge and 30 m^3/d TWAS inlet flow assuming ROPEC TWAS at 6 % TS.

Table 7.5: Energy requirements for different scenarios

Scenario	$E_{pretreatment}$†	E_{heat}	$E_{digester}$	E_{mixing}	$E_{dewatering}$	E_{CH4}	E_{sink}	E_{net}
(1)	-	$2.99*10^3$	$6.84*10^3$	$1.14*10^3$	$7.39*10^2$	$5.03*10^3$	-	$1.85*10^3$
(2)	$2.83*10^4$	$1.20*10^3$	$2.71*10^3$	$2.84*10^2$	$7.39*10^2$	$5.13*10^3$	$1.23*10^4$	$1.58*10^4$
(3)	$2.83*10^4$	$1.20*10^3$	$2.54*10^3$	$2.57*10^2$	$7.39*10^2$	$4.88*10^3$	$1.23*10^4$	$1.59*10^4$

† Unit is MJ/d for all data.

Even at a conversion efficiency of 95% for MW energy transfer into the sludge, MW irradiation is an energy intense pretreatment method but requires less energy than conventional thermal heating. Due to the high energy requirement for MW pretreatment, net energy demands for scenarios (2) and (3) were found to be higher than digestion of untreated sludge. On the other hand pretreating sludge with MW improved many aspects of sludge management. First of all, due to improvements in hydrolysis, SRT could be decreased to 5 days without any significant changes in the digestate characteristics which would decrease the digester mixing energy and energy loss though external digester walls. There is no need for heating sludge prior to entering the digester moreover there is extra heat (E_{sink}) that could also be used throughout the plant. This analysis assumed E_{sink} which is 43% of the $E_{pretreatment}$ could be recovered in the plant to offset heat requirements to heat primary sludge as well as heat loss in the digester and other energy demands. These results are based on TWAS which

was highly biodegradable with a young age (5 d SRT). If older and less biodegradable TWAS were used, MW pretreatment could have more impact on increasing biogas production and improving sludge stabilization more. Another very important advantage of digestion of MW pretreated sludge is that it can be used in land application due to its Class A designation. Supernatant digestion had the highest energy requirement overall; however, it is important to acknowledge that the biogas production values for this analysis were taken from batch tests and due to mild inhibition this value was lower than would likely be achieved.

Although the net energy requirement is higher with MW pretreatment it is important to consider other parameters such as lower polymer requirements, less and more concentrated sludge for disposal and associated decrease in transportation costs and landfill tipping fees to assess the overall picture. Due to difficulties in quantifying the energy requirement of transportation and landfill tipping fees, energy requirements were converted to dollar costs for the Ottawa region. The electricity cost was taken from Hydro Ottawa as $0.05/kWh. For transportation to a landfill the distance was assumed to be 30 km from the WWTP and a typical truck can hold 12.3 m^3 of sludge (Baaj *et al.*, 1996). According to Statistics Canada average truck fuel consumption was estimated to be 2.8 km/L in 2001. Price of diesel fuel was assumed to be $1.3/L. Therefore the fuel cost of one round trip to the landfill was calculated to be $27.86. The overhead transportation cost including the driver's wage and truck cost was assumed to be $90/h. With an average speed of 50 km/h and 20 minutes of waiting time at the landfill, the transportation cost for one round trip to the landfill was calculated to be $135. According to Ottawa Valley Waste Recovery center for residential

organic materials, the landfill tipping fee is $55/tonne. For landfill tipping cost calculations a more generous $45/tonne fee was used. Previously it was reported that biosolids concentration after dewatering was improved 5-7% when ultrasound pretreatment method was used prior to digestion (Barber, 2005). Decrease in polymer consumption was also reported as 31%. Using this information, improvement in biosolids concentration was taken as 6% (from 13 to 19% TS) for dewatering digestate of mesophilic digestion with MW pretreatment. Polymer consumption was not taken into consideration.

Cost analysis was done for three different sizes of communities with daily WWTP sludge flow rates for 25,000, 500,000 and 1,000,000 residential populations. Primary sludge production was assumed to be 80 g/cap/d. As a rule of thumb in secondary sludge production, for every kg of BOD_5 removed 0.6 kg TS is produced (Droste, 1997, Metcalf & Eddy, 1991). If 0.01 kg BOD_5/cap/d was assumed, then for populations of 25,000, 500,000 and 1,000,000, daily primary sludge production would be 2, 40 and 80 m^3/d and daily secondary sludge production (5% TS) would be 3, 60 and 120 m^3/d, respectively. Table 7.6 shows net energy requirements, cost of electricity, transportation, fuel, landfill fees and overall cost for these three sludge flow rates.

As long as the excess energy (E_{sink}) can be used efficiently, digestion with MW pretreatment becomes very feasible for all sludge flow rates. For all flow rates studied, digestion of primary sludge combined with whole TWAS pretreated with MW pretreatment at 175°C was found to be the most economical digestion scenario which reduces overall cost more than 58% since the end product is a valuable product which eliminates the transportation and landfilling.

Table 7.6: Cost analysis of different scenarios for different sludge flow rates

Daily total sludge flow rate (Q_s)	Scenario	E_{net} (MJ/d)	Electricity cost ($/d)	Biosolids volume (m^3/d)	Transportation cost ($/d)	Fuel cost ($/d)	Landfill tipping cost ($/d)	Total cost ($/d)	Cost per unit flow ($/$m^3$)
5 m^3/d	(1)	$1.46*10^3$	20.2	0.77	6.8	1.4	34.6	63.0	12.6
	(2)	$1.89*10^3$	26.3	0.53	-	-	-	26.3	8.8
	(3)	$2.22*10^3$	30.8	0.69	-	-	-	30.8	10.3
100 m^3/d	(1)	$1.05*10^4$	146.2	15.38	135.8	23.0	692.3	1002.4	10.02
	(2)	$3.05*10^4$	423.8	10.52	-	-	-	423.8	7.1
	(3)	$3.75*10^4$	520.9	13.81	-	-	-	520.9	8.7
200 m^3/d	(1)	$1.66*10^4$	230.2	30.77	271.7	56.1	1384.6	1942.5	9.7
	(2)	$5.92*10^4$	822.9	21.05	-	-	-	822.9	6.9
	(3)	$7.33*10^4$	1098.7	27.62	-	-	-	1098.7	8.5

Supernatant digestion with MW pretreatment appears to be energy intense. The disadvantage of scenario (3) is that biosolids were not stabilized completely; therefore, it may require alterations to be classified as Class A which was not taken into consideration during cost analysis; however, it has a potential for other purpose usage due to pathogen removal by MW treatment. Cost per unit flow of supernatant digestion is higher than that of primary and whole TWAS digestion with MW pretreatment but it is still less than that of digestion with no pretreatment. It appears to be 43% more efficient than untreated sludge digestion. This makes supernatant digestion also economical option for sludge stabilization and due to its smaller reactors it requires less space in a wastewater treatment plant which is also another advantage of this process.

Cost per unit flow for all scenarios slightly decreases as flow rate increases which was expected. Digestion of primary sludge and TWAS MW pretreated at 175°C was found to be the most economical option among the scenarios studied.

