Enhancement of Anaerobic Digestion of Organic Fraction of Municipal Solid Waste by Microwave Pretreatment

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Abstract

This study evaluates the enhancement of anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) by microwave pretreatment (MW) at high temperatures (115, 145 and 175°C). The highest level of solubilization was achieved at 175ºC, with a supplemental water addition of 30% (SWA30). Pretreatments combining two modalities; MW heating in presence or absence of hydrogen peroxide (H_2O_2) was also investigated. Biochemical methane potential (BMP) tests were conducted on the whole OFMSW, as well as on the liquid fractions.

The whole OFMSW pretreated at 115 and 145 ºC showed little improvement in biogas production over control. When pretreated at 175 ºC, biogas production decreased due to formation of refractory compounds, inhibiting digestion. For the liquid fraction of OFMSW, the effect of pretreatment on the cumulative biogas production (CBP) was more pronounced for supplemental water addition of 20% (SWA20) at 145 ºC. Combining MW and H_2O_2 modalities did not have a positive impact on OFMSW stabilization and enhanced biogas production.

Based on the BMP assay results, the effects of MW pretreatment (145 ºC) on the AD of OFMSW (SWA20) were further evaluated in single and dual stage semi-continuous digesters at hydraulic retention times (HRTs) of 20, 15, 12 and 9 days. Overall, MW pretreatment did not enhance the AD of the whole waste at the HRTs tested. However, the use of a dual stage reactor digesting non pretreated whole OFMSW had the best performance with the shortest HRT of 9 days. Conversely, for free liquid after pretreatment in two stage reactors at 20 day HRT methane production was tripled. In general, the performance of the dual stage digesters surpassed that of the single stage reactors.

Cyclic BMP assays indicated that using an appropriate fraction of recycled effluent leachate can be implemented without negatively effecting methanogenic activity and biogas production.

Based on the results obtained in this study, digestion of OFMSW by dual stage reactors without pretreatment appears to provide the best potential for waste stabilization in terms of biogas production and yield, process stability and volumetric loading rates.

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Nomenclature

AD	Anaerobic Digestion
ADS	Anaerobic Digester Sludge
ASBR	Anaerobic Sequencing Batch Reactor
BLF	Bioreactor Landfill
BMP	Biochemical Methane Potential
BOD	Biological Oxygen Demand
BSA	Bovine Serum Albumin
BTA	Biotechnische Abfallverwertung GmbH & Co KG
C/N	Carbon to Nitrogen ratio
CBP	Cumulative Biogas Production
CH	Conventional Heating
COD	Chemical Oxygen Demand
DS	Dried Solid
F/M	Food to Microorganism ratio
GHG	Green House Gases
HA	Humic Acid
HASL	Hybrid 2-stage Anaerobic Solid–Liquid
HRT	Hydraulic Retention Time
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
LCA	Life Cycle Assessment
LCH	Lignin-Carbohydrate
MAD	Mesophilic Anaerobic Digestion
MBM	Meat and Bone Meal
M-OFMSW	Model OFMSW
MSW	Municipal Solid Waste
MW	Microwave
OFMSW	Organic Fraction of Municipal Solid Waste
OLR	Organic Loading Rate
ORP	Oxidation Reduction Potential
OWS	Organic Waste Systems Inc.
POME	Palm Oil Mill Effluent
PS	Primary Sludge
PWAS	Pretreated WAS
R	MW intensity or ramp
RCF	Relative Centrifugal Force
RDF	Refuse Derived Fuel
SBR	Sequencing Batch Reactors
SCOD	Soluble COD
SEBAC	Sequential Batch Anaerobic Composting
SFW	Simulated Food Waste
SORDISEP	SORting, DIgestion and SEParation
SRT	Solids Retention Time

SS	Suspended Solids
SWA	Supplement Water Addition
SWA20	SWA of 20%
SWA30	SWA of 30%
T	Temperature
TCOD	Total COD
TDH	Thermal Hydrolysis
TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solids
TWAS	Thickened Waste Activated Sludge
US	Ultrasound
VFA	Volatile Fatty Acid
VOA	Volatile Organic Acid
VS	Volatile Solids
VSS	Volatile Suspended Solids
WAO	Wet Air Oxidation
WAS	Waste Activated Sludge

CHAPTER 1

Introduction

Solid waste management has become a major issue in the last decade due to environmental and economical concerns. Landfilling is still the main approach for waste management, and about 54% of the US's annual production of municipal solid waste (MSW), about 243 million tonnes (2009), is still landfilled. MSW consists of a non-biodegradable portion and a biodegradable organic fraction (Figure 1.1) which typically includes paper (28%), yard trimmings (14%) and food scraps (14%). Accordingly, in the United States (USEPA 2009) food scrapes alone account for almost 34 million tonnes per year which must be managed. In 2008, only 2.5% of food scraps was diverted while the remainder was landfilled (USEPA 2009). Food scraps which make up a significant component of the organic fraction of municipal solid waste (OFMSW) is characterised by a high moisture content that results in the production of large amounts of leachate with in landfills as it biodegrades anaerobically. If the leachate that is produced in the landfill is not managed and treated properly, it can present a serious pollution hazard to groundwater and surface water resulting in contamination of the local environment. Additionally, anaerobic degradation of OFMSW in landfills has resulted in them being one of the largest human-related sources of fugitive methane (CH_4) emissions, accounting for 17% of all anthropogenic CH_4 emissions in the USA (USEPA 2011). Methane is 23 times worse than CO_2 as a green house gas (GHG), concomitantly it has been argued that recovery of biogas for energy from landfills is a poor environmental strategy since fugitive methane emissions prior to energy generation are excessive and contribute to the GHG effect. Therefore, scarcity of land, potential leachate contamination of the environment and uncontrolled fugitive GHG emissions has made landfilling an undesirable option in many countries, especially European countries and Japan. The most stringent rules are enforced in Germany which now has a complete ban on landfilling of organic solid waste.

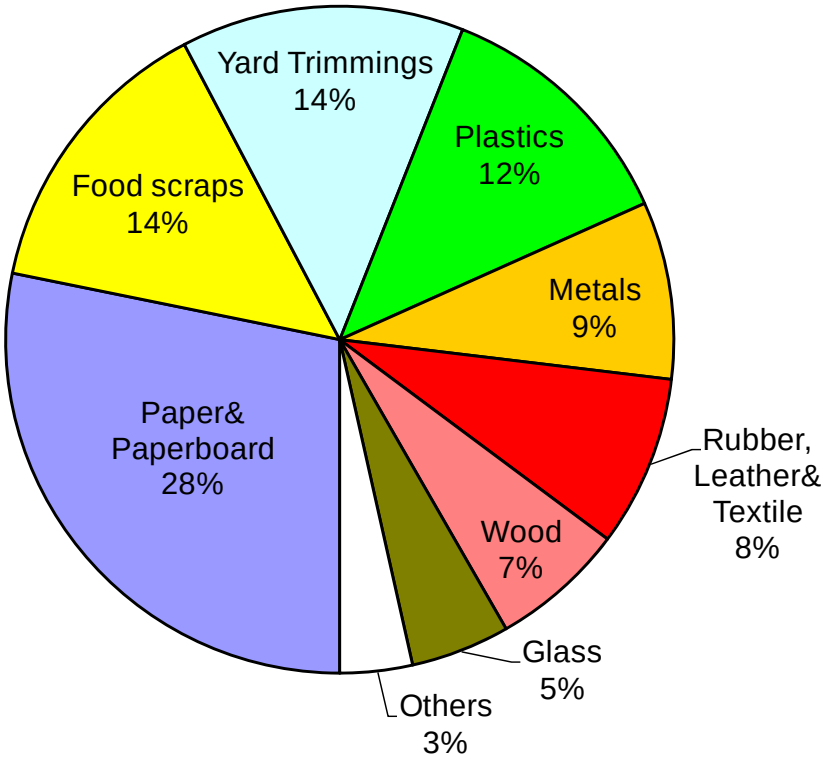

Figure 1.1: Different Fractions of MSW (USEPA 2009)

However biological processes can still offer sustainable methods to address the problems associated with OFMSW management and a source of sustainable energy if implemented under controlled conditions such as standalone anaerobic digestion (AD) processes. Life Cycle Assessment (LCA) of different waste disposal strategies described by Cherubini et al. (2009) included landfilling, AD, composting and waste incineration showed that landfilling is the least favourable option and standalone AD is very likely one of the best options for OFMSW management. By comparing different studies related to composting and AD of OFMSW, Mata-Alvarez (2003) concluded that AD will gain more attention in the future for both energetic and ecological reasons. The reasons are apparent: mass and volume reduction, odour removal, pathogen reduction, lower energy requirements, and more significantly, control of GHG emission and energy recovery in the form of methane. AD of OFMSW has become a reliable standalone technology in recent years with a number of processes available mostly in Europe. It has been stated that "AD has a great future amongst the biological technologies and will become one of mainstream processes for sustainable waste management throughout the 21st century, working with nature to maintain the natural carbon cycle to the benefit of mankind" (ADC 2007).

AD of OFMSW can be divided into four main stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The first step of AD is hydrolysis, in which suspended solids (SS) are solublized so they can be metabolized by an anaerobic bacterial consortium. For wastes that have a high SS component such as OFMSW this is the rate-limiting step (Eastman and Ferguson 1981; Pavlostathis and Giraldogomez 1991). As a result, AD of OFMSW in conventional anaerobic digesters usually requires a long retention time of more than 20 days (Climent et al. 2007) with concomitant large reactor volume requirements per unit mass of OFMSW digested. Exacerbated by the shear mass and volume of OFMSW that needs to be managed, new technologies and techniques are being developed to enhance AD and decrease reactor volume requirements per unit mass/volume of OFMSW digested. One approach is to minimize the rate limiting hydrolysis step by pretreatment in order to accelerate the overall stabilization of OFMSW, thus reducing AD retention time and increasing methane production. Pretreatment methods including mechanical treatment (Mshandete et al. 2006), ultrasound (Koksoy and Sanin 2010), chemical treatment (Li et al. 2011), thermal hydrolysis (Bougrier et al. 2008), thermochemical pretreatment (Chou et al. 2010) and microwave (MW) pretreatment (Yu et al. 2010), have been shown to increase biodegradability of thickened waste activated sludge (TWAS) and other organic solid wastes with varying degrees of success. In the case of OFMSW, conventional thermal pretreatment using high temperatures (160-175 °C) and pressure (6-8 MPa) have improved AD performance in terms of both rate of reaction and extent of degradation.

MW pretreatment is a novel heating technology that looks promising and could be applied to OFMSW. Compared to conventional heating (CH) it is attractive due to its environmental and energy conservation properties (Decareau 1985; Kingston and Jassie 1988), since it can be switched on and off and it minimizes heat losses that occur in energy transmission during normal heating. As an alternative and innovative method to CH of organic waste MW irradiation pretreatment is an emerging energy efficient technology. So far, publications regarding the effect of MW pretreatment on waste solubilization and improved AD have been limited to and focused on waste activated sludge (Eskicioglu et al. 2008a; Toreci et al. 2010). Recent studies have also shown synergic solubilization effects for TWAS when MW heating is combined with the oxidizing agent H_2O_2 (dual modality). Wong et al (2006a) reported that dual modality MW/H_2O_2 pretreatment of TWAS converted a larger fraction of total chemical oxygen demand (TCOD) into soluble chemical oxygen demand (SCOD) than either single

modality pretreatment. Application of single modality MW pretreatment as well as combined modality pretreatment (MW/H_2O_2) has not been extended to OFMSW.

It has also been reported that advantages in the AD process can be gained by staging of the two main metabolic steps involved in AD, particularly the acid and methanogenic steps. Mata-Alvarez et al. (1992) reported that in conventional one-step AD of solid wastes, 2 types of problems may occur. If the substrate has a large component of easily degradable organics this can lead to rapid acidogenesis and an accumulation of volatile fatty acids (VFAs). In solid waste digestion, this is attributed to the inability of the system to accumulate or retain the correct consortia of microbial biomass within the reactor, resulting in the overfeeding and inhibition of slower growing methanogens. When substrate feeding rate is increased, acidogenic microbial growth and activity increases at a faster rate than the slower growing methanogenic population resulting in the accumulation of VFAs, decreasing pH and decreasing digester performance. High organic loading rates (OLRs) cause system imbalance and considerable reduction of methane production reducing the overall efficiency of the reactor. On the other hand for solid wastes such as OFMSW single stage reactor conditions may be sub optimal for hydrolysis of SS leading to this being the rate limiting step. In addition in the first step of two stage reactors alternate strategies can be implemented that would not be possible in a single reactor system. Establishment of microaerophilic condition and/or bioaugmentation in the acid phase reactor may be a simple way to increase hydrolysis. Jagadabhi et al., (2010) applied microaerophilic acidification for grass-silage and reported 4 fold increase in total VFAs (TVFAs) production.

Staging of the AD process in which 2 individual reactors are used to provide optimum growth conditions for acidogens and methanogens can provide alternate operational management strategies or can be a solution to circumvent the hydrolytic rate limiting step issue while also overcoming the microbial consortia imbalance mentioned above (Li et al. 2010). Staging, pretreatment and acid phase management strategies offer the potential to successfully digest OFMSW at higher OLRs which would result in smaller reactor volumes per unit mass/volume of OFMSW treated. No studies are available for OFMSW that attempt to evaluate and compare the advantages of various management strategies, single and dual modality MW pretreatment, and single vs. two stage digestion to enhance anaerobic stabilization.

Alternatively, another approach to OFMSW management may be to MW pretreat the OFMSW and only digest the liquefied component. This strategy is only applicable if the

majority of the biodegradable components in the original OFMSW can be solubilized into the free liquid phase. The literature documents one example of this strategy in which kitchen waste was thermochemically liquidized (175 ^{o}C and 4 MPa) then separated into the suspended and filtrate fractions. Biogas yield from the filtrate was reported to be similar to the unseparated pretreated waste (Sawayama et al. 1997; Sawayama et al. 1999). AD of liquefied wastes has the advantage that a variety of high rate AD reactors specific for liquid waste are available that can be operataed at high OLRs which again can translate in to smaller reactor volumes per unit mass/volume of OFMSW treated. This strategy has potential to produced methane from the OFMSW as well as a pretreatment that minimizes the suspended material that would be sent to landfill.

Finally for all the strategies above dilution of OFMSW is an important issue in wet AD. Due to the high solids content and low moisture component wet digestion of OFMSW can only be performed in conventional reactor systems by incorporating OFMSW dilution either by addition of fresh and/or recycled process water (De Laclos et al. 1997) or by co-digestion with a more liquid type waste if available. One time use of fresh water for dilution is not a sustainable or feasible option both environmentally and/or economically. Recycling of process water is a good solution but there are restrictions and limits for water reuse. Effects of multiple water reuse cycles on the digestion and stabilization of OFMSW has not been studied.