7.5 CONCLUSIONS

From BMP tests on the soluble portion of sludge pretreated with high temperature MW:

The degree of inhibition was very small for 6% TWAS supernatant pretreated at 175°C with both MW intensities, whereas that for 11.85% TWAS supernatant pretreated with the same conditions was higher.

MW temperature had greater impact on removing supernatant from sludge than MW intensity. The overall improvement in dewaterability for 6% TWAS treated with MW and

concentrated sludge first to 11.85% and then microwaving showed similar results; however, at lower treatment temperatures the difference on degree of separation between these two methods was more pronounced.

At day 20, pretreatment at 150°C with low MW intensity showed better results in supernatant digestion in terms of higher biogas production percentage. Supernatant pretreated at this condition produced 90% more biogas than obtained from the same volume of supernatant obtained from raw TWAS.

Energy calculations showed that MW pretreatment requires 944 MJ/m^3 sludge. A case study for cost analysis reveals that the most feasible scenario is the digestion of primary sludge combined with TWAS pretreated with MW at 175°C which reduces cost more than 58% due to Class A biosolids production. Digestion of only supernatant was also found to be more economical than untreated digestion which reduces cost more than 43%.

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CHAPTER 8:

Conclusions and Recommendations

8.1. CONCLUSIONS

This research was conducted to understand the effect of high temperature (>100°C) microwave (MW) pretreatment on thickened waste activated sludge (TWAS) characteristics as well as mesophilic anaerobic digestion (MAD) efficiency. The experiments were performed in three major phases to achieve this objective, and can be described as batch, semi-continuous and ultrafiltration (UF) tests. The main conclusions can be summarized as the following:

- TWAS solubilization improves as MW pretreatment temperature increases and MW intensity decreases. The highest increase in solubilization was observed with MW pretreatment at 175°C with 3.75°C/min intensity. At this condition, TWAS had soluble chemical oxygen demand (sCOD) to total COD (tCOD) ratios of 0.46 ± 0.06 and 0.57 ± 0.04 which were 4.5 ± 0.8 and 8.8 ± 0.9 fold greater than untreated TWAS for 6.0 and 11.8% total solids (TS) concentrations, respectively.

- According to three-factor fixed effect ANOVA, the main effects or MW temperature (T), MW intensity (I), sludge concentration (C) and T:I and T:C interactions as well as T:I:C interaction are significant on COD solubilization at a 94% confidence interval.

- Good acclimation is very important to minimize and/or eliminate methanogenic inhibition.

- 31 ± 6% more biogas can be produced with TWAS pretreated to 175°C at the 18th day of the BMP test.

- BMP assay for the soluble portion of TWAS showed that TWAS pretreated to 150°C at low MW intensity can produce 90% more biogas than that obtained from the same volume of supernatant obtained from raw TWAS.

- From semi-continuous digestion experiments it was concluded that sludge retention time (SRT) can be reduced to 10 and 5 days with MW pretreatment at 175°C with similar VS removal efficiency of untreated sludge single-stage digestion.

- MW pretreatment with low MW intensity (1.25°C/min) showed negative effect on semi-continuous MAD.

- Dual -stage digestion compared to single-stage digestion had a slight advantage on MAD VS stabilization efficiency when no MW pretreatment was applied. However, with MW pretreatment single stage digesters preformed better than dual stage digesters.

- Capillary suction time (CST) values of digestate from MW pretreated digesters were considerably shorter in all digester configurations at all SRTs compared to that of digestates from untreated TWAS systems.

- Although for high and low MW intensities sCOD concentrations were very similar their soluble organic (sCOD, soluble protein, soluble sugar and total volatile fatty acid

(tVFA)) distributions were very different to each other confirming that MW intensity has an impact on molecular breakdown path.

- First-order model fit was found to underestimate the rate constants and tended to underestimate the exponential phase biogas production but fit the tail section of the biogas curve more accurately. Zero-order kinetics better explained the nature of initial rapid degradation phase. It was concluded that high temperature MW pretreatment improves degradation rate; however, lowering MW intensity from 3.75 to 1.25 °C/min did not have an effect on degradation rate.

- MW intensity between 1.25 and 3.75 °C/min has an effect on overall biodegradability (Mw < 5 μm) and refractory organic concentration; however, it does not have a significant affect on overall cumulative biogas production (CBP).

- Energy calculations showed that MW pretreatment requires 944 MJ/m^3 sludge. MW irradiation is an energy intense pretreatment method but less than conventional thermal heating.

- Due to the high energy requirement for MW pretreatment, for daily flow rate of 20 m^3/d primary sludge and 30 m^3/d TWAS the net energy demands for scenarios (2) and (3) were found to be higher than digestion of untreated sludge. But it is important to acknowledge the advantages of MW pretreatment method such as lower SRT, smaller digester concurrently a decrease in the digester mixing energy and energy loss though external digester walls, probability of producing Class A sludge, better dewaterability

characteristics of digestate concurrently lower transportation costs and landfill tipping fees, etc.

- From cost analysis it was found that as long as the excess energy (which was 43% of pretreatment energy) can be used efficiently digestion with MW pretreatment becomes 58% more economical for all sludge flow rates studied since the end product is a valuable product which eliminates the transportation and landfill tipping costs.

- Digestion of only supernatant was found to be more economical than untreated sludge digestion and it reduces more than 43% of overall cost however it is more expensive than primary sludge and MW pretreated whole TWAS digestion.

- At this time, MAD of TWAS with MW pretreatment at 175°C with 3.75°C/min MW intensity is recommended as the best and economical way to increase solubilization and enhance biogas production from TWAS digestion.

8.2. RECOMMENDATIONS

MW pretreatment is still a new method for sludge stabilization and there are many issues that still need to be explored.

Studies with MW pretreatment for sludge stabilizations were initially focused on temperatures lower than 100°C and this research is the only one that explored high temperature (> 100°C) MW irradiation. Most of these studied sludge that has a very young age (5-7 days of SRT). It is recommended to examine the effects of MW pretreatment on more mature sludge that has has a longer SRT and will be relatively less biodegradable.

Research done on MW pretreatment has been applied to mesophilic digestion. MW pretreatment and its effect on thermophilic digestion should also be considered. Combination of mesophilic and thermophilic dual digestion with MW pretreatment which has the potential to improve the efficiency of digestion should also be investigated.

Other pretreatment alternatives such as addition of chemical agents with MW pretreatment at different temperatures and intensities could enhance solubilization and biodegradability as well as dewaterability. The effects of these combinations of pretreatment methods should be examined with mesophilic and thermophilic digestion.

There is still need for better understanding of interaction of extracellular polymeric substances and cations with MW pretreatment. More exploration should be done on floc matrix and its interaction to MW irradiation.

Knowledge on athermal effect of MW irradiation on sludge is still very limited which needs to be explored for better understanding of organic materials' hydrolysis by MWing.

Impact of MW at other frequencies (ie.10 MHz) is also unknown and should be investigated.

APPENDIX A:

Experimental Setup

A.1 MICROWAVE PRETREATMENT

Through out the research, microwave (MW) pretreatments were carried out with a Mars 5© (MW Accelerated Reaction System; CEM Corporation) MW oven (Figure A-1). Mars 5© has a frequency of 2450 MHz and can deliver 1200 W±15% of MW energy at full power with complete MW penetration of the 100 mL sample vessels (Figure A-2). With its fiber optic (the Thermo-Optic™) temperature and electronic sensor pressure sensors it is possible to monitor and control operating conditions up to 250°C and 34.5 bar. Pressure vessels were filled with 70 mL of TWAS and a temperature and pressure profile was programmed and monitored.

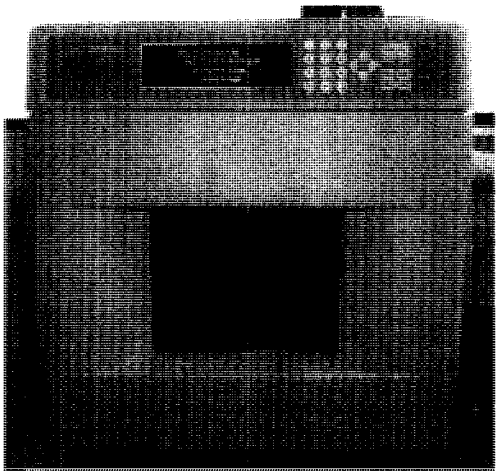


Figure A-1: Mars 5 microwave oven

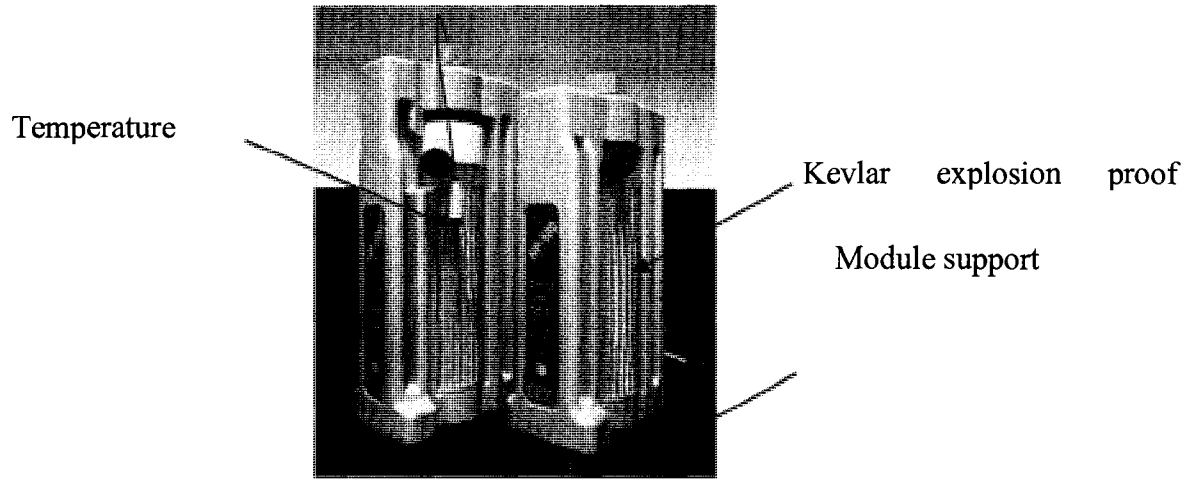


Figure A-2: Control vessel and standard vessel

A.2 INOCULUM ACCLIMATION

10 L anaerobic semi-continuous reactor was used for inoculum and it was fed with MW-irradiated sludge at 175°C for acclimation (Figure A-3). It was run at approximately 20 d SRT by gradually increasing the influent flow rate over a period of more than 4 months. The initial source of inoculum was from effluent line of the MAD at ROPEC where primary sludge and TWAS are treated in a 58/42 (v/v) ratio at a SRT of 15- 20 days. Organic loading rate (OLR) of acclimation reactor was 2.0 ± 0.04 g TCOD/ L. d. The concentration of feed was 3% TS (w/w), which can be considered as a typical sludge concentration in a full-scale sludge digester. When the inoculum was being acclimatized to the MW-irradiated WAS, daily biogas production, biogas composition and VFA readings reached a stable value.

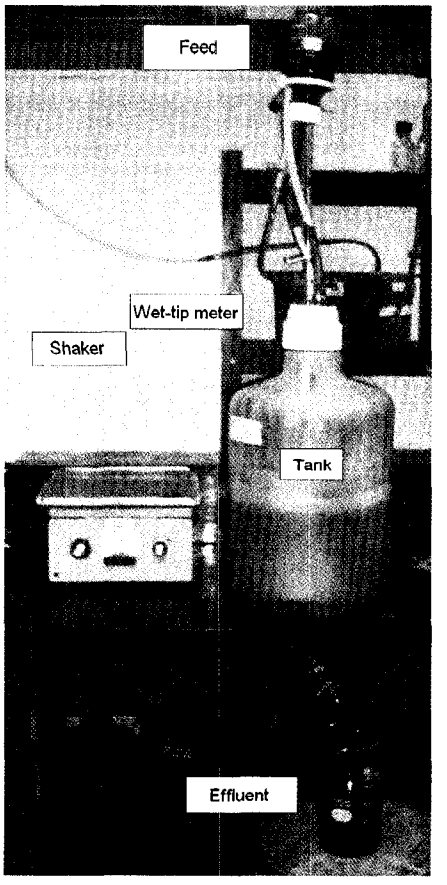


Figure A-3: Inoculum reactor set up

A.3 BATCH ANAEROBIC DIGESTION

The BMP analysis was performed using 500 mL and 250 mL Kimax glass bottles with butyl rubber stoppers (Wheaton (22400-503) lyophilization stopper with screw cap size of 43 mm, VWR, Montreal, QC, Canada) and propylene caps (Wheaton (240746) screw cap size 45 mm, VWR, Montreal, QC, Canada) as reactors. For sludge digestion, the concentration of TWAS used in the BMP reactors was set at 3% which necessitated diluting the sludge distilled water after pretreatment. A 280 mL volume of diluted (as needed), pretreated

TWAS was added to 70 mL of acclimated inoculum in each 500 mL reactor and mixed. For supernatant digestion, TWAS was centrifuged at 6513 RCF for 30 minutes and it was filtered through 0.45 μm GF/C grade binder free glass microfibre filters. A volume of 140 mL of supernatant was mixed with 35 mL of acclimated inoculum in 250 mL glass bottle. Nitrogen was bubbled through the BMP mixture to prevent air exposure. An equal volume mixture of potassium and sodium bicarbonate was added to provide 4000 mg/L of bicarbonate alkalinity and the reactors were sealed. BMP tests were performed in duplicate at 35 ± 1°C on a New Brunswick rotary shaker at a speed of 95 rpm (Figure A-4).