1.1. The Hypothesis

This thesis proposes MW pretreatment technology in combination with reactor staging as a new and alternative OFMSW management strategy that will enhance AD of OFMSW by reducing the volume of AD reactors and increasing biogas production per unit mass/volume of OFMSW managed. It is hypothesized that

MW pretreatment can increase the efficiency of AD by increasing the solubility and bioavailability of organic waste, concomitantly increasing hydrolysis and biogas production rates as well as the extent of waste stabilization.

Extensive solubilization of OFMSW by MW pretreatment will result in a substantial proportion of the organics being transferred into the free liquid fraction. Digestion of the liquid fraction only can result in efficient waste stabilization and concomitant biogas production as an alternative management strategy for AD of OFMSW.

Combining MW pretreatment with a two-stage acidogenic/methanogenic reactor system will optimize hydrolysis and overcome the microbial consortia imbalance associated with single stage reactors. Combined MW pretreatment and staged bioreactor management strategy will produce the highest waste stabilizations and volumetric waste stabilization rates (i.e. smallest reactor volumes per unit mass/volume of OFMSW treated).

Hydrolysis and acid fermentation in the first stage of a two stage AD system can be accelerated by bioaugmentation (adding TWAS) under microaerophilic condition.

An appropriate fraction of recycled effluent and fresh make up water for AD of OFMSW can minimize fresh water use without a substantial decrease in waste stabilization, methanogenic activity and biogas production.

The following sections of this report contain a literature review on AD and existing pretreatment methods and propose an experimental design plan to prove these hypotheses.

1.2. Research Objectives

The specific objectives of this research can be summarized as follows:

Determine the effects of high temperature/pressure MW irradiation on solubilization of OFMSW using different temperatures (T), temperature ramp profiles (R), and supplemental water additions (SWA).

Determine the effects of MW pretreatment on enhancement and/or inhibition of biogas production for the whole OFMSW and supernatant fraction, using the biochemical methane potential (BMP) assay.

Determine the applicability and performance of a two-stage semi-continuous mesophilic AD (MAD) process vs. single stage with and without MW pretreatment.

Determine the potential for increasing the rate of hydrolysis and acid fermentation in the first stage of two-stage AD system by bioaugmentation (adding TWAS) under microaerophilic condition.

Determine the impacts of using effluent water for process make up water and effect of multiple effluent water reuse cycles on the digestion and stabilization of the OFMSW treatment process using BMP assays.

1.3. Thesis Organization

This thesis is organized as a paper format thesis. Chapter 2 gives information and reviews the literature on fundamentals of AD, MW technology and some of the existing pretreatment methods. Additional literature and the main results and discussion are presented in chapters 3 to 6 which were prepared in a journal manuscript format. Overall conclusions and recommendations are given in Chapter 7.

Chapter 3 focuses on the effect of different operating conditions (MW temperatures, MW intensities based on temperature ramp times and two SWAs) on M-OFMSW characteristics such as SCOD, soluble sugar, soluble protein and TVFAs. Statistical analysis with a three-factor fixed effect ANOVA model was used to analysis 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 GeoHalifax 2009, the 62nd Canadian Geotechnical Conference and 10th Joint CGS/IAH-CNC Specialty Groundwater Conference in Halifax, Canada, September 20-24, 2009 and the manuscript shown as Chapter 3 was published by International Journal of Environmental Technology and Management (IJETM), Vol.14, issue 1-4, page 67-83.

Chapter 4 presents the results obtained from BMP assays of M-OFMSW pretreated at different MW temperatures and SWAs. It also presents pretreatment combining two modalities, microwave heating in presence or absence of hydrogen peroxide (H_2O_2). BMP tests were conducted on the whole OFMSW, as well as the liquid fraction. The kinetics of biogas production was predicted by a first order reaction. A summary paper that contains a portion of results included in this chapter has been accepted and will be presented at the 13th International symposium On Waste Management and Landfill Issues, Sardinia, Italy, October 3-7, 2011. The full manuscript was accepted by the Journal of Waste Management, manuscript number WM-11-306.

Chapter 5 presents the results of semi-continuous digestion tests that were carried out to obtain better understanding of the effect of MW pretreatment of OFMSW on performance of single and dual stage reactors and evaluate the effect of MW on enhancement of AD of the whole waste and free liquid extracted from the waste. The secondary focus of this part was to further increase the rate of hydrolysis and acidification by bioaugmentation with TWAS and resulting

microaerophilic conditions in the first reactor in dual stage digesters. This manuscript was submitted to the Journal of Environmental Management.

Chapter 6 provides insight in to the use of effluent for process make up water and investigates the impact of recycling treated water/fresh water mixtures on biogas production and stabilization of a wet OFMSW treatment process. The study used BMP assays with various water/effluent mixtures and multiple water reuse cycles to evaluate the impact on digestion of OFMSW. This manuscript was submitted to the Journal of Waste Management, manuscript number WM-11-558.

A summary of chapter 3, 4 and 5 was accepted to Anaerobic Digestion of Solid Waste and Energy Crops 2011, International IWA- ADSW and EC Symposium, Vienna, Austria, August 28 - September 1, 2011.

CHAPTER 2

Literature Review

2.1. Anaerobic Digestion

Anaerobic digestion (AD) is a naturally occurring process of decomposition which takes place when bacteria reduce organic matter in the absence of oxygen to CH_4 (65%) and CO_2 (35%). This is a complex process that involves many different classes of bacteria and several intermediate steps which are represented schematically in Figure 2.1. Performance of AD can best be evaluated by monitoring the products of the digestion process. As shown in Figure 2.1, the AD process can be split into four main stages: hydrolysis, acidogenesis (fermentation), acetogenesis, and methanogenesis. Each of these four processes are described below.

If the substrate is a complex organic material with a significant suspended solids (SS) component, it must first be hydrolysed to simple organic compounds before it can be fermented to volatile fatty acids (VFA) by the acidogenic bacteria (acid formers). During hydrolysis insoluble organic molecules are solubilized by extracellular enzymes so that they can eventually be consumed by other microorganisms in the anaerobic microbial consortium. A great variety of common types of facultative and anaerobic microorganisms mediate this hydrolytic step. Hydrolytic microorganisms decompose long chain organic polymers such as proteins, polysaccharides and lipids in to their simpler monomeric base compounds such as long chain fatty acids and glucose. In the case of simple organic compounds, such as glucose, hydrolysis is not necessary but the hydrolytic activity is of significant importance in wastes with high suspended organic content as this step becomes the rate limiting step of the overall reaction (Verma 2002). These smaller molecules facilitate transport across the cell membrane. Reaction products of the hydrolysis step are then available for the second step of AD, acidogenesis. The longer chained fatty acids (i.e. acids with more than one carbon) are then converted to acetic acid and hydrogen gas by obligate hydrogen producing acetogens. Finally,

the acetic acid, carbon dioxide and hydrogen gas can be converted to methane by methanogenic bacteria (methanogens) (Speece 1996).

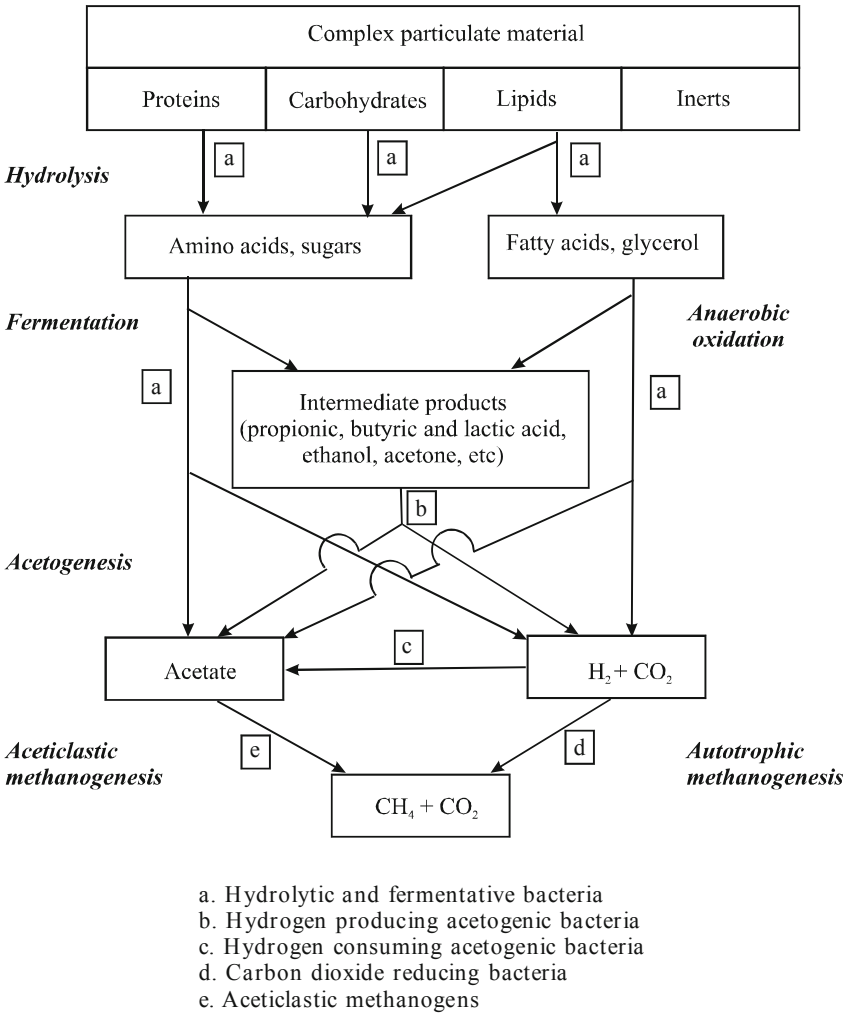

Figure 2.1: Anaerobic digestion processes, adapted from Manariotis et al. (2010)

Bacterial methanogenesis is a ubiquitous process in most anaerobic environments. The generation of CH_4 is performed by two unique groups of strictly anaerobic Archaea (Rittmann 2008). The first group of Archaea are aceticlastic methanogens, which are responsible for biogas production directly from acetate, and the second group are hydrogen scavenging hydrogenotrophic methanogens. It has been well established that acetate is the major methanogenic precursor in most anaerobic ecosystems (Horan 2003). It has been reported that aceticlastic methanogens are responsible for 70% of methane production, while hydrogenotrophic methanogens account for the remaining 30% (Sawayama et al. 2004).

This complex series of operations is rate controlled by the various anaerobic bacterial groups with the hydrolysis step being limiting for complex suspended solids wastes like organic fraction of municipal solid waste (OFMSW) followed by the microbial consortia with the slowest growth rates and therefore the slowest metabolism rates, namely the acetic and propionic acid utilizing methanogens. Within a single digestion tank or environment all four of the stages involved in AD occur simultaneously and synergistically, but require ideal reaction conditions for all stages to occur at the same time.

2.2. Factors Affecting Anaerobic Biodegradation

In order to maintain the stability of an anaerobic digester, the complex and interdependent bacterial consortium necessary for AD must exist in equilibrium. Disruptions in environmental conditions can cause the system to shift away from equilibrium, resulting in the build up or depletion of intermediaries, ultimately inhibiting bacterial populations, or shutting down the entire system.

Several digestion parameters affect the physical system and consequently the rate of digestion and production of biogas (CH_4 and CO_2). The following parameters must be monitored and maintained at acceptable levels to ensure process stability: temperature, pH and alkalinity, carbon to nitrogen (C/N) ratio, retention time, and organic loading rate (OLR). Deviations from the acceptable ranges for these parameters can result in digester failure and it is essential to understand the importance of each parameter.

2.2.1. Temperature

Temperature is one of the critical parameter to maintain the anaerobic biodegradation in a desired range. It has an effect upon anaerobic operations similar to all other biological systems as depicted in Figure 2.2. In this figure the rate of the anaerobic biodegradation process shown is measured by gas production rates, growth rates and substrate degradation performance.

Anaerobic bacteria have the ability to survive in a wide range of temperatures: from 0 °C to 70 °C, and are typically divided into the following classifications: psychrophilic (0 °C to 20 °C), mesophilic (20 °C to 40 °C) and thermophilic (50 °C to 65 °C) (Sakar et al. 2009), with optimum temperatures of 35 °C and 55 °C for mesophilic and thermophilic digestion

respectively. Both mesophilic and thermophilic digestions have advantages and disadvantages associated with them.

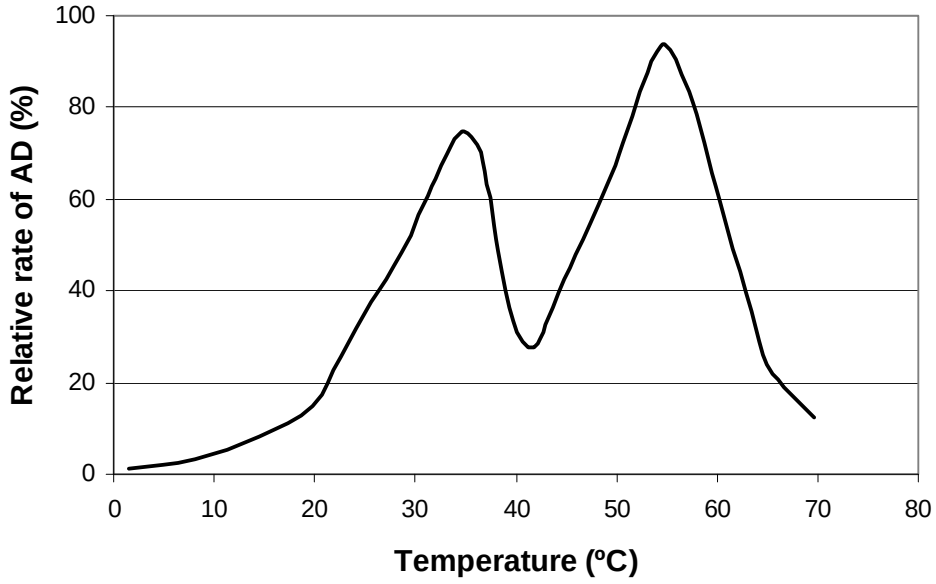

Figure 2.2: Effect of temperature on rate of anaerobic biodegradation, Golueke (2002)

Thermophilic digestion is advantageous as it allows for higher loading rates with lower retention times and achieves a higher rate of pathogen destruction (Six and Debaere 1992; Engeli et al. 1993; Bendixen 1994) as well as an increased degradation of the substrate compared to mesophilic digestion. However, thermophilic systems are more sensitive to toxicity and environmental changes than mesophilic systems. From an energetics perspective, thermophilic is also less favourable than mesophilic systems, as they require a greater heat input. Despite its theoretical short comings, in practice thermophilic digestions have outperformed mesophilic digestions in some studies. Thermophilic AD remains controversial and while some plants continue to use this method (Vancouver, Canada), others have discontinued the practice (Chicago, USA).

Mesophilic bacteria are thought to be more robust and able to tolerate greater environmental changes in comparison to thermophilic bacteria. Despite the longer retention times required, mesophilic bacteria have demonstrated considerable stability in many different applications, which makes them the bacterial population of choice in most AD facilities.

2.2.2. pH and Alkalinity

pH is a primary indication of system health and a stable pH indicates digester equilibrium and stability. The optimal pH for growth of anaerobic bacteria lies between 6.5 and 7.8 (Horan 2003; Sakar et al. 2009). To maintain efficient methanogenesis a suitable and stable pH should be maintained within a digester (Horan 2003).

The accumulation of acids in a reactor can be particularly problematic, resulting in a declining pH and unstable digester. A sharp increase in the volatile solids (introduced to a digester as fresh waste) will result in these conditions. As a consequence of increased availability of volatile solids (VS), there is an increase in the activity of acidogenic bacteria present in the system. This can lead to a drop in pH which can destabilize the microbial consortium. Further, this pH drop would tend to adversely affect the methanogenic stage disproportionately to the other groups (acidogenic stage), compounding the problem, which would further lower the pH. This phenomenon is known as reactor souring. Reactor souring can be avoided through careful monitoring of reactor pH, VFA levels and by buffering of the feed with bicarbonate alkalinity. Alkalinity refers to the ability of a system to resist changes in pH. This is important to an anaerobic system, as when acids are produced or added to the system, alkalinity present will contribute hydroxide ions, helping to neutralize the acids present (Sakar et al. 2009). At the first sign of increased VFA concentrations and/or decrease in pH levels in conventional single stage digesters, the feed rate to the reactor can be decreased or stopped and the reactor set to recycle only, thus allowing the bacterial consortia to consume the excess VFA without having the simultaneous production of VFA from incoming substrate. Separation of the acidogenic and methanogenic stages (staging) is another solution, that recently has been practiced, that will be discussed in more details.

2.2.3. Carbon to Nitrogen Ratio

The low growth rate of anaerobes from a given amount of substrate result in lower nutrient requirements compared to aerobes. The optimum C/N ratio is between 20-30 (25 as the ideal level) (Verma 2002; Monnet 2003). A low C/N ratio, or too much nitrogen, can cause ammonia to accumulate which would lead to pH values above 8.5. Additionally, the quality of the anaerobic digestate is lessened with high ammonia production. A high C/N ratio will lead to a rapid consumption of nitrogen by the methanogenic bacteria and lower gas production

rates. Optimum C/N ratios of the digester materials can be achieved by mixing materials of high and low C/N ratios, such as organic solid waste mixed with sewage or animal manure.

2.2.4. Retention Time

The longer a substrate is kept under proper reaction conditions, the more complete its degradation will be. The rate of the reaction, however, will decrease with increasing residence time, indicating that there is an optimal time that will achieve the benefits of digestion in a cost effective way. The appropriate time depends on the feedstock, environmental conditions, and intended use of the digestate. The retention time for most dry processes (total solids (TS) >20%) ranges between 14 and 30 days and for wet processes (TS < 20%) can be as low as 3 days. Recent research has shown that volatile suspended solids (VSS) in a digester could be reduced by 64- 85% after only 10 hours, but typically a retention time of 10 days is required for complete digestion (Lin et al. 1997; Vlyssides and Karlis 2004). A shorter retention time will lead to a higher biogas production rate per reactor volume unit, but a lower overall degradation. These two effects have to be balanced in the design of the full-scale reactor.

2.2.5. Mixing

Babbite and Baumann (1958) recognized the importance of mixing to improve anaerobic process performance. Mixing is an important factor in pH control and maintenance of uniform environmental conditions. Without adequate mixing, unfavorable conditions for microorganism growth can occur. Mixing distributes buffering agents and nutrients throughout the reactor and prevents local buildup of high concentrations of intermediate metabolic products that can be inhibitory to methanogens (Droste 1996).

2.2.6. Organic Loading Rate

OLR determines how much VS are continuously inputted to the digester. A higher OLR will increase acidogenic bacteria populations, which produce acids rapidly. The methanogenic bacteria, which take longer to increase their populations, would not be able to consume the acids at the same pace. An early indication of this imbalance is a lowering of pH and eventually lowered biogas production (Verma 2002). Many plants have reported system failures due to overloading.

2.2.7. Food to Microorganism Ratio

Another key factor controlling AD is the food-to-microorganism (F/M) ratio (Burke 2001). The F/M ratio expresses the ratio of substrate (F) to the amount of inoculum (M) present in a system (Koksoy and Sanin 2010). It can be described in the units of grams (g) of VS of substrate per g VSS of the bacterial population (inoculum) present. It is an important parameter to use to evaluate the potential VS loading, as at a given temperature bacteria are only capable of consuming a limited amount of food each day (Prashanth et al. 2006; Koksoy and Sanin 2010). In a biological treatment system, efficiency can be improved either by increasing the bacterial biomass present or decreasing the amount of substrate provided thereby lowering the F/M ratio. Research has indicated that too high an F/M ratio results in toxic conditions, while too low an F/M ratio also may inhibit digestion (Prashanth et al. 2006).

2.3. Anaerobic Biodegradation in a Landfill

Anaerobic biodegradation in a landfill is a natural process. Waste in a municipal solid waste (MSW) landfill does not have a single age because waste is placed gradually over the life of the landfill. The different MSW landfill stabilization phases often overlap and can be viewed together. As shown in Figure 2.3, the initial phase results in aerobic decomposition followed by four stages of anaerobic decomposition.

All MSW landfills and bioreactor landfills (BLF) undergo these five stages of stabilization but BLFs decrease the duration of the stabilization phases (Kim and Pohland 2003; Sun et al. 2011). The application of these phases to a MSW landfill is discussed below.

2.3.1. Phase I (Initial Adjustment)

As moisture becomes available and the microbial population density increases, the biochemical decomposition under aerobic conditions is started. Compaction of the waste decreases the O_2 content of solid waste in the landfill. This phase is sometimes called the lag phase.

2.3.2. Phase II (Transition)

This stage is a transition from aerobic to anaerobic conditions. During this phase, the primary electron acceptors become nitrates and sulfates, rather than O_2, with the displacement of O_2 by CO_2 in the effluent gas.

Measurable concentrations of chemical oxygen demand (COD), volatile organic acids (VOAs) and ammonia (due to the hydrolysis and fermentation of protein compounds) can be detected in the leachate, by the end of this phase.

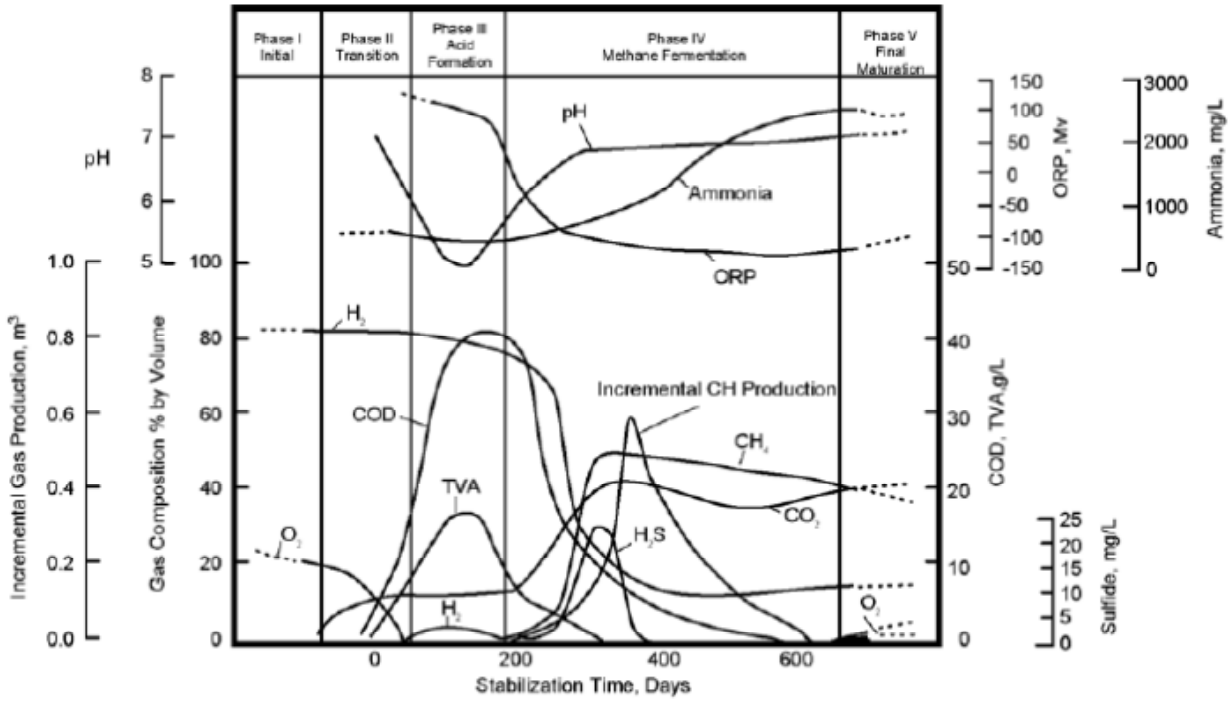

Figure 2.3: Phases of anaerobic decomposition in MSW landfills (Pohland and Kim 1999)

2.3.3. Phase III (Acid Formation)

In this phase the concentration of VFAs in the leachate increases because of the hydrolysis of the biodegradable fraction of the solid waste thus pH decreases from approximately 7.5 to 5.6. The drop in pH may cause concomitant mobilization and the possible complexation of metal species that are more soluble at a low pH.

During this phase, the decomposition intermediates such as VFAs contribute to a high COD and the long-chain VOAs are converted to acetic acid ($C_2H_4O_2$), CO_2, and H_2. The H_2 generation phase is terminates by the end of this phase. This phase is also marked by an

increase in the biomass of acidogenic bacteria as well as a rapid consumption of substrates and nutrients.

2.3.4. Phase IV (Methane Fermentation)

Intermediary products appearing during the acid formation phase (i.e., mainly acetic, propionic, and butyric acids) are converted to CH_4 and CO_2 by methanogens. As a result the pH is elevated to neutrality. The organic strength of the leachate biological oxygen demand (BOD) is dramatically decreased in correspondence with increases in gas (i.e., CH_4 and CO_2) production. Heavy metals removed from the leachate by complexation and precipitation and transported to the solid phase. This phase also signifies the longest overall time duration and represents the period when the majority of the waste decomposes.

2.3.5. Phase V (Final Maturation and Stabilization)

The final stage of solid waste decomposition is characterized by a lower rate of biological activity due to the limiting of nutrients such as phosphorus. During this stage, landfill CH_4 production is almost negligible. O_2 and oxidized species may slowly reappear as O_2 permeates from the atmosphere with a corresponding increase in oxidation-reduction potential (ORP) in the leachate. It is hypothesized that residual organic materials may slowly be converted to gas in this phase, with the possible production of humic-like substances. In a large-scale landfill the waste stabilization phases tend to overlap and the leachate and gas characteristics reflect this phenomenon.

2.4. Anaerobic Biodegradation in Bioreactor Landfill

Although the landfilling disposal option is advantageous in many aspects, conventional landfills actually cause negative environmental impacts including high net emissions of green house gases (GHG), high potential to impact land resources and sensitive natural habitats, and great potential to consume non-renewable resources and affect land uses. Moreover, conventional landfills usually include environmental barriers such as landfill liners and covers, which exclude moisture that is essential to waste biodegradation. Consequently, wastes are contained in a “dry tomb” and remain intact for long periods of time ranging from 30 to 200 years, possibly in excess of the life of the landfill barriers and covers. Liner failure could

happen in conventional dry landfills sometime in the future, which could cause serious groundwater and surface water contamination (Warith et al. 2005).

These drawbacks as well as the advances in enhancing techniques for landfill performance have motivated researchers to develop operation changes in conventional landfills by engineering the inputs and outputs in such a way that the negative impacts are minimized. From here, the new concept of BLFs evolved took place as one of the future alternatives to conventional landfilling.

A BLF is a sanitary landfill that uses enhanced microbiological processes to transform and stabilize the readily and moderately decomposable organic waste constituents within 5 to 10 years of bioreactor process implementation (Figure 2.4). The BLF significantly increases the extent of organic waste decomposition, conversion rates and process effectiveness over what would otherwise occur within the landfill. Microbial degradation may be promoted by adding certain elements (moisture, nutrients, or oxygen) and controlling other elements (such as temperature or pH). Anaerobic BLFs have the same stages of normal landfills, but with more favourable environmental conditions for the microorganisms responsible for biodegradation of waste, digestion will be faster. A key component in operating a landfill as a bioreactor is the introduction of moisture into the landfill from internal (i.e., leachate) and external (e.g., precipitation, storm water, groundwater, and industrial liquid waste streams) sources.