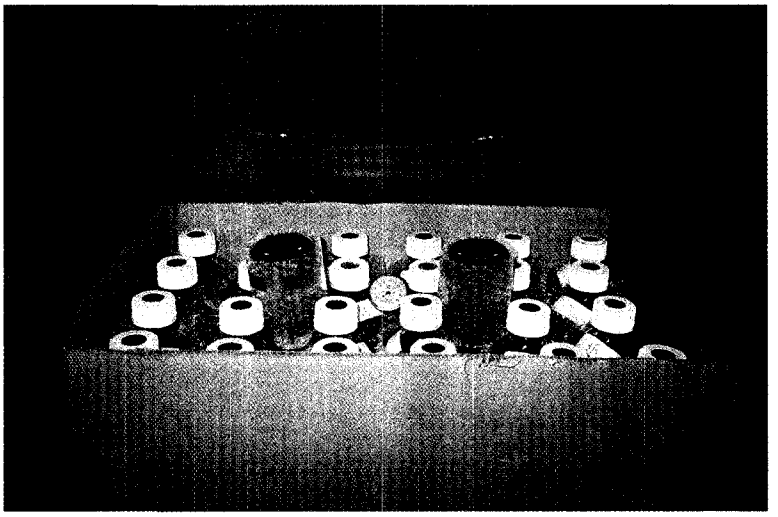
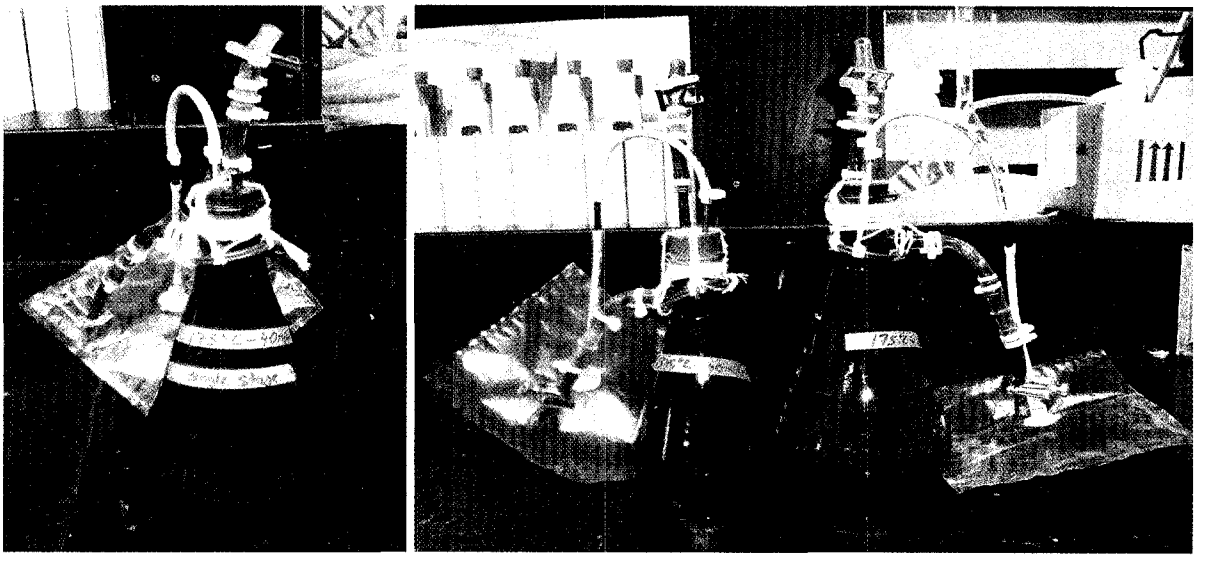


Figure A-4: Batch reactors in rotary shaker

A.4 SEMI-CONTINUOUS ANAEROBIC DIGESTION

Side armed Erlenmeyer flasks which were sealed with two-hole rubber stoppers were used as digesters. The volume of the flasks used for single stage and secondary dual stage digesters were 1 L and the acid phase digesters of the dual stage were 0.5 L flasks

(Pyrexplus plastic coated graduated flasks, VWR, Montreal QC, Canada) (Figure A-5). Ports in the rubber stopper (two-hole black rubber stoppers, VWR, Montreal, QC, Canada) were used to collect biogas and to withdraw sludge. Digesters were fed semi-continuously (i.e. one feeding everyday) by using the side arm of the flask. 1 L tedlar bags (Tedlar gas sampling bags, Chromatographic Specialties Inc., ON, Canada) were used for biogas collection and biogas production was measured daily by using a manometer. All digesters were started with acclimatized inoculum and TWS was diluted to 3% total solids (TS) prior to feeding. All reactors were kept at 35°C in a New Brunswick incubator at a rotational speed of 95 rpm (Figure A-6). Single stage reactors were started at typical 20 day SRT. In the two phase digesters the primary acid phase digester was maintained at a 2 day SRT and its effluent was transferred to the secondary dual stage digester which was initially operated at an 18 day SRT.



(a) **(b)**

Figure A-5: Semi continuous (a) single and (b) dual anaerobic digesters

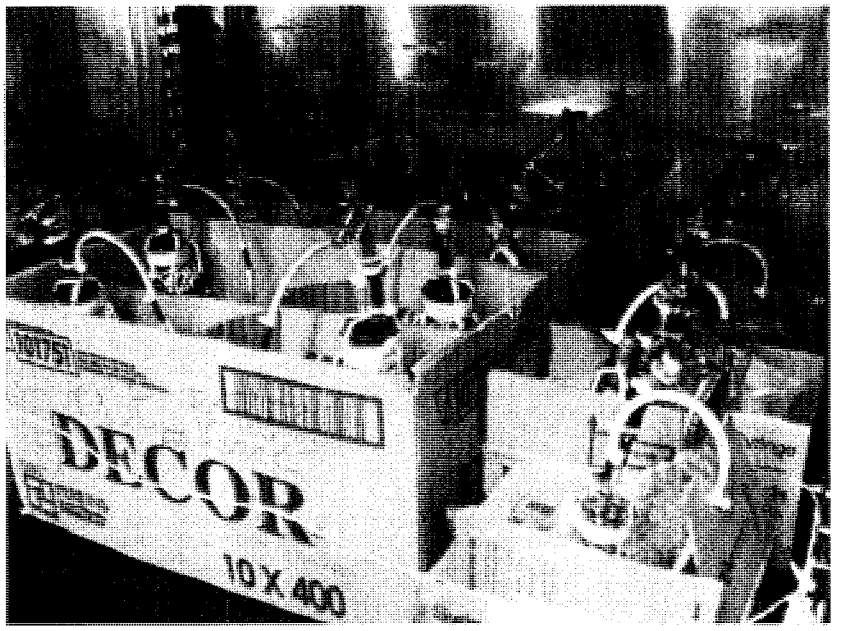


Figure A-6: All semi-continuous digesters in incubator

A.5 BATCH DIGESTION FOR SOLUBLE FRACTION OF TWAS

Samples were centrifuged at 5856 relative centrifugal force (RCF) for 20 minutes to remove supernatant. Supernatants primarily filtered through 5 μm pore size to discard any biomass residuals from the soluble phase. Due to clogging problems supernatant filtered through 5 μm were diluted with Milli-Q water with a ratio of 4.19:1 then filtered through 0.45 μm pore size (GN-6 Metricel S-Pack membrane) disc filters. For ultrafiltration (UF), 400 mL Amicon model 8400 stirred cells (Amicon Corp., MA, USA) with high recovery, low organic adsorption hydrophobic membranes (7.6 cm dia., Millipore, MA, USA) were used (Figure A-7). Supernatants filtered through 0.45μm were ultra-filtered from higher Mw cutoff to lower. Mw cutoffs used for UF are 300 kDa (PES300), 100 kDa (YM100), 10 kDa (YM10) and 1 kDa (YM1).

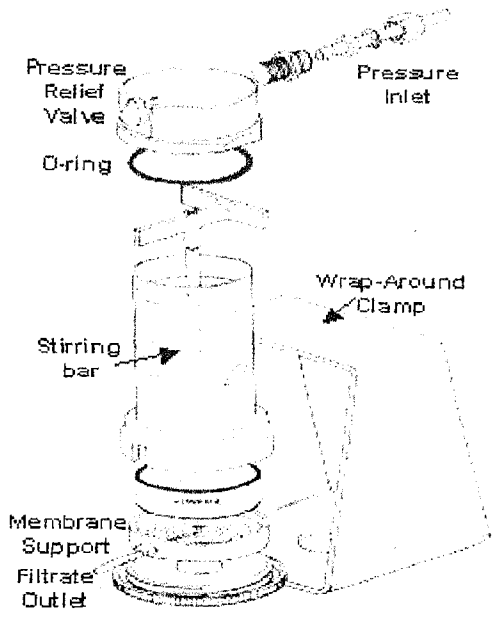


Figure A-7: Schematic diagram of Amicon model 8400 stirred UF cell

APPENDIX B:

Raw Data

In Appendix B data that has not been shown in the thesis is presented.

B.1 Batch Anaerobic Digestion of Sludge

B.2 Semi-Continuous Anaerobic Digestion

B.3 Batch Anaerobic Digestion of Supernatant

B.1 BATCH ANAEROBIC DIGESTION OF SLUDGE

Table B-1: Volatile fatty acid values during batch anaerobic digestion of sludge

	Before BMP April27, 2006			Week 1 May 4, 2006			Week 2 May 10, 2006			Week 3 May 19, 2006			Week 4 May 24, 2006			Week 5 May 31, 2006		
	AA*	PA	BA	AA	PA	BA	AA	PA	BA	AA	PA	BA	AA	PA	BA	AA	PA	BA
control	355	29		966	1087	52	781	53					45	3		0		
control	334	24		1069	1107	90	157	3		60			8			0		
110 °C-7.5 °C/min	2314	916	541	1991	1121		54			20			4			30		
111 °C-7.5 °C/min-d	2240	937	547	2015	1102		20			19	1		0			0		
150°C-7.5 °C/min	2562	798	705	2353	1195	319	25	1031		17			0			0		
150°C-7.5 °C/min-d	2998	941	821	2482	1203	368	15	890		17			6			0		
175°C-7.5 °C/min	3147	924	608	2710	1181	547	222	1490		18			4			75		
175°C-7.5 °C/min-d	3260	953	639	2650	1156	570	78	1405		73	17		10			0		
110 °C-3.75°C/min	2721	1393	719	2418	1147	319	23	26		20			14			0		
111 °C-3.75°C/min-d	2725	1394	717	2203	1106	273	23	5		23			14			0		
150°C-3.75°C/min	2527	1255	759	2304	1108	404	16	1407		22	2		5			0		
150°C-3.75°C/min-d	2469	1236	749	2352	1096	524	20	1299		21			0			0		
175°C-3.75°C/min	2333	1116	799	2768	1065	624	313	1421	41	30	1678		13			0		
175°C-3.75°C/min-d	2212	1078	780	2889	1061	654	157	1373		34	1660		9			19		
control-c	574	210	169	1029	904	264	37	44		12	5		19			0		
control-c	625	210	169	1021	872	70				8			0			0		
110°C-7.5 °C/min-c	4401	1718	1093	1622	909	225	39	142		12			20			0		
110°C-7.5 °C/min-c-d	4438	1679	1136	1710	929	322	39	519		12			7			0		
150°C-7.5 °C/min-c	4148	1248	723	2146	978	492	33	1436		20			8			0		
150°C-7.5 °C/min-c-d	4250	1232	744	2195	990	510	41	1342		22			15			0		
175°C-7.5 °C/min-c	3187	796	442	2119	911	434	17	1287					8			61	3	
175°C-7.5 °C/min-c-d	3812	983	527	1776	909	330	9	1106		16			12			0		
110°C3.75°C/min-c	3347	1611	929	1690	917	168	5	26		10			7			0		
110°C3.75°C/min-c-d	3546	1670	980	1754	903	374	81	900		12			8			0		
150°C-3.75°C/min-c	4428	1202	513	2128	1020	497	36	1271		19			16			0		
150°C-3.75°C/min-c-d	4864	1298	548	2210	1040	541	234	1412		7			8			0		
175°C-3.75°C/min-c	4216	1609	736	2448	961	504	104	1144		29	1439		8			0		
175°C-3.75°C/min-c-d	4384	1702	785	2534	905	532	74	1048		36	1402		21			0		

*AA=acidic acid, PA=propionic acid, BA=butyric acid in mg/L

Table B-2: Methane production (%) during batch anaerobic digestion of sludge

	Week 1 May 4, 2006	Week 2 May 10, 2006	Week 3 May 19, 2006	Week 4 May 24, 2006	Week 5 May 31, 2006
control	62.3	60.2	56.6	57.1	56.4
control	62.3	60.2	56.6	57.9	56.7
110 °C-7.5 °C/min	55.0	65.0	58.5	58.1	59.8
111 °C-7.5 °C/min-d	58.3	64.8	58.7	58.9	60.3
150°C-7.5 °C/min	49.7	66.4	61.8	59.7	59.4
150°C-7.5 °C/min-d	51.3	65.9	62.6	58.6	62.0
175°C-7.5 °C/min	44.0	68.1	67.0	60.6	61.5
175°C-7.5 °C/min-d	43.8	69.1	66.0	62.5	62.1
110 °C-3.75°C/min	55.5	68.6	57.4	57.4	58.2
111 °C-3.75°C/min-d	53.2	70.1	59.0	58.5	58.6
150°C-3.75°C/min	45.4	65.6	65.1	63.5	63.4
150°C-3.75°C/min-d	45.5	66.7	64.4	61.3	64.0
175°C-3.75°C/min	31.8	71.0	63.3	66.7	66.3
175°C-3.75°C/min-d	30.3	73.8	63.5	66.7	66.6
control-c	59.1	62.1	57.4	56.7	61.2
control-c	58.8	63.6	57.2	57.0	60.3
110°C-7.5 °C/min-c	46.6	69.1	60.6	59.4	57.2
110°C-7.5 °C/min-c-d	44.4	69.4	60.5	57.7	57.6
150°C-7.5 °C/min-c	35.9	73.1	70.9	62.7	56.5
150°C-7.5 °C/min-c-d	35.6	71.2	66.3	62.8	62.4
175°C-7.5 °C/min-c	34.3	66.6	70.0	62.7	62.9
175°C-7.5 °C/min-c-d	48.3	64.8	65.0	60.2	59.3
110°C3.75°C/min-c	55.8	73.2	62.2	57.4	56.9
110°C3.75°C/min-c-d	40.1	67.1	56.4	65.3	61.2
150°C-3.75°C/min-c	38.2	67.8	67.6	60.4	61.2
150°C-3.75°C/min-c-d	38.6	68.0	67.2	62.5	64.0
175°C-3.75°C/min-c	33.6	68.6	64.0	62.8	62.4
175°C-3.75°C/min-c-d	28.6	69.2	67.0	65.3	62.9