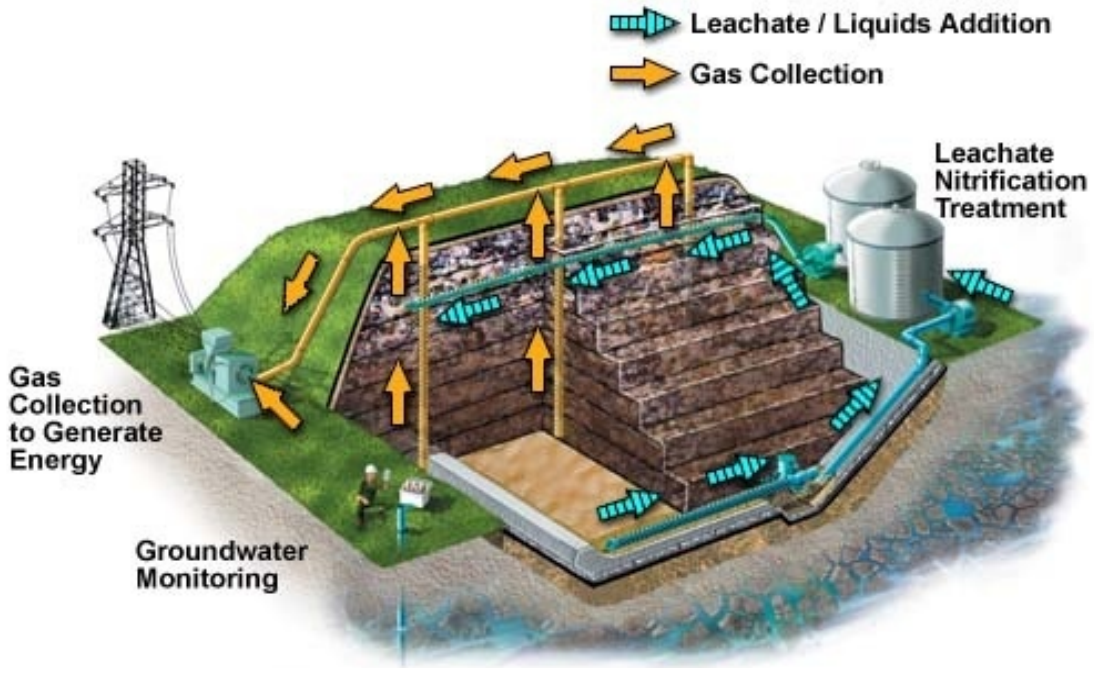

Figure 2.4: Configuration of Anaerobic Bioreactor Landfill

The optimum moisture content for biological degradation is reported to be greater than 40 percent (Reinhart and AlYousfi 1996). In general, the decomposition and stabilization rate of biodegradable solid wastes increases with increasing moisture content of the waste (El-Fadel 1999; Mehta et al. 2002; Sponza and Agdag 2004). Moreover, some studies indicated that moisture movement could also affect waste stabilization. Therefore, moisture control (i.e., moisture content and movement) is essential for landfill operation. Leachate recirculation has been demonstrated to be a superior management strategy for moisture control (Kumar et al. 2011). Through leachate recirculation, liquid movement distributes the inocula, minimizes local shortages of nutrients, provides better contact between insoluble substrates, soluble nutrients, and the microorganisms, dilutes potential toxins, and transfers heat. As a result, microbial activities are increased. The advantages of leachate recirculation can be listed as (Warith et al. 2005).

- Providing in-situ leachate treatment instead of off-site treatment, thus saving costs
- Enhancing waste settlement, thus decreasing the risk of damage to the final cover and permitting recovery of valuable landfill air space
- Increasing gas generation rate which make energy recovery more favorable
- Accelerating waste decomposition, thus shortening the post closure monitoring period and reducing the overall landfill operation cost.

2.5. Process of Anaerobic Digesters

In order to further accelerate the benefits of the BLF concept stand alone anaerobic digester facilities have been proposed and designed to accelerate and optimize the four steps of anaerobic biodegradation by providing the most accommodating conditions for all the microorganisms involved, thereby increasing waste stabilization and bioenergy production. In addition to the characteristics of the waste used, reactor process design and management can significantly influence the practical biogas yield from anaerobic biodegradation of OFMSW. Anaerobic digesters can be classified into the following general categories:

- Thermophilic versus mesophilic conditions
- Wet versus dry fermentation
- Two-phase versus single-phase treatment.

2.5.1. Two-phase versus single-phase treatment

Single stage reactors make use of one reactor for both the acidogenic phase and the methanogenic reactions of AD. The main idea of a multi-stage or multi phase AD process is to optimize the conditions for the individual biological reactions of AD, with the hydrolytic bacteria in one reactor and the methanogens in another reactor. The operating strategies of the separate stages can then be manipulated separately to increase gas production and waste stabilization rates. Staging typically involves separation of the microbial consortia based on hydraulic separation with a short residence time acid phase digester followed by a longer residence time methanogenic phase reactor.

Studies by Hamzawi et al. (1999) found that a two-phase AD treatment process for dry fermentation of OFMSW could be operated at significantly shorter hydraulic retention time (HRT) and higher OLR than a conventional single-stage system. However, other studies by Chynoweth et al. (1992) disagreed. Using a sequential batch anaerobic composting (SEBAC) process consisting of three reactors for the treatment of high-solids resulted in the majority of the total methane produced coming from stage 1, which indicated that this system did not benefit by dividing the process into three reactors. Similar results were obtained when Mtzviturtia et al. (1995) compared a single-step and a two-phase wet system which consisted of a hydrolyzing reactor followed by a methanization reactor for digestion of fruit and vegetable wastes. The overall performance showed no improvement when compared to a single-stage system.

Other studies contradict the results described above for single and two stage digestion. Digestion of OFMSW, particularly kitchen refuse has indicated that, the digestion process is best performed in a two stage process with a concentration unit between the two stages. Under these process conditions a 90% removal of the organic matter was reported at lower overall retention times compared to single stage controls (Schober et al. 1999). Similarly Demirer and Chen (2005) investigated the advantages of two-phase AD for unscreened dairy manure. A two phase reactor at a HRT of 10 days (2 days of acidogenic reactions and 8 days of methanogenic reactions) resulted in 50 and 67% higher biogas production at OLRs of 5 and 6 g VS/L.day, respectively, compared to a conventional one-stage reactor with HRT of 20 days. In addition, an OLR of 12.6 g VS/L.day was achieved with the dual stage reactor which was not possible with the conventional one-phase configuration. Likewise, Mohan and Bindhu

(2008) studied the AD of kitchen waste in single-phase digestion and two-phase digestion systems. The two-phase AD system performed well at an OLR of 8.0 kg VS/m^3.day and total HRT of 10 days, while the single phase system failed at OLRs beyond 4.5 kg VS/m^3.day and HRTs of less than 15 days. The two-stage VS and COD removal efficiency was 94% and 92% compared to 79% and 81% for one stage, respectively at an HRT of 15 days and OLR of 4.5 kg VS/m^3.day. By considering the higher ORLs that could be achieved at shorter HRTs in the two-stage reactors, the waste stabilizaton efficiency and concomitant biogas production of the two-stage reactor process was increased by another 33% compared to the single reactor process.

Other studies have combined two stage reactors with thermal microwave (MW) pretreatment to enhance biogas production. Coelho et al. (2011) investigated the effects of MW pretreatment of thickened waste activated sludge (TWAS) to 96 ºC on AD in one and two stage reactors under thermophilic and mesophilic conditions at four different HRTs (5, 10, 15, 20 days). In two phase reactors, both steps operating under thermophilic conditions with an SRT of 5 days, a 106% enhancement in biogas production was observed compared to the one stage mesophilic reactor. The one stage mesophilic and thermophilic reactors that were fed with MW pretreated sludge had 44 and 83% higher biogas production respectively compared to the control reactor (single stage mesophilic reactor with no MW pretreatment) at an HRT of 20 days. Overall, the study confirmed that for single stage reactors improved waste stabilization efficiency resulting from MW pretreatment decreased at shorter HRTs conversely, for two stage reactors operated at the same HRTs waste stabilization was increased with and without MW pretreatment.

Despite lower OLRs and biogas production rates, single phase digestion remains the predominant AD treatment applied in full scale for the OFMSW. Two-phase digestion has, so far, not been able to prove its benefit in the market place (De Baere 2000) and is limited to a small market share.

2.6. Commercial Anaerobic Digesters for treating MSW

During the period of 1991–1995, annual world wide stand alone AD capacity was 38,800 tonnes MSW per year. From 1996–2000, AD capacity increased to 223,500 tonnes MSW per year which was further increased to 415,590 tonnes MSW per year in the period 2001–2005

of. In the period of 2006–2010 the overall world capacity has approximately doubled year over year at an annual increase of about 345,540 tonnes MSW per year being added. The new capacity added each year is by about 11 new plants with an average size of each being about 32,000 tonnes per year.

A typical AD facility has six major components. The first is a tipping floor where trucks deliver organic waste. In the second stage, the waste is pretreated and contaminants removed. The next stage is the anaerobic digester where biological degradation occurs. The fourth component treats the solid product and the fifth cleans and consumes the biogas. The final part is a biofilter, which ensures that odors do not leave the facility. Four types of continuous anaerobic digesters that are widely used will be introduced in the following section.

2.6.1. BTA

The BTA (Biotechnische Abfallverwertung GmbH & Co KG) Process which was developed in Germany in the 1980s, combines sophisticated waste pretreatment and separation techniques with advanced methods of AD, all within a fully enclosed and highly automated facility. The first BTA plant for the digestion of 20,000 tonnes per year of bio-waste (source separated OFMSW) started its operation in Elsinore (Denmark) in 1991.

The process consists of two major steps: mechanical pretreatment and biological conversion. The BTA process begins with mechanical wet pretreatment, where feedstock and recirculated process water (confidential information) are mixed and pulped in a hydropulper. Contaminants are separated mechanically by using a rack and a heavy fraction trap. From the original waste material a homogenous, pumpable 10% TS organics pulp is produced which is pumped into the digester.

Several different designs for the biological conversion are offered by BTA according to the plant capacity and the use of the biogas and compost (digestate). For smaller plants a one-stage version combining the pretreatment with a completely mixed digester (mesophilic or thermophilic) is normally recommended (Figure 2.5). After grit removal the pulp gets fed directly into the digester for degradation; without any preceding additional steps.

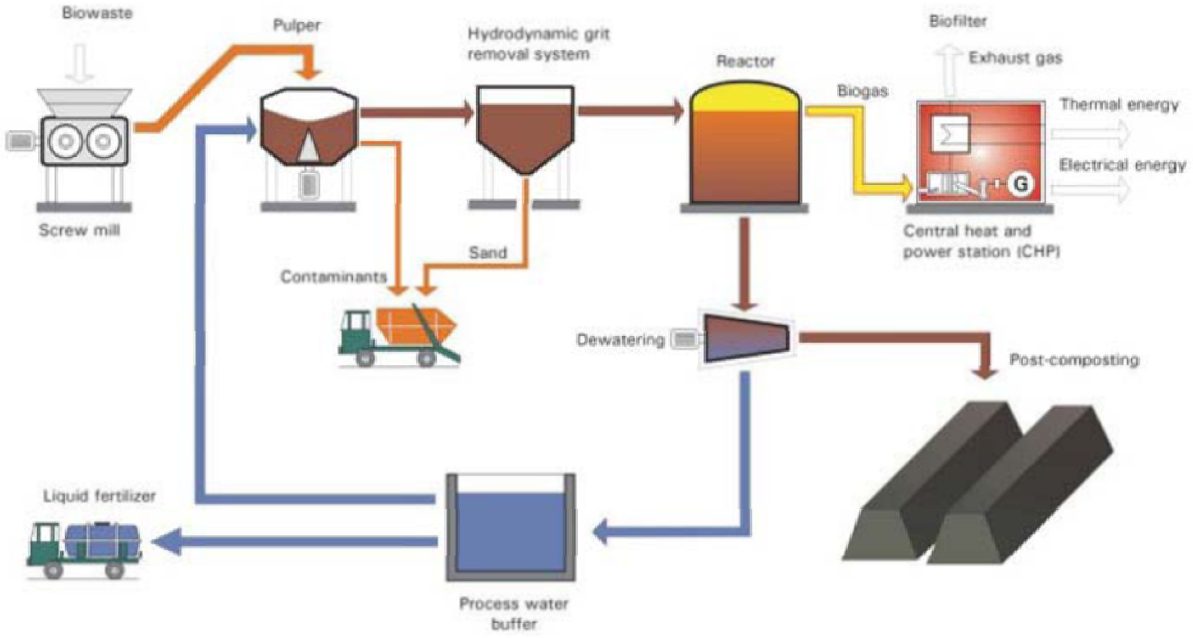

Figure 2.5: BTA Single Stage Reactor (www.canadacomposting.com)

For plants with a capacity of more than 50,000 tonnes per year, the multi-stage digester was developed, including separation of the pulp by dewatering in to a high solids mass fraction and a liquid phase fraction. The dewatered solid fraction is mixed with fresh water/recirculated process water (confidential information) to increase the moisture content then fed into the first stage hydrolysis reactor (4 day HRT). After hydrolysis, the solids are again dewatered, and the liquid fraction is pumped into a fixed film methane phase reactor along with liquid from the original pulp dewatering. The retention time in the methane reactor is 2 days. This process is shown in Figure 2.6. As a further variation a two-stage version may be used for plants with medium capacity, based on the multi-stage concept but without a solid/liquid separation. The biogas produced at BTA plants is 60-65% methane and the solid digestate is aerobically cured for 1-3 weeks.

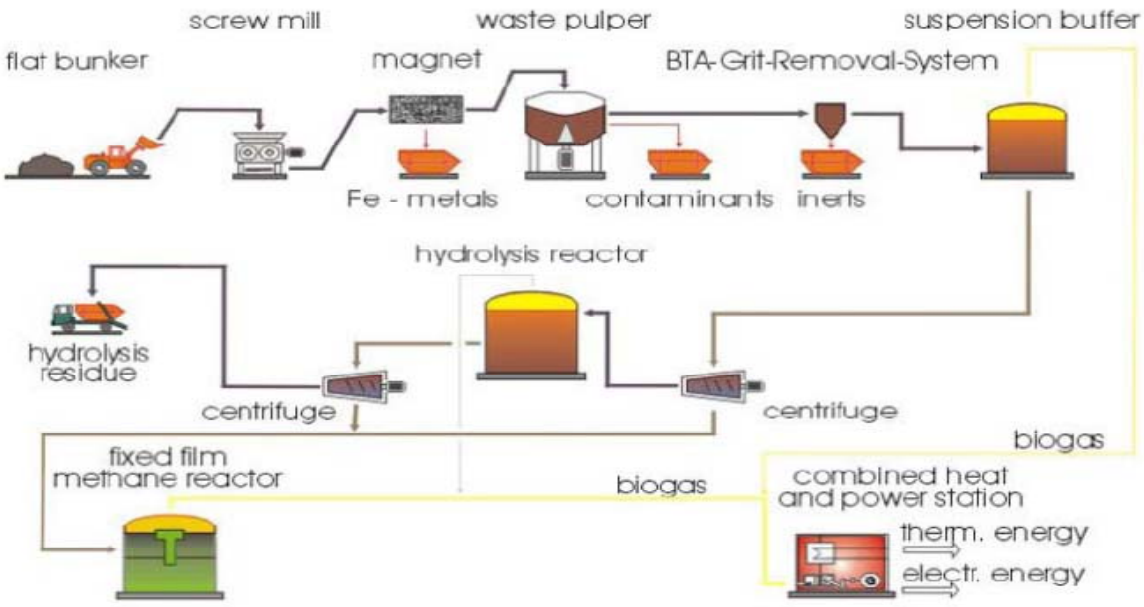

Figure 2.6: BTA Multi-stage Reactor (Canada Composting, 2004)

2.6.2. Kompogas

The Kompogas process was developed by W. Schmid of Glattbrugg, Switzerland in the 1980s and the first plant was put through a trial phase in 1991. Solid organic waste is shredded into approximately 30 mm nominal diameter size. Metal in the shredded waste is removed by magnetic separator. The shredded waste is mixed with process water in a mixer (confidential information) then placed in intermediate storage to ensure a homogenous organic mixture and constant flow into the feeder. The homogenous mixture is next introduced in to the anaerobic digester with a positive displacement piston pump. After passing through a heat exchanger, it is sent to a horizontal plug-flow thermophilic reactor equipped with a slowly rotating agitator. The thermophilic process takes place at 55 to 60 ºC and lasts for 15 to 20 days. The long HRT and elevated temperatures under AD conditions are reported to result in a significant kills of pathogens as well as undesirable rootlets and seeds (Figure 2.7).

The system must be carefully monitored to maintain the solid content between 23 and 28% so that flow can continue unimpeded and heavy particles remain in suspension (Nichols 2004). Due to the mechanical requirements of the system, the size of the reactors is limited. Added capacity at one site is satisfied by installing additional reactors that are operated in parallel. This modular design reduces capital construction costs as well as allowing for a wide range of

facility sizes, from 5,000 to 100,000 metric tonnes per year. The process can recover and utilize the biogas which consists of approximately 60% CH_4 and 40% CO_2. The methane yield is between 80 and 120 m^3/metric tonne of feedstock.

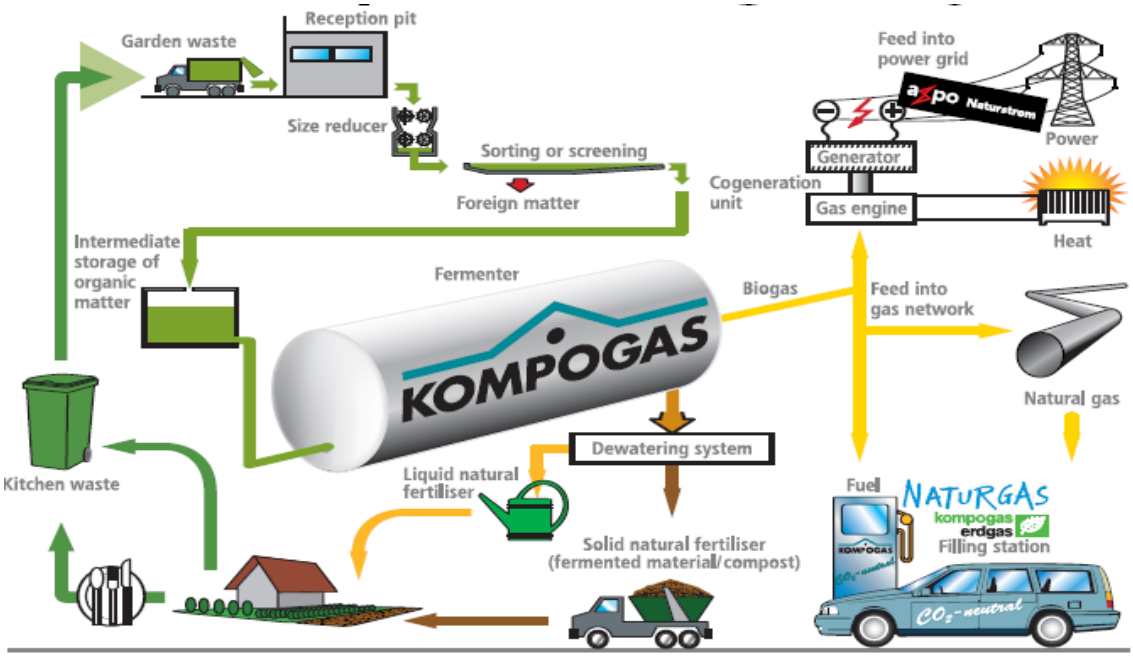

Figure 2.7: Kompogas anaerobic digester (Partl 2007)

2.6.3. Valorga

The first Valorga process pilot plant was built in 1982 in France. The pretreatment in the Valorga process uses an automatic separator to divide the waste into the organic fraction, including fermentable material, paper and cardboard, and nonorganics. The crushed waste is mixed into a thick sludge, with a TS content of 25-35%, and introduced at the bottom of the reactor, which can be thermophilic or mesophilic. The single stage reactor is a vertical, plug-flow cylinder with an inner wall that forces material to go up and over it before being extracted from the bottom on the other side (Figure 2.8). This geometry guarantees that waste has a residence time of 18 to 25 days in the fermentation chamber. Recycling gas to the base of the digester induces mixing. The digestate removed from the digester pass into screw presses and/or centrifuges to separate the solids from the liquid digestate. Part of the extracted liquid is used to dilute incoming waste (confidential information) and the rest is discharged in

the sewage. The solid fraction (with a TS content of about 40%) produced is transferred to the aerobic post-treatment unit. The biogas is used for heat, electricity, or is purified to natural gas. A biofilter treats the aerobic gases produced to eliminate odour. The methane yield is between 80 and 160 m^3/metric tonne of feedstock.

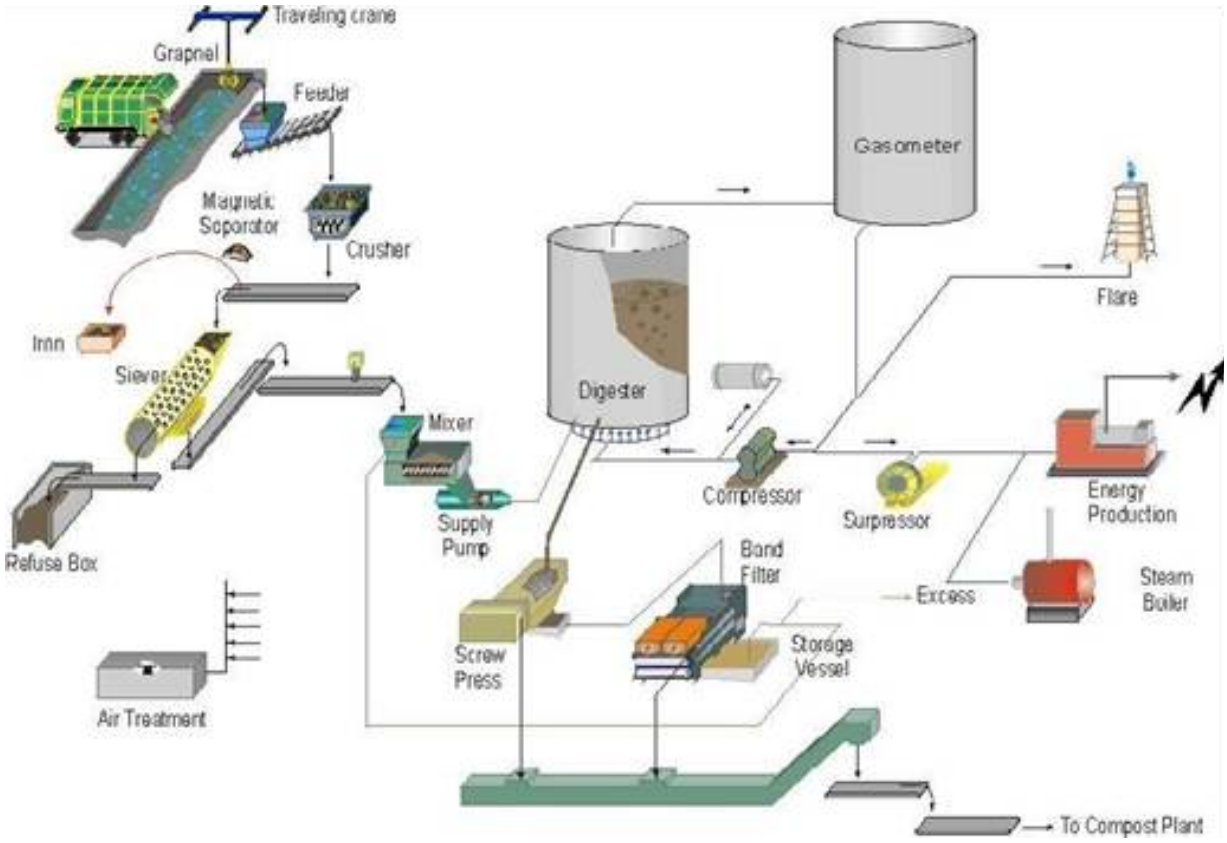

Figure 2.8: Valorga anaerobic digester (Valorga 2004)

2.6.4. Dranco

The first DRANCO facility on an industrial scale began operating in Brecht, Belgium in 1992. Organic Waste Systems Inc. (OWS) currently operates twenty full scale plants worldwide using the DRANCO process.

OWS also developed a sorting, digestion and separation system named the SORDISEP process (SORting, DIgestion and SEParation) for municipal and industrial solid waste treatment for maximum recovery of recyclables and energy. In the dry sorting step, Refuse Derived Fuel (RDF), ferrous and non-ferrous metals are recovered. The remaining feedstock is

mixed with digested material to form a mixture with a15-40% TS content; there is no further mixing in the vessel. DRANCO digestion is a single stage, vertical gravity driven plug flow system, where the waste is introduced at the top of the chamber and removed at the bottom with no other means of mixing. The system is run at thermophilic temperatures with a 15-30 day retention time. Biogas production ranges from 100 to 200 m^3/tonnes of waste feed stock which can be stored and purified before being used for a variety of purposes. The solid digestate is dewatered to about 50% and then further stabilized aerobically (approximately 2 weeks).

2.7. Existing Pretreatment Methods

"When considering particulate substrates like MSW and OFMSW, both the accessibility of hydrolytic microorganisms to the solid matter and hydrolysis of complex polymeric components constitute the rate limiting step" (Eastman and Ferguson 1981). One way of improving the performance of MSW and OFMSW digesters is to increase the hydrolysis of organic matter by pretreatment of the substrate. Regardless of pretreatment, the objectives are: a) to obtain an extension and acceleration of the anaerobic process; b) to increase the amount and yield of the biogas produced and; c) to reduce the volume of the anaerobic digestate and d) reduce the digestion time of the process. Satisfying these criteria occurs by breaking insoluble polymer chains into soluble components, thus making the reaction products more biodegradable as well as more accessible for bacteria to digest. Major pretreatment methods covered in this review. Include: mechanical, thermal, physic-chemical, chemical, thermo-chemical and MW pretreatment.

2.7.1. Mechanical Pretreatment

In mechanical pretreatment of TWAS, the disruption of cell walls occurs within seconds or minutes instead of days by applying mechanical disruption. The intracellular components of the cells are immediately available for biological degradation which has the potential to accelerate the AD process (Muller et al. 1998).

2.7.2. Size Reduction

Many studies have investigated mechanical pretreatment with size reduction. Muller et al. (1998) and Kopp et al. (1997) tested (laboratory scale) four methods of mechanical cell disintegration using sewage sludge with SS content of 1%-4% and VSS of 70% of total suspended solids (TSS). The sludge was disintegrated using a stirred ball mill, a high-pressure homogenizer, an ultrasonic homogenizer, and a shear-gap homogenizer. Overall the research concluded that disintegration leads to a higher degree of biodegradation, higher gas production, and reduction in the volume of sludge to be disposed. In addition it was found that the extent of cell disruption depends on the operational parameters of the disintegration machines and on the initial SS content. Disintegration rates near 90% were obtained for optimal operating conditions with all methods tested except when using the shear gap homogenizer. When considering power consumption, the stirred ball mill and high pressure homogenizer demonstrated to be the most economical disintegration techniques. These results are in agreement with the findings of Baier and Schmidheiny (1997), who used a stirred ball mill and a high speed cutting mill for enhancement of AD by disintegration of TWAS. The stirred ball mill showed more significant disintegration vs. the cutting mill. Under optimized conditions the initial soluble COD (SCOD) of samples increased from 5.5% to 22% of the total COD (TCOD) after using the stirred ball mill, in addition, the milling led to a 10% increase in biogas production based on mesophilic batch biochemical methane potential (BMP) assays. Another study by Machnicka et al. (2005) evaluated a high pressure homogenizer for pretreatment of WAS prior to mesophilic AD (MAD). A high pressure pump (10 MPa), which recirculated sludge from a 25 L container through a 1.2 mm nozzle. SCOD increased about 2, 3 and 3.5 times, respectively, compared to initial SCOD after 15, 30 and 60 minutes of pretreatment, respectively. An 82% improvement in cumulative biogas production (CBP) was observed after 14 days of mesophilic batch AD when 20% (v/v) pretreated sludge was added to WAS. A recent study by Lee et al. {, 2010 #593}further investigated the effects of ball mill pretreatment on the solubilization of sewage sludge. They observed a rapid increase of SCOD as a function of the specific energy input; however the rate of increase slowed gradually as more specific energy was applied, especially at low TS content of 1%. Optimal conditions were achieved at high TS of 4%. When the TS was 4%, the increase in SCOD (SCOD of untreated sludge- SCOD of treated sludge) was approximately 9,000 mg/L

with a specific energy input of 75.8 KJ/g TSS treated. The higher increase in SCOD for high TS sludge was attributed to increased contact between cells and milling beads. The research was limited to solubilization tests and AD after pretreatment was not studied.

Hartmann et al. (2000) extended mechanical pretreatment studies to examine treatment of cow manure. Pretreatment of cow manure in a macerator resulted in an increase in mesophilic biogas production of up to 25%. Results from the macerators indicated that the biodegradability of fiber material in the manure feedstock is enhanced by shearing which is not necessarily reflected by a change in fiber size. Degradable cellulose and hemicellulose was released from the damaged fibers into the liquid fraction, making it more readily available for degradation.

Palmowski and Muller (2000) investigated the effect of comminution of organic material using various machines on anaerobic biodegradability. These investigations demonstrated two positive effects of the comminution of organic solids on their biodegradability under single stage mesophilic anaerobic conditions. Pretreatment of substrates like maple leaves and hay stems containing a large percentage of fibres which are difficult to digest resulted in up to an 18% increase in biogas production as a result of the comminution. This is while mixtures of apples, carrots and potatoes and meat, which have low fibre contents and are very biodegradable, showed no improvement in overall biogas production. The second effect occurs with all the substrates and particularly substrates which are not easy to digest. Samples pretreated by comminution demonstrated a clear reduction in the digestion time which was decreased by 23-59% with little to no reduction in organic removal efficiency. This is in agreement with studies by Mshandete et al. (2006), who carried out batch MAD of sisal fibre waste in 1 L digesters with an average fibre length of 50 mm. The sisal fibre waste was reduced to lengths of 2 mm by grinding using a laboratory mill. Total fibre COD degradation via AD increased from 31% to 70% for the 2 mm fibres, compared to untreated sisal fibres. In addition, methane yield increased to 0.22 m^3 CH_4/kg VS (2 mm), compared to 0.18 m^3 CH_4/kg VS with no size reduction that shows by 22% increase in methane yield. These studies provided quantified evidence of the impact of size reduction on bioavailability of substrate.