B.2 SEMI-CONTINUOUS ANAEROBIC DIGESTION

Table B-3: Sludge characteristics during semi-continuous anaerobic digestion

	20 day SRT					10 day SRT				5 day SRT		
Alkalinity												
	13-Jun	20-Jun	27-Jun	03-Jul	11-Jul	1-Aug	8-Aug	14-Aug	21-Aug	15-Sep	19-Sep	21-Sep
C	4659	4894	5108	4820	5040	4109	4494	3838	3467	2800	3153	3153
High Int.	4863	4950	5154	5235	5400	5332	5512	5200	5363	4117	4656	4630
Low Int.	4630	4950	5134	5681	5477	4788	4992	5051	5403	3480	4009	4189
C-A	2445	2652	2376	2489	2676	2370	2600	1618	1790		2474	2478
High Int.-A	2661	2510	3472	3687	3001	2880	3170	2866	3231		2900	2928
Low Int.-A	2326	2663	2815	3467	2912	3159	2713	2976	3413	2217	2515	2520
C-M	4417	4532	4653	4810	4531	4687	4550	4286	3989	3339	3328	3451
High Int.-M	4455	4785	5289	5489		2896	5233	4931	5342	3816	3999	4089
Low Int.-M	5460	4611	5164	5383	5274	4724	4900	5111	5128	3313	3523	3731
C-F				1998	1580		1878		1185		1685	1667
High Int.-F				2054	1357		1589	2011	1453		2150	2144
Low Int.-F				2614	1739			2790	2967		2071	2071
Ammonia												
	15-Jun	20-Jun	26-Jun	4-Jul	13-Jul	2-Aug	8-Aug	15-Aug	22-Aug	15-Sep	19-Sep	21-Sep
C	1276	1458	1923	1932	1686	1629	1127	1350	1081	2501	1547	1574
High Int.	1181	1543	1696	1681	1657	1534	1881	1518	1673	2136	1900	1800
Low Int.	1338	1436	1836	1609	1638	1238	1357	1535	1507	1703	1504	1477
C-A*	1017	977	1060	1029	1140	836	849	624	647		1201	1155
High Int.-A	1280	1200	1777	1997	1301	990	1297	1204	1295	1574	1295	1347
Low Int.-A	1107	1307	1441	1643	1016	1150	1183	1318	1472	1211	1306	1319
C-M	1295	1285	1539	1497	1490	966	1309	1217	1249	1111	1153	1210
High Int.-M	1336	1529	1747	1681	1469	1157	1612	1444	1759	1329	1400	1443
Low Int.-M	561	1459	1685	1701	1470	1189	1384	1509	1565	994	1508	1453
C-F			904	694	732		747	240	409		642	686
High Int.-F			1113	507	966		755	880	726		1080	1093
Low Int.-F			1183	971	709		766	1246	1423		873	1013

VFA												
	3-Jul	6-Jul	10-Jul	13-Jul	17-Jul	14-Aug	17-Aug	21-Aug	24-Aug	18-Sep	21-Sep	24-Sep
C	88	58	70	67	79	41		41	0	1087	1251	1232
High Int.	23	8	28	20	11	0	0	0	70	98	71	87
Low Int.	20	16	15	16	10	0	0	0	25	658	744	789
C-A	3098	3319	2399	2380	2692	1878	1829	1805	1936	1271	1421	1760
High Int.-A	3381	3513	3174	3174	3310	3402	2972	3875	3930	2899	2642	2479
Low Int.-A	4108	3578	2803	3092	3846	4292	4620	4747	4767	3324	3101	3095
C-M	102	45	36	14	51	28	0	347	361	649	809	1109
High Int.-M	17	17	18	29	16	5	25		9	988	945	1264
Low Int.-M	34	29	26	26	9		19	4	6	1350	1346	1483
C-F	2616	2822	1906	1957	2103	914	946	1285	1428	1993	1835	1884
High Int.-F	2868	1853	2088	2721	2530	3675	3729	3500	3387	3169	2834	3185
Low Int.-F	3594	1879	2400	2319	3331	4067	3832	3985	4631	2843	2716	2954
pH												
	26-Jun	29-Jun	3-Jul	6-Jul	10-Jul	10-Aug	14-Aug	17-Aug	21-Aug	18-Sep	21-Sep	25-Sep
C	7.5	7.5	7.4	7.5	7.5	7.3	7.3	7.2	7.2	7.0	7.0	7.1
High Int.	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.4	7.4	7.4
Low Int.	7.5	7.4	7.5	7.5	7.6	7.5	7.5	7.5	7.5	7.3	7.3	7.4
C-A	6.6	6.7	6.7	6.7	6.7	6.6	6.4	6.5	6.6	6.8	6.9	6.8
High Int.-A	6.9	6.9	6.7	6.7	6.7	6.7	6.8	6.8	6.8	6.8	6.9	6.9
Low Int.-A	6.7	6.8	6.8	6.6	6.9	6.6	6.7	6.6	6.7	6.6	6.6	6.7
C-M	7.5	7.5	7.5	7.5	7.6	7.5	7.4	7.3	7.3	7.2	7.2	7.3
High Int.-M	7.7	7.6	7.6	7.7	7.6	7.5	7.5	7.6	7.5	7.4	7.3	7.5
Low Int.-M	7.6		7.6	7.7	7.6	7.5	7.5	7.6	7.5	7.2	7.2	7.3
C-F		7.0	7.0	7.3	7.1	7.2	7.3	7.1	7.3	6.5	6.5	6.6
High Int.-F	7.2	7.4	7.2	7.2	7.2	7.1	7.2	7.2	6.8	6.6	6.5	6.6
Low Int.-F	7.3	7.0	7.0	7.4	7.1	7.1	7.2	7.2	6.9	6.5	6.6	6.5
VS/TS												
	15-Jun	22-Jun	29-Jun	6-Jul	13-Jul	10-Aug	17-Aug	24-Aug	29-Aug	14-Sep	21-Sep	28-Sep