2.7.3. Ultrasound Pretreatment

The frequency range for ultrasound (US) is between 20 kHz and 10 MHz. In an aqueous environment, the application of US at frequencies between 20 to 40 kHz results in the formation of small bubbles due to localized pressure drops below the vapor pressure of the aqueous phase. The bubbles oscillate, grow, and collapse in a nonlinear manner and create cavitations. The cavitations, in turn, cause strong mechanical shear forces and extreme temperature increases inside and around the bubbles (Chu et al. 2001). US disintegration is essentially a physical process, and therefore it neither generates secondary toxic compounds nor contributes additional chemical compounds. (Khanal et al. 2007).

The use of US pretreatment can effectively reduce the particle size of sludge and other suspended organic materials. The size reduction efficiency is dependent upon the sonication time (Tiehm et al. 1997), ultrasonication density (El-Hadj et al. 2007; Show et al. 2007; Laurent et al. 2009), sonication power (Mao and Show 2006), sludge or sample volume and sludge or sample characteristics (Cao et al. 2006).

Tiehm et al. (2001) reported that disintegration of WAS was most effective at lower frequencies (41 kHz) when they examined a range of frequencies between 41 and 3217 kHz. Disintegration of WAS was assessed based on reductions in the median sludge particle size, the increase in turbidity of the sludge samples, and the increase in SCOD of the sample which was used to determine the disintegration ratio (ratio of COD increase of sample vs. control). The most effective frequency was found to be at 41 kHz with a sonication time of 7.5 minutes. By increasing the sonication time from 7.5 minutes to 30, 60 and 150 minutes, further improvements in WAS disintegration were also obtained (SCOD has compared with a reference that was pretreated by sodium hydroxide, further details have explained in Tiehm et al. (2001)). For sonication times of 30, 60, and 150 minutes, the extent of disintegration was increased by 4.7, 13.1, and 23.7%, respectively compared to 7.5 minutes. Additionally, biogas production and VS reduction based on batch MAD for the one hour sonicated sludge increased by approximately 31% and 46%, respectively, compared to the control. Other studies by Chu et al. (2001) examined the effect of different sonication densities (W/mL) and times on WAS floc size at a consistent frequency of 20 kHz and a maximum power input of 110 W. The original sludge floc exhibited a mean diameter of 98.9 mm and when the power level had exceeded to 0.22 W/mL the particle size apparently decreased. At 0.33 W/mL, the floc

diameter was reduced to 22 mm after 20 minutes and approximately 4 mm after 120 minutes of sonication. At 0.44 W/mL, the floc size decreased to less than 3 mm after 20 minutes of sonication. Further sonication resulted in only slight reduction in the floc size. The study concluded that ultrasonic density was more important than the sonication time for effective sludge disintegration. At 0.33W/mL about 20% of the suspended COD had been transformed into SCOD after 120 minutes of sonication at 20 kHz. The increase of the BOD/TCOD ratio from 0.66 to 0.80, indicated that most of the newly solubilized COD was biodegradable. An additional study by Mao and Show (2006) confirmed the findings of both Tiehm et al. (2001) and Chu et al. (2001). Working with WAS, Mao and Show (2006) showed that the sludge particles were disintegrated from a mean size of about 51 mm to 33, 24, and 18 mm at sonication densities of 0.18, 0.33 and 0.52 W/mL, respectively when using a frequency of 20 kHz, and exposure time of one minute and maximum power output of 1500W. The results indicated that the SCOD also increased to 929, 1135 and 1385 mg/L after treatment at the respective sonication densities, compared with SCOD 723mg/L in untreated sludge. Correspondingly, the ratio of SCOD/TCOD expressed as percent also increased from an initial of 3.5% to 4.2%, 5.3% and 6.0%, respectively. The results again illustrated that higher degrees of WAS disintegration occur at higher US density. The impact of sonication on the MAD of pretreated sludge at HRTs of 8, 4, and 2 days was also assessed. Biogas production was increased by 2.0, 2.5 and 2.4 times, respectively compared to the control. An increase in methane composition by 10% was also observed which may be related to elevated pH associated with solubilisation and digestion of protein material. The improved biogas production was supported by the increase in VS removal efficiency which was 68% in digesters with pretreated sludge at HRT of 2 days, while the control showed only 40% efficiency.

The relationship between WAS sample solubilization and energy has been reported by Khanal et al. (2007), who studied effects of specific energy input on SCOD increase at a frequency of 20 kHz, a maximum power of 1.5 kW, a TS content of 3% and an US density of 1.07 W/mL. The SCOD increased with longer sonication times, and thus at a higher specific energy input. However, the release in SCOD slowed at energy inputs of over 35 kJ/g TS which were likely due to re-flocculation of the particles. Initially floc sizes are reduced but further increase in sonication time causes more intracellular polymers to be released from cell lysis, creating favourable conditions for re-flocculation (Gonze et al. 2003; El-Hadj et al. 2007). Based on

this finding, an energy input of 35 kJ/g TS was found to be optimal for maximal sludge disintegration at 3% TS content. Wang et al. (2006a) had similar findings when comparing SCOD, protein, polysaccharide and DNA of pretreated sludge and untreated sludge after different sonication times. Using an ultrasonic density of 0.768 W/mL, and exposure times of 5, 15 and 20 minutes, the SCOD increased to 2581, 7509 and 8912 mg/L, respectively vs. the control SCOD concentration of 52 mg/L. Longer exposure times more than 20 minutes did not significantly further increase the SCOD concentration. It was also observed that the release of protein, polysaccharide and DNA in to the soluble phase also occured quickly during the first 20 minutes (50 kJ/g TS), and then the increase slowed as the time increased.

Other studies have examined the use of US applied to different TS concentrations. Akin (2008) used US for disintegration of WAS at different TS concentrations with low US frequency of 20 kHz. A SCOD release of about 329 mg SCOD/g TS was obtained at a TS content of 2% and specific energy input of 5 kJ/g TS which decreased to 248 and 124 mg SCOD/g TS at TS contents of 4 and 6%, respectively at the same specific energy input indicating the role of TS concentration on waste solublization.

In the recent study by Koksoy and Sanin (2010) the effect of the F/M ratio was compared for sonicated and unsonicated sludge using batch MAD assays. Sonicated reactors treating sonicated sludge always produced higher cumulative amounts of methane compared to unsonicated reactors with the same F/M ratio indicating that the extent of waste degradation was increased by US pretreatment.

On the industrial scale, full-scale installations using high-powered ultrasound probes for conditioning sludge have been installed by Sonix™ in sludge plants in the UK, US and Australia. Biogas production rates in these plants has increased by 40–50%, and VS reduction increased by 30–50% compared to controls (Pilli et al. 2011).

2.7.4. Thermal Pretreatment

Heat treatment alters the structure of the insoluble fraction of sludge and suspended solid sample to make them more amenable to biodegradation. The main advantages of thermal pretreatment of sludge are: improvements in VS biodegradability and biogas production; better dewaterability of the treated sludge; as well as an increase in pathogen reduction and odour control (Bougrier et al. 2006; 2007; Jeong et al. 2007).

Research by Li and Noike (1992) focused on the thermal pretreatment of secondary sludge, and they concluded that a temperature of 170 ºC for 60 minutes was the most favorable pretreatment conditions over the range that was examined in terms of increased COD removal and gas production during MAD. The retention time for AD of WAS thermally pretreated at 170 ºC for 60 minutes, could be safely reduced by 5 days. With these conditions, COD removal increased by 60%, with a almost two fold increase in biogas production compared to the control. Bougrier et al. (2007) also used high temperatures for the pretreatment of sludge. They concluded that a thermal treatment at 190 ºC was more efficient than treatment at 135 ºC in terms of TCOD, lipids, carbohydrates, and protein removal as well as for methane production using MAD conditions. However, treatment at 190 ºC produced refractory soluble COD, and AD effluent SCOD increased 75% compared to the control. This phenomenon was not observed for treatments at 135 ºC.

Similar studies investigated thermal hydrolysis with temperatures ranging from 60 to 210 ºC with six different waste-activated sludge samples from municipal and industrial wastewater treatment plants working at high load, medium load, or extended aeration conditions. Results showed that the SCOD concentration increase was linearly correlated with the treatment temperature over the entire temperature range studied and was independent of the sludge sample composition, The MAD biodegradability was however related to sludge type. As might be expected higher organic matter content was associated with higher AD biodegradability. Using BMP assays, it was found that biodegradability of samples increased with pretreatment temperature up to 190 ºC after which it slightly decreased (Bougrier et al. 2008; Carrere et al. 2009) suggesting the release or formation of recalcitrant or inhibitory compounds at the higher temperatures.

Using thermal pretreatment, Minowa et al. (1995) changed the phase state of model OFMSW (M-OFMSW) from solid to a liquid slurry by thermal liquefaction, at temperatures of 150, 200, or 250 ºC. Sedimentation of the particulates was also observed to increase at the higher temperatures. The liquidized waste was regarded as a pseudo plastic fluid from viscosity measurements, and the apparent viscosity decreased significantly as the temperature increased. Inoue et al. (2002) also used high temperature for liquefaction of OFMSW. They liquidized M-OFMSW using thermochemical process temperatures between 150 ºC and 250 ºC and pressures varying between 3.5 and 7.0 MPa and also by a mechanical disruption process. It was demonstrated that a reaction temperature of 175 ºC is optimal for the liquidization of the

waste as a pretreatment prior to AD. The waste that was transformed to liquid slurry had a greater proportion of lower molecular weight organic acids compared with the mechanically disrupted M-OFMSW. Optimum mesophilic methane production was observed after pretreatment at 175 ºC, which quantitatively resulted in an increase in methane production of 27% compared to the control. At more elevated temperatures, total organic carbon (TOC) in the liquid phase decreased compared to control, which might considered that organics in the liquid phase were converted into oil and/or gas. In a different study, Sawayama et al. (1997) investigated the effect of thermochemical liquidization with sodium carbonate (5% on a dry solid basis) as a pretreatment for the AD of kitchen waste. Model kitchen waste was thermochemically liquidized at 175 ºC and 4 MPa with one hour holding time. The liquidized waste was separated into a suspended solid fraction and a soluble filtrate. The filtrate was then anaerobically digested in a mesophilic batch system. The biogas yield from the filtrate after 4 days of digestion was almost 2 times higher than that produced from the mechanically disrupted garbage. The percent composition of methane in the biogas from the liquidized waste was 64% and the soluble filtrate was 62% after 7 days of incubation both of which were higher than that for the whole mechanically disrupted waste which had a methane content of 48%. The energy balance of the liquidization and AD treatment process has been analyzed to be less energy intensive than direct incineration indicating an alternate management strategy for this type of waste.

Schieder et al. (2000) used thermal hydrolysis (TDH) as a pretreatment method for the digestion of organic waste (canteen and gastronomic food wastes). Reactor temperatures between 160 ºC and 200 ºC, pressures up to 4 MPa and residence times of up to 60 minutes were most successful for a raw material mash with dry matter of 10–15%. TDH and MAD, showed a conversion of 60–80% of the feed organic waste material at a total treatment time of less than 10 days, which consisted of less than 1 hour in the TDH reactor and 6–9 days in a fixed bed methane reactor. Using this system COD removal of 65-76% and the specific gas production of 500 L/kg COD added was obtained in 10 days, whereas the raw material required 20 days to reach a similar COD removal and gas production of 470 L/kg COD added. Similarly, Wang et al. (2006b) developed the hybrid 2 stage anaerobic solid–liquid (HASL) system to minimize the amount of food waste for disposal. The thermal pretreatment of food waste at 70 ºC for 2 hours (E1) or at 150 ºC for 1 hour (E2) accelerated the hydrolytic and acidogenic processes in the acidogenic reactor and methanogenesis in the methanogenic

reactor in the HASL system. The average rate of SCOD production in the acidogenic reactor increased by 1.4% for E1 and 5.5% for E2 in comparison with the control. The SCOD in the effluent from the methanogenic reactor was lower (less than 1000mg/L) in experiments E1 and E2 than that in the control (>1500 mg/L). The use of thermally pretreated food waste halved the time to produce the same quantity of methane in comparison with AD of fresh food waste.

Rafique et al. (2010) studied the effect of thermal pretreatment from 75-150 ºC on MAD of dewatered swine manure . Highest biogas production and highest yield was obtained at the pretreatment temperature of 100 ºC. After pretreatment at 100 ºC CBPs were 30%, 29% and 30% higher than the control after 7, 19 and 29 days respectively. Biogas production from thermally treated samples at 130 and 150 ºC were less than control due to the formation of complex recalcitrant or inhibitory organic compounds at the higher temperatures (Hendriks and Zeeman 2009).

2.7.5. Physico-Chemical Pretreatment

Wet air oxidation (WAO) is a physico-chemical process that oxidizes solid waste with high organic matter content, using high temperatures (150-370 ºC) and high pressures (5-15 MPa). The principle of this method is to enhance the contact made between molecular oxygen and the organic matter. The high temperatures in a closed system prepares the waste for oxidation, under high pressure oxygen reacts with organic matter to produce inorganic salts and simpler forms of biodegradable and non-biodegradable compounds.

Khan et al. (1999) used WAO for solubilization of WAS prior to AD. Temperatures ranging from 200 to 300 ºC, and retention times of 10, 30 and 60 minutes, under stoichiometric oxygen conditions were tested. Temperature showed to be the most significant parameter, followed by retention time and oxygen pressure. At 200 ºC and for retention times of 10 and 30 minutes, the generation of SCOD was 9 and 4 times greater than the control respectively, whereas at 300 ºC the value was only 1 fold greater which was assumed to be due to the production of recalcitrant compounds at the more extreme condition. Another study by Liu et al. (2002) utilized pressurized steam (240 ºC, 5 minutes) as a disruptive pretreatment step for lignocellulosic-rich biomass including MSW. There was no lag phase in gas production when pretreated substrate was digested at mesophilic anaerobic conditions. In addition, treated

samples provided a 40% improvement in methane yield and a 40% increase in VS reduction indicating that the MSW had been made more biodegradable substrate. In other research, Lissens et al. (2004) studied the effect of WAO at temperatures ranging between 185 ºC and 220 ºC, pressures between 0 and 1.2 MPa and constant reaction time of 15 minutes on AD enhancement for a variety of solid biowastes including; food waste, yard waste and digested biosolids. Compared to the controls, SCOD concentrations were 4.8 to 5.9 times higher at high pressures, whereas it was only a factor 2.3 to 3 times higher for low pressures. Overall, higher oxygen pressures during WAO of digested biowastes (in a full-scale plant) increased the total methane yield and stabilization kinetics by 35-40%. These results were in agreement with Wang et al. (2010) who demonstrated that the anaerobic digestibility of bulrush plants can be significantly enhanced by steam explosion pretreatment. Under optimum conditions of 11% moisture, 1.72 MPa steam pressure and a holding time of 8.14 minutes, 205.3 mL methane/g TS added was obtained compared to 164.5 mL/g TS added for untreated bulrush.

2.7.6. Chemical Pretreatment

Chemical pretreatment at ambient temperatures have been proposed using acids, bases, or extracellular enzymes. In comparing acidic with alkaline treatment, the latter is more compatible, especially when such pretreatment is to be followed by AD as acid pretreatment generally requires pH adjustment by increasing alkalinity prior to digestion (Liu et al. 2002).
Solubilization of WAS under different chemical dosages of NaOH at different mixing times (3, 4 and 5 hours) followed by MAD was conducted and it was observed that for dosages less than 15 meq/L all AD reactors had the same performance in terms of VS and COD reduction at HRTs of 7.5 or 20 days. From pilot scale experiments the best biogas production was observed when WAS at 1% TS was pretreated with 12.5 meq/L NaOH. Mesophilic retention time was reduced from 25 to 10 days without effecting WAS stabilization overall process performance and effluent quality (Knezevic et al. 1995). Penaud et al. (1999) also investigated solubilization of municipal sludge by chemical addition. Alkali treatment enhanced solubilization of microbial biomass with 63% of suspended COD solubilization achieved at ambient temperature, when 4.6 g of NaOH/L was added and held for 3 hours. Greater NaOH addition (more than 5 g NaOH/L) did not lead to further significant increases in COD solubilization. It signifies an optimum concentration of NaOH for solubilization.

In a study from Pavlostathis and Gossett (1985), wheat straw was treated with NaOH then underwent MAD. All pretreatment experiments were conducted at room temperature and four solids concentrations were tested: 2.5, 5, 7.5, and 10% (w/v). The alkali level ranged from 0.02 to 0.5 g NaOH/ g dry matter and the treatment time ranged from 0 to 24 hours. The highest biodegradability achieved was 280 mL CH_4/g COD added when pretreatment conditions were 7.5% TS, 0.5 g NaOH/g TS and 24 hours exposure compared to the control at 120 mL CH_4/g COD added. Alkaline treatment resulted in a greater than 100% improvement in wheat straw biodegradability. In a recent study, NaOH was used for pretreatment of rice straw (He et al. 2008b) prior to AD. Biogas yield of rice straw during AD was substantially increased through NaOH pretreatment. The biogas yield of 6% NaOH-treated rice straw increased by 64.5, 44.4, 27.3, and 42.9% at initial loadings of 35, 50, 65, and 80 g TS/L compared to controls, respectively. It was shown that a large proportion of the cellulose (16.4%), hemicellulose (36.8%), and lignin (28.4%) in the NaOH-treated rice straw were solubilised as indicated by a 122% increase of water-soluble extractives and subsequently degraded as indicated by the increase in biogas yields. The decrease of LCH (lignin-carbohydrate complexes), cellulose, hemicellulose, and lignin contents as well as the increase of water-soluble substances made the NaOH-treated rice straw more digestible.

Similarly, Heo et al. (2003) reported that the particulate solubilization of simulated food waste (SFW) and WAS was proportionally increased with the increasing temperature and alkali dosage. The maximum solubilization was 27.2%, 31.4% and 38.3% after a reaction time of 4 hours at 25, 35 and 55 °C with 45 meq NaOH/L, respectively. The ultimate methane yields of SFW and WAS without pretreatment were 430 and 165 mL CH_4/g VS added, and the methane production of the pretreated WAS (PWAS) at 25, 35 and 55 °C was more than 66%, 73% and 88% of the cumulative methane yield of 165 mL CH_4/g VS added for WAS without pretreatment, respectively. Additionally, methane production during anaerobic co-digestion was affected by different fractions of SFW and PWAS. Torres and Llorens (2008) also studied the effect of alkaline pretreatment on AD of OFMSW. 11.5% of the COD was solubilized under the optimal condition that was 62.0 meq $Ca(OH)_2$/L (equivalent to 2.3 g $Ca(OH)_2$/L) and contact time of 6 hours. The maximum methane yield with AD of the PWAS was 0.15 m^3 CH_4/kg VS that is 172% of the control, also SCOD and VS removal of 93.0% and 94.0% was achieved, respectively. Further addition of $Ca(OH)_2$ decreased solubilization, which may be associated with instability and formation of complex, non-soluble compound.

Another study using chemical pretreatment was completed by Pang et al. (2008) who used NaOH to pretreat corn stover to improve biodegradability and anaerobic biogas production. NaOH doses of 4, 6, 8, and 10%, based on dry matter of corn stover, were tested. Four loading concentrations of 35, 50, 65, and 80 g/L (dry weight) of corn stover loaded per litter effective volume of digester (g TS/L)) were examined. At high loading concentrations of 50, 65, and 80 g/L, the CBPs treated corn stovers were 26.8-40.4%, 39.8-48.5%, and 58.0-69.1% higher than controls at corresponding loadings, respectively. The optimal condition for pretreatment was 6% NaOH and loading concentration of 65 g/L, under this condition corn stover produced 48.5% more biogas compared to the untreated control.

Kim et al. (2010) studied the effect of alkaline (6 N KOH), ultrasonic and bimodal or combined (alkaline & ultrasonic) pretreatment on the disintegration of sewage sludge. Increases in solubilization were limited to 50% with individual pretreatment techniques, but it increased to 70% with the combined pretreatment. When pretreated sludge (pH of 9 +7500 kJ/kg TS) was used to feed an mesophilic anaerobic sequencing batch reactor (ASBR), CH_4 significantly increased, from 81.9 CH_4/g COD added before pretreatment to 127.3 mL CH_4/g COD added after combined pretreatment, which was a 55% increase in biogas generation from the same feed stock and is an indicator of the synergistic improvements possible from combining pretreatment technologies.

2.7.7. Thermo - Chemical Pretreatment

Valo et al. (2004), studied different pretreatment conditions to evaluate the effects of temperature, pH and treatment time on WAS solubilization, and AD of sludge. SCOD increased from 59.5% to 83% at 170 ºC with pH of 12 after 1 hour of treatment. 170 ºC compared with 130 ºC at pH of 10 demonstrated better performance for continuous AD, as it led to 71% of COD degradation and 59% of TS degradation, with an improvement of 54% in biogas production compared to control.

Kim et al. (2003) studied enhancement of AD of WAS with different pretreatment techniques including thermal, chemical, ultrasonic and thermochemical. The thermal and thermochemical pretreatment methods showed the great improvement in solubilization and biogas production in mesophilic BMP assays. Under optimum conditions for thermal (30 minutes at 121 ºC) and thermochemical pretreatment (7g/L NaOH and heating for 30 minutes at 121 ºC) the

SCOD/TCOD ratio increased from 8.1% to 17.6% and 85.4% after pretreatment, respectively. Increases in biogas production were 35.2% and 34.3% higher compared to the control. The increase in gas production was not as high as the increase in solubilization, and it was suggested that maybe part of the generated SCOD was refractory.

Wu et al. (2009) conducted a study on thermochemical pretreatment of meat and bone meal (MBM) prior to MAD. At two tested temperatures (55 °C and 131 °C), five alkaline conditions were tested by adding 1.25, 2.5, 5, 10 and 20 g/L of NaOH to the samples. The SCOD concentration increased with higher dosage of NaOH but no further increase was observed with NaOH dosage above 5 g/L. With the same dosage of NaOH SCOD production at 131 °C was higher than at 55 °C. By adding NaOH, the reaction was accelerated, the reaction time was shortened from 24 hours to 8 hours at 55 °C and 0.5 hours at 131 °C. The CH_4 production of pretreated MBM was in the range of 389 to 503 mL CH_4/g VS MBM and 464 to 555 mL CH_4/g VS MBM at 55 °C and 131 °C, respectively. At 55 °C, alkaline pretreatment enhanced the AD of MBM however, inhibition was observed at 131 °C which did not coincide with the increase in SCOD at the higher temperature. This study showed that an increase in solubilization is not always paralleled by the same enhancement in biogas production by AD.

Chou et al. (2010) evaluated the effect of thermochemical pretreatment on solubilization of palm oil mill effluent (POME). Experiments were carried out at a temperature range between 30 to 60 ºC with NaOH concentration ranging from 0 to 16 g/L with the reaction times between 7 and 89 hours. The optimum condition based on response surface methodology for solubilization was 32.5 ºC with 8.83 g/L of NaOH after 41.2 hours of incubation which resulted in the highest SCOD/TCOD ratio of 82.63%, which was more than 2 fold greater than for the raw POME (36.97%).

Fdez-Guelfo et al. (2011) used thermochemical and biological pretreatments to enhance solubilization of OFMSW (TS of 30%). Mature compost, fungus *Aspergillus awamori* and activated sludge were used for biological pretreatments. Dual modality NaOH (1-5g/L) addition and thermal pretreatment (120-180 °C) in oxidizing atmospheres (N_2 and air) with a contact time of 30 minutes were tested. Thermochemical pretreatment showed higher solubilization compared to the individual biological pretreatments. The maximum solubilization was observed by thermochemical pretreatment at 180 °C with 3 g NaOH/L and 3 bar pressure which was 2.5 fold higher than the control.

2.7.8. Microwave Pretreatment

MWs are electromagnetic waves with wavelengths ranging from 1 mm to 1 m, or frequencies between 300 MHz and 300 GHz (Figure 2.9). Practically, MW frequencies start at 1 GHz according to both International Electrotechnical Commission (IEC) standard 60050 and Institute of Electrical and Electronics Engineers (IEEE) standard 100. MWs radiation leads to a thermal effect through the interaction of MWs and the dielectric material (Decareau 1985).

MW radiation causes molecular and ionic motion of molecules and ions of certain types of materials discussed below. This agitation or mechanical energy is directly transferred into thermal energy. A MW oven passes (non-ionizing) MW radiation (at a frequency near 2.45 GHz and at a wavelength of 12.25 cm) through the food, this causes dielectric heating by the absorption of energy by the water, fats, and sugars contained within the food. MW ovens became common kitchen appliances in western countries in the late 1970s, following development of inexpensive MW magnetrons.

The behavior of a sample when subject to MW heating, depends on its chemical and physical properties. Materials are classified according to their characteristic reaction to MW exposure. The material can be:

- Reflective: reflects all MW energy and does not increase the temperature of the sample. Metals are reflective materials.
- Transparent: transparent to MW energy and does not increase in temperature. Transparent materials, such as glass are good insulators.
- Absorptive: absorb MW energy and increase in temperature. One example of an absorptive material is water.

Some solids and liquids have the ability to transform electromagnetic energy into heat. This is called the dissipation factor, 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 $\tan\Delta = \varepsilon''/\varepsilon'$ where, $\tan\Delta$ is the dissipation factor, ε'' is the dielectric loss factor (amount of the input power lost from the sample by heat dissipation) and ε' is the dielectric constant of the material.

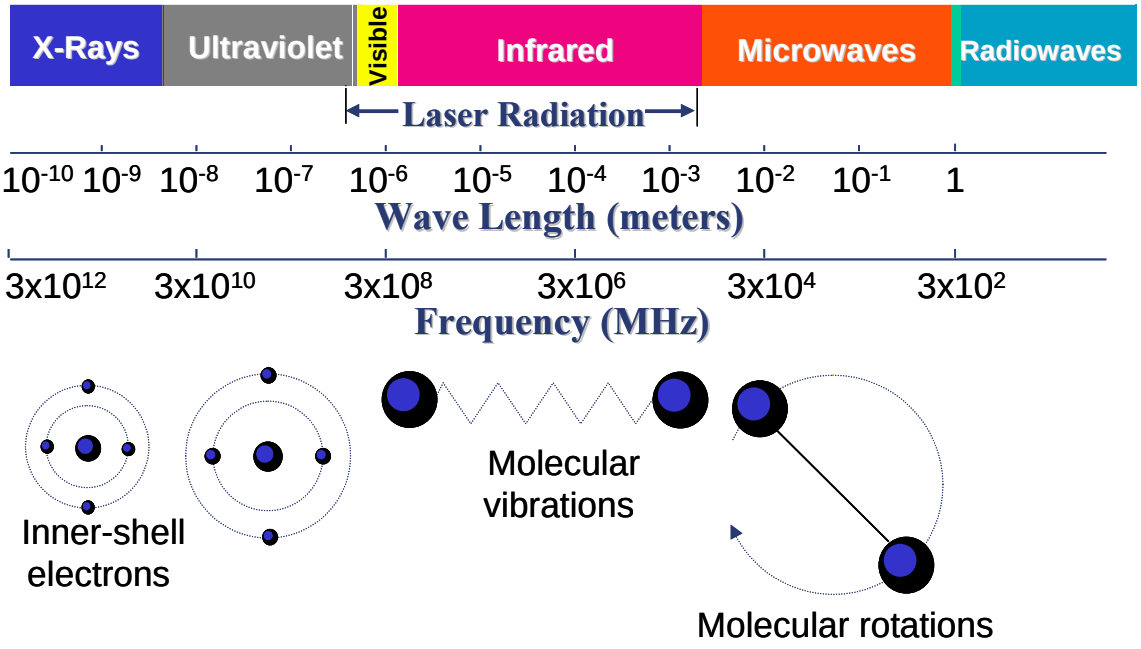

Figure 2.9: Electromagnetic spectrum (Kingston and Jassie 1988)

The higher the loss factor of a substance, the faster the substance can be heated in a MW field. At 2.45 GHz, the heating rate of water by microwaving is maximized and the dielectric constant of water increases with decreased frequency. The dielectric constant of water drops to zero very rapidly when the frequency reaches 30 GHz (Fini and Breccia 1999).

In conventional or conductive heating, energy transfers through the vessel and is then dissipated throughout the medium. Hot plates remain active after the completion of the sample heating and pose a risk of heating the sample to dryness. In contrast, in MW heating, the vessel wall is transparent to energy and, as a result, direct activation of the molecules of the sample is possible. Localized superheating maximizes heat transfer upon reaction completion as energy addition stops. This process is illustrated in Figure 2.10.