C	0.54	0.54	0.54	0.52	0.54	0.58	0.57	0.57	0.55	0.59	0.59	0.59
High Int.	0.53	0.52	0.51	0.49	0.51	0.55	0.55	0.55	0.56	0.55	0.55	0.53
Low Int.	0.52	0.52	0.50	0.57	0.51	0.56	0.56	0.56	0.55	0.56	0.56	0.55
C-A	0.62	0.62	0.69	0.63	0.64	0.64	0.64	0.63	0.61	0.61	0.62	0.61
High Int.-A	0.60	0.57	0.56	0.62		0.62	0.62	0.61	0.60	0.59	0.59	0.58
Low Int.-A	0.61	0.60	0.57	0.62	0.61	0.63	0.63	0.63	0.62	0.60		0.60
C-M	0.54	0.54	0.54	0.54	0.54	0.57	0.57	0.56	0.55	0.56	0.56	0.57
High Int.-M	0.52	0.52	0.50	0.51	0.52	0.57	0.54	0.56	0.57	0.56	0.56	0.55
Low Int.-M	0.52	0.52	0.51	0.51	0.52	0.57	0.56	0.57	0.56	0.58	0.58	0.56
C-F	0.64	0.65	0.67	0.68	0.69	0.66	0.67	0.67	0.65	0.66	0.66	0.66
High Int.-F	0.60	0.66	0.67	0.69	0.69	0.67	0.67	0.66	0.65	0.65	0.64	0.64
Low Int.-F	0.68	0.66		0.69	0.69	0.68	0.68	0.67	0.66	0.66	0.64	0.64

*A = (acidogenic) first reactor of dual digesters, M = (methanogenic) second reactor of dual digesters, F = feed

B.3 Batch Anaerobic Digestion of Supernatant

Table B-4: Volatile fatty acid values during batch anaerobic digestion of supernatant

	Before BMP April27, 2006			Week 1 May 4, 2006			Week 2 May 10, 2006			Week 3 May 19, 2006			Week 4 May 24, 2006			Week 5 May 31, 2006		
	AA*	PA	BA	AA	PA	BA	AA	PA	BA	AA	PA	BA	AA	PA	BA	AA	PA	BA
control	355	29	0	2246	996	643	65	193	0	1674	0	0	467	9	0	0	0	0
control	334	24	0	1987	967	164	72	247	0	2107	0	0	3	0	0	50	3	0
110 °C-7.5 °C/min	2314	916	541	2743	1222	564	60	1415	0	9	0	0	0	0	0	0	0	0
111 °C-7.5 °C/min-d	2240	937	547	2662	1165	715	126	1326	0	19	0	0	2	0	0	0	0	0
150°C-7.5 °C/min	2562	798	705	3360	1265	811	301	1355	0	35	1440	0	20	0	0	0	0	0
150°C-7.5 °C/min-d	2998	941	821	3404	1306	854	324	1465	124	0	1325	0	53	4	0	0	0	0
175°C-7.5 °C/min	3147	924	608	3865	1317	961	778	1345	656	44	2444	0	216	1963	0	841	0	0
175°C-7.5 °C/min-d	3260	953	639	3784	1256	979	1735	1366	1011	0	0	0	55	2204	0	281	1262	0
110 °C-3.75°C/min	2721	1393	719	2875	1251	807	372	1158	0	0	1484	0	18	5	0	4	0	0
111 °C-3.75°C/min-d	2725	1394	717	3093	1391	825	151	1228	0	192	0	0	2	0	0	0	0	0
150°C-3.75°C/min	2527	1255	759	3946	1397	972	764	1361	618	0	3037	0	161	1716	0	288	0	0
150°C-3.75°C/min-d	2469	1236	749	3503	1209	960	1106	1461	702	183	2506	0	112	2024	0	566	336	0
175°C-3.75°C/min	2333	1116	799	4021	1361	1092	14766	6842	3765	7245	2237	1607	58	2388	0	56	1869	0
175°C-3.75°C/min-d	2212	1078	780	3948	1342	1154	17632	7846	3748	4880	2256	1523	188	2581	0	124	2258	0
control-c	574	210	169	2091	1019	504	56745	42934	842	1593	1170	0	11	0	0	6	0	0
control-c	625	210	169	1726	1053	175	149722	12834	0	0	0	0	0	0	0	0	0	0
110°C-7.5 °C/min-c	4401	1718	1093	4044	1807	1328	2757	8179	2007	57	2783	0	64	2110	0	2	0	0
110°C-7.5 °C/min-c-d	4438	1679	1136	4422	1849	1639	2212	8483	3158	61	2894	0	191	2233	0	1	0	0
150°C-7.5 °C/min-c	4148	1248	723	5086	1921	1668	7238	7724	4436	93	3254	0	0	3228	0	184	2660	0
150°C-7.5 °C/min-c-d	4250	1232	744	4832	1786	1569	11064	8241	4954	2193	2508	121	312	3293	0	0	2967	0
175°C-7.5 °C/min-c	3187	796	442	5171	1679	1656	21241	6185	4502	0	0	0	5964	1804	1282	5211	1851	921
175°C-7.5 °C/min-c-d	3812	983	527	4848	1624	1691	22351	6628	4646	0	0	0	2514	1834	343	580	1890	0
110°C3.75°C/min-c	3347	1611	929	4199	1529	1407	1938	7431	3812	0	0	0	527	2497	0	187	64	0
110°C3.75°C/min-c-d	3546	1670	980	4126	1478	1331	0	0	0	134	322	2628	35	2859	0	178	1606	0
150°C-3.75°C/min-c	4428	1202	513	4816	1621	1123	365	1579	1132	341	3032	26	97	2936	0	0	2820	0
150°C-3.75°C/min-c-d	4864	1298	548	4787	1808	1638	1630	1976	1739	112	2443	0	91	4082	51	226	3658	0
175°C-3.75°C/min-c	4216	1609	736	4822	1851	1797	5015	2034	1804	5729	2380	1573	3513	2304	1572	773	2209	115
175°C-3.75°C/min-c-d	4384	1702	785	5020	1863	1842	5197	1959	1847	0	2434	1538	1293	2211	64	680	2439	0

*AA=acidic acid, PA=propionic acid, BA=butyric acid in mg/L

Table B-5: Methane production (%) during batch anaerobic digestion of supernatant

	Week 1 May 4, 2006	Week 2 May 10, 2006	Week 3 May 19, 2006	Week 4 May 24, 2006	Week 5 May 31, 2006
control	47.9	78.4	72.5	66.9	66.5
control	47.9	79.6	69.0	94.5	66.0
110 °C-7.5 °C/min	35.1	72.7	69.5	66.4	62.9
111 °C-7.5 °C/min-d	34.0	72.7	70.2	63.6	64.4
150°C-7.5 °C/min	26.9	75.8	71.1	70.3	62.9
150°C-7.5 °C/min-d	27.5	74.3	67.9	67.7	61.1
175°C-7.5 °C/min	21.4	7.4	67.2	66.6	69.3
175°C-7.5 °C/min-d	19.9	66.9	73.0	66.0	69.2
110 °C-3.75°C/min	32.5	76.1	71.9	65.0	61.0
111 °C-3.75°C/min-d	35.4	73.4	68.2	63.6	59.9
150°C-3.75°C/min	21.5	72.8	68.6	72.2	70.5
150°C-3.75°C/min-d	21.5	71.6	73.4	67.3	72.1
175°C-3.75°C/min	19.2	57.7	82.1	68.2	72.8
175°C-3.75°C/min-d	17.8	50.6	73.8	71.5	70.0
control-c	44.1	78.5	72.7	31.5	69.2
control-c	47.2	79.3	68.9	68.4	67.8
110°C-7.5 °C/min-c	25.1	75.8	65.9	69.1	68.8
110°C-7.5 °C/min-c-d	23.6	79.2	66.2	68.6	68.5
150°C-7.5 °C/min-c	17.7	72.7	70.7	68.5	70.1
150°C-7.5 °C/min-c-d	13.7	71.0	61.1	75.1	70.1
175°C-7.5 °C/min-c	12.6	16.3	17.5	22.4	54.0
175°C-7.5 °C/min-c-d	12.9	14.7	25.1	84.0	62.4
110°C3.75°C/min-c	23.9	73.9	68.0	64.6	77.7
110°C3.75°C/min-c-d	22.6	74.5	69.5	49.8	73.2
150°C-3.75°C/min-c	18.6	74.4	73.0	62.1	65.1
150°C-3.75°C/min-c-d	18.4	71.4	70.0	65.0	61.5
175°C-3.75°C/min-c	12.4	15.5	24.2	64.9	76.7
175°C-3.75°C/min-c-d	12.7	21.9	75.1	74.6	65.9