Nowadays, MW heating is used in many fields, such as the food industry for baking, thawing, tempering, pasteurising, sterilizing and drying; wood and particle board manufacture for drying, and in the medical industry for sterilization. MW technology is capable of faster and more uniform heating of polar molecules, such as water, while using less energy than conventional heating.

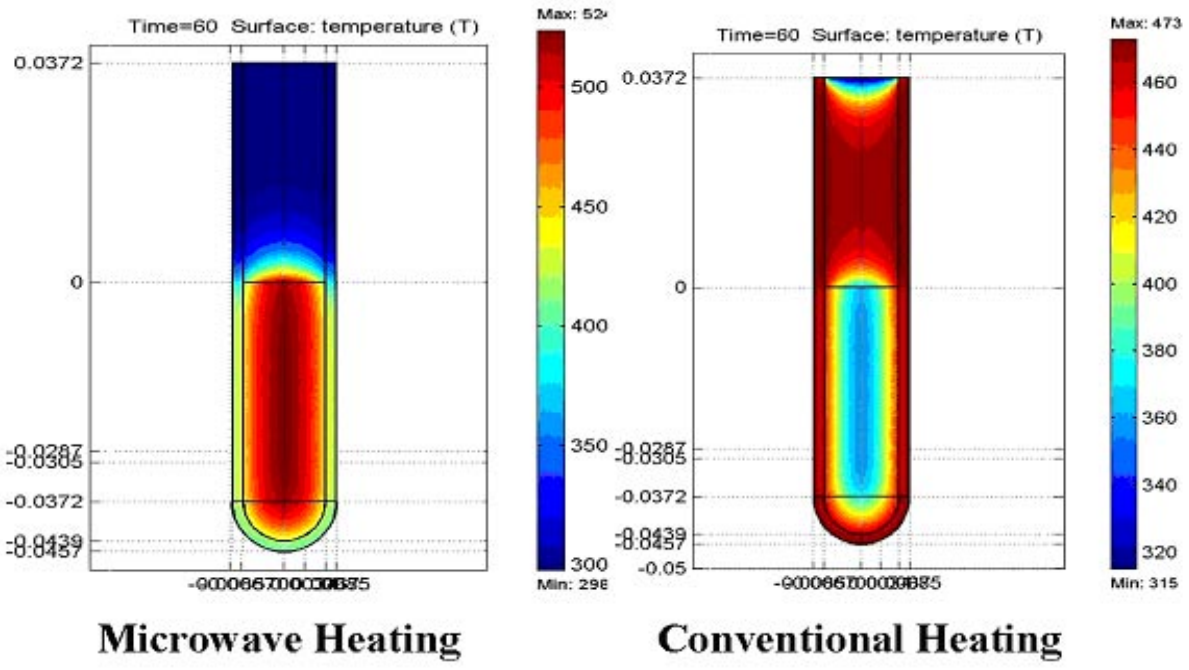

Figure 2.10: Comparison of Conventional and Microwave Heating (CEM Inc.)

2.7.9. Application of Microwave in Organic Waste Treatment

Conventional thermal or thermo-chemical treatment is a time-consuming process. With the purpose of heating organic waste, MW irradiation offers an alternative method. In recent years, MW as a novel technique for sludge pretreatment has attracted interest as it may simultaneously improve digestion and decrease the pathogen content. Sludge is a multiphase medium containing water, mineral and organic substances, proteins, and cells of microorganisms. Due to its high water content, sewage sludge absorbs MW irradiation effectively.

Park et al. (2004) investigated the effect of MW irradiation on domestic wastewater sludge for AD. The ratio of SCOD/TCOD increased from 2 to 22%, when sludge was irradiated with MW to its boiling temperature. AD of pretreated sludge with MW resulted in almost 2.5% increase of VS reduction under mesophilic conditions. Maximum rates of COD removal and methane production with the pretreated sludge were 64% and 79% higher than those of the control system, respectively. The MW pretreatment of sludge also resulted in a decrease in the HRT of the AD from 15 to 8 days, since the biogas production and VS removal rates were still high and the concentration of VFAs in the effluent was low. Hong et al. (2006) also observed desirable effects using MW pretreatment. When primary sludge (PS), WAS and anaerobic

digester sludge (ADS) were irradiated with MWs to reach a temperature of approximately 70 ºC, the SCOD increased by 16%, 125% and 45%, respectively. Microwaving of PS at 85 ºC and 100 ºC resulted in an increase of 11.9% and 22.7% respectively for biogas production. While WAS irradiated to 85 ºC and 100 ºC produced 11.4% and 15% more biogas, respectively. Likewise, Zheng and Kennedy (2006), while working with PS of 3 to 4% TS reported that MW irradiation to 65 ºC and 90 ºC at various MW intensities resulted in a 2 to 3 fold increase of SCOD and a 15% to 30% improvement in the rate of biogas production, however the ultimate degradability of PS remained unchanged. Similar conclusions were also reported by Eskicioglu et al. (2007b) who investigated, low temperature (50-96 ºC) MW irradiation of TWAS. Results showed that microwaved WAS, had 3.6 and 3.2 fold increase in SCOD/TCOD ratio and 13% and 17% increase in CBP at concentrations of 1.4 and 3% TS, respectively. All samples showed similar improvement in VS destruction compared to the controls. Solubilization was always slightly higher at 50% than at 100% MW intensities for both sludge concentrations at the same pretreatment temperatures, possibly due to longer exposure time to the MW field at low MW intensities. The most important factors affecting WAS solubilization were temperature, intensity, and sludge concentration. Eskicioglu et al. (2007a) also studied continuous systems. It was observed TCOD removal efficiency of pretreated digesters increased as the HRT was gradually shortened from 20days to 5days, and as the pretreatment temperature was increased from 50 ºC to 96 ºC. TWAS pretreated at 96 ºC by MW and CH achieved 29% and 32% higher TS and 23% and 26% VS removal efficiencies compared to control at HRT of 5days, respectively. MW and CH digesters fed by pretreated sludge at 96 ºC had 80% and 96% higher SCOD and 120% and 56% higher effluent ammonia-N at HRT of 5 days compared to control respectively.

Kennedy et al. (2007) found MW irradiation improved the anaerobic biodegradability of combined aerobic sequencing batch reactors (SBR) sludge with high HRT. The SCOD/TCOD ratio of control samples was approximately 1.4%. Increasing the MW temperature from 45 to 85 ºC had a positive effect on the solubilization, as the SCOD/TCOD ratio approximately doubled when sludge was MW heated to 85 ºC. Over all, temperature had the most significant effect on solubility in comparison to sludge concentration and MW intensity. The maximum increase in mesophilic biogas production (16.2%) resulted when 100% of SBR sludge received MW pretreatment to 85 ºC. Multiple MW irradiation cycles and maintaining sludge at 85 ºC showed no increase biodegradation.

In a recent study, Qiao et al. (2008) investigated the treatment of sludge by MW irradiation combined with alkali addition. 50–70% of VSS was dissolved into solution at 120 ºC to 170 ºC with a dose of 0.2 g NaOH/g-DS (dried solids) within 5 minutes, and 80% of the TCOD was transformed to SCOD. For the fresh sludge, MW heating alone reduced VSS by an additional 40% at 170 ºC within 1 minutes. Adding 0.05 g NaOH/g-DS increased the VSS dissolution ratio to 50%. Also settleability improved after 1 minutes MW treatment combined with alkali addition. Similarly, Yu et al. (2010) studied physical and chemical characteristics of WAS after MW pretreatment to determine the optimum conditions for microwaving to achieve high SS disintegration. Combination of power (500, 750, and 900 W) and contact times in the range of 0-140 seconds was tested. The highest supernatant turbidity for treated sludge was observed at the highest energy input, probably due to the release of biopolymers. With the increase in the MW energy and contact time, VSS solubilization increased. After 140 seconds of pretreatment, VSS solubilization was 24.7%, 25.7% and 29.6% at 500 W, 750 W and 900 W, respectively. This might result from disruption of the sludge floc and cells causing the release of organic matter into the soluble phase. The SCOD/TCOD ratio increased from 0.0622 (raw sludge) to 0.1571, 0.1581 and 0.1611 at energies of 500 W, 750W and 900 W, respectively, after 140 seconds irradiation. The results showed that the SCOD increased gradually, becoming asymptotic as the maximum solubilisation was approached and no further increases in solubilisation occurred. They concluded 900 W and 60 seconds is a good option for optimizing sludge digestibility and energy consumption.

Zhu et al. (2005) examined the effects of combined modality MW/alkali pretreatment and alkali pretreatment alone for the TSS weight loss and composition of rice straw. The rice straw had a TSS weight loss of 44.6% composed of cellulose 69.2%, lignin 4.9%, and hemicellulose 10.2% after 30 minutes MW/alkali pretreatment at 700 W while it only had a weight loss of 41.5% and composition of cellulose 65.4%, lignin 6.0%, and hemicellulose 14.3% after 70 minutes for alkali pretreatment only. The rice straw pretreated by MW/alkali had a higher hydrolysis rate and glucose content in the hydrolysate in comparison with the alkali pretreatment. Similarly, Hu and Wen (2008) studied the enhancement of the enzymatic digestibility of switchgrass by MW-assisted alkali pretreatment. In this study, MW was used to pretreat switchgrass, which was then hydrolyzed by cellulase enzymes. When switchgrass was soaked in water and treated by MW, the total sugar yield from the combined treatment and hydrolysis was 34.5 g/100 g biomass (58.5% of the maximum potential sugars released).

This yield was 53% higher than the CH of switchgrass. In addition, the effect of alkali addition was also tested. When switchgrass was presoaked in alkali solution (0.1 g alkali/g biomass) and treated by MW heating (190 ºC, TS of 5% for 30 minutes), a sugar yield of 99% of maximum potential sugars was achieved. The advantage of MW over CH was attributed to the disruption of recalcitrant structures. Another study by Dogan and Sanin (2009) concentrated on alkaline solubilization (NaOH) and microwave irradiation (final temperature 171 ºC and duration 16 minutes) of WAS for the enhancement of AD. In this study, the ratio of SCOD/TCOD increased from 0.005 to 0.18, 0.27, 0.34 and 0.37 with MW/pH of 10, MW/pH of 11, MW/pH of 12 and MW/pH of 12.5, respectively which were higher than the effect of MW or NaOH alone. Further, with BMP tests were carried out for pH of 10, pH of 12, MW, MW/pH of 10 and MW/pH of 12. Dual modalities MW/pH of 12 had the greatest methane production, which were 18.9% improvements over the control. In semi continuous study of WAS with MW/pH of 12 at an HRT of 15 days, 55% more methane was produced compared to the control reactor. Furthermore, the VS and TCOD removal were increased by 35.4% and 30.3%, respectively.

MW technology has not been fully tested as a pretreatment method for AD of OFMSW. This report proposes MW technology as an alternative to existing pretreatment techniques for enhancing AD of OFMSW.

2.8. Potential of water recycle for OFMSW anaerobic digestion

A common trend in the published literature concerning digestion of concentrated high strength organic waste and wastes with low moisture content like OFMSW is the need for long retention times, due to the high organic strength of the material to be treated (Eskicioglu et al. 2011) or dilution in order to achieve a concentration appropriate for AD (Kaparaju et al. 2010). As it is, the digestion of OFMSW can be a water intensive process just from the shear volume (34 million tonnes of food scraps per year) of material that needs to be treated (USEPA 2009). There appears to be very little literature available on the impact of using digested effluent as a means to reduce fresh water use for substrate dilution prior to AD.

Recent research conducted by Sun et al. (2010) examined the potential for integrating AD into a water-recycled cassava bioethanol process. AD of cassava thin stillage by thermophilic and mesophilic digesters prior to use as backset water in the upstream bioethanol processes was

carried out. The effects on fermentation were observed and the authors found that the use of anaerobic digester effluent had a positive impact on yeast growth. Also, improved microbial biomass inventory was observed when compared to fermentation of substrate diluted with tap water only. It was also concluded that the use of effluent expedited sugar consumption and positively impacted ethanol fermentation and was attributed to residual enzymes and co-factors that were beneficial to the microbial culture materials. This study indicates a significant potential for water savings and emission reductions if similar benefits from the use of digested OFMSW effluent for dilution could be obtained with OFMSW digestion.

A study by Nordberg et al. (2007) investigated the recirculation of process liquid for AD of alfalfa silage in semi-continuous continuously mixed reactors. With 100% recirculation of process liquid used for substrate dilution the reactors were able to operate without the need for an extra supply of water. However, the authors found that this resulted in an accumulation of organic and inorganic compounds and an increase in pH and alkalinity. Initially the increases in pH and alkalinity made it possible for the authors to achieve the desired OLR while maintaining hydrolysis and a stable methane yield, however 100% recirculation eventually led to inhibition. Interestingly, when a 50% process liquid, 50% water ratio was used for substrate dilution there was an observed improvement in process performance. Nordberg et al. (2007) indicated that this meant that an optimal process can likely be obtained by adjusting the degree of process liquid recirculation. The authors were able to make some interesting observations and there appears to be promise for the use of digested process water for substrate dilution to reduce fresh water consumption. However, the HRT at which Nordberg et al. (2007) achieved these results was rather long at 26 days.

CHAPTER 3

Effect of Microwave Temperature, Intensity and Moisture Content on Solubilization of Organic Fraction of Municipal Solid Waste

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3.1. Abstract

High temperature and pressure microwave (MW) irradiation pretreatment of the organic fraction of municipal solid waste (OFMSW) enhanced solubilisation prior to anaerobic digestion (AD). Three temperatures (175 ºC, 145 ºC and 115 ºC), three MW intensities based on temperature ramp times (20, 40 and 60 minutes) and two supplemental water additions (SWA) of 20% and 30% were evaluated. MW irradiation resulted in higher concentrations of soluble chemical oxygen demand (SCOD), proteins and sugars in the supernatant phase. The highest level of solubilization was achieved at 175 ºC and resulted in 1.61±0.05, 1.62±0.01 and 1.58±0.03 times higher SCOD concentrations at SWA of 30% versus controls for MW intensity ramp times of 20, 40, and 60 minutes, respectively. Additionally for the same conditions, the free liquid volume released from the municipal solid waste (MSW) into the supernatant were observed to be 1.39±0.01, 1.34±0.02, and 1.37±0.01 times greater than the control, respectively. Concomitantly potentially bio-available SCOD available for AD increased more than 2 fold compared to controls.

Keywords: microwave; municipal solid waste; organic fraction; pretreatment; anaerobic digestion

3.2. Introduction

In the United States, approximately 251 million tons of municipal solid waste (MSW) was generated in 2006 and its management is a high environmental priority. MSW consists of a non-biodegradable portion and a biodegradable organic fraction