APPENDIX C:

Sample Calculation for Cost Analysis

C.1 ANAEROBIC DIGESTER DESIGN

A simple anaerobic digester was used for energy calculation purposes (Figure 1).

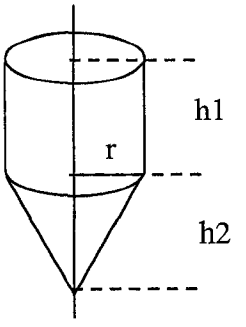


Figure 1: Schematic diagram of the reactor

Assumptions:

$$\left.\begin{array}{l} H = h1 + h2 \\ H/2r = 3/2 \text{ (based on egg-shaped reactors)} \\ r/h2 = 1/2 \end{array}\right\} \begin{array}{l} h1 = r \\ h2 = 2r \end{array}$$

Volume of the reactor:

$$V_{total} = V_{cylinder} + V_{cone} = \pi r^2 h1 + \frac{1}{3}\pi r^2 h2 = \pi r^3 + \frac{2}{3}\pi r^3 = \frac{5}{3}\pi r^3 = V_s * 5/4$$

Surface area of the reactor:

$$SA_{total} = SA_{cylinder} + SA_{cone} = 2\pi r^2 + \pi r^2 + \pi r\sqrt{r^2 + h2^2} = 3\pi r^2 + \pi r^2\sqrt{5} = \pi r^2(3 + \sqrt{5})$$

C.2 ENERGY CALCULATIONS

For 100 m^3/d sludge flow rate for MW pretreatment to 175°C with 5 day SRT:

Assumptions: $T_i = 25°C$

$$\rho_s = 1000 \frac{kg}{m^3}$$

$$T_a = -15°C$$

$$M_s = 100 \frac{m^3}{d} * 1000 \frac{kg}{m^3} = 100{,}000 \frac{kg}{d}$$

$$r = \left(\frac{3V_s}{4\pi} \right)^{1/3} = \left(\frac{3 * SRT * Q_s}{4\pi} \right)^{1/3} = \left(\frac{3 * 5d * 100 \frac{m^3}{d}}{4\pi} \right)^{1/3} = 4.92m$$

$$SA = \pi r^2 (3 + \sqrt{5}) = \pi * 4.92m^2 (3 + \sqrt{5}) = 398.8m^2$$

$$V_s = Q_d * SRT = 100 \frac{m^3}{d} * 5d = 500m^3$$

$$E_{net} = E_{pretreatment} + E_{heat} + E_{digester} + E_{mixing} + E_{dewatering} - E_{CH_4} - E_{\sin k}$$

$$E_{pretreatment} = k_e * k_{MW} * M_s * C_{p,s} * (T_p - T_i)$$

$$= \frac{1}{0.7} * \frac{1}{0.95} * 100{,}00 \frac{kg}{d} * 4.186 * 10^{-3} \frac{MJ}{kg.°C} * (175°C - 25°C) = 9.44 * 10^4 \frac{MJ}{d}$$

$$E_{heat} = M_s * C_{p,s} * (T_r - T_i) / k_h$$

$$= 0 \frac{MJ}{d}$$

$$E_{digester} = U * SA * (T_r - T_a)$$

$$= 0.216 \frac{MJ}{d.m^3.°C} * 398.8 m^3 * (35°C - -15°C) = 4.31 * 10^3 \frac{MJ}{d}$$

$$E_{mixing} = k_m * V_s$$

$$= 1.138 \frac{MJ}{d.m^3} * 5.00 * 10^2 m^3 = 5.69 * 10^2 \frac{MJ}{d}$$

$$E_{CH_4} = h_m * Q_s * (S_{VS,i} - S_{VS,e}) * M$$

$$= 37 \frac{MJ}{m^3 methane} * 100 \frac{m^3 sludge}{d} * \left(19.4 \frac{kgVS}{m^3 sludge} - 12.8 \frac{kgVS}{m^3 sludge} \right) * 0.6984 \frac{m^3 methane}{kgVS}$$

$$= 1.71 * 10^4 \frac{MJ}{d}$$

$$E_{\sin k} = M_s * C_{p,s} * (T_p - T_r) * k_h$$

$$= 100{,}00 \frac{kg}{d} * 4.186 * 10^{-3} \frac{MJ}{kg.°C} * (175°C - 35°C) * 0.70 = 4.10 * 10^4 \frac{MJ}{d}$$

$$E_{dewatering} = k_d * M_s$$

$$= 11.48 \frac{MJ}{m^3} * 100 \frac{m^3}{d} = 1.48 * 10^3 \frac{MJ}{d}$$

$$E_{net} = (9.44*10^4 + 0 + 4.31*10^3 + 5.69*10^2 + 1.48*10^3 - 1.71*10^4 - 4.10*10^4)\frac{MJ}{d}$$

$$= 4.27*10^4 \frac{MJ}{d}$$

C.3 COST ANALYSIS

For scenario (a)

$$C_{electricity} = \frac{\$0.05}{kWh} * E_{net} = 0.05*1.08\frac{kWh}{d} = \frac{\$53.85}{d}$$

$$V_{biosolid} = \frac{TS_i * Q}{TS_e} = \frac{3\%*100m^3/d}{13\%} = 15.38\frac{m^3}{d}$$

$$\#trip = \frac{V_{biosolid}}{V_{truck}} = \frac{15.38m^3/d}{12.3m^3/truck} = 1.006/d$$

$$C_{transportation} = \frac{135\$}{trip} * \#trip = \frac{135\$}{trip} * 1.006/d = \frac{\$135.81}{d}$$

$$C_{fuel} = \frac{60km}{trip} * \frac{\$1.3/L}{2.8km/L} * \#trip = \frac{\$27.86}{trip} * 1.006/d = \frac{\$28.03}{d}$$

$$C_{landfilltipping} = \$45/tonne * V_{biosolid} * 1tonne/m^3 = 45*15.38*1 = \frac{\$692.31}{d}$$

$$C_{total} = C_{electricity} + C_{transportation} + C_{fuel} + C_{landfilltipping} = 53.87 + 135.81 + 28.03 + 692.31 = \frac{\$910.02}{d}$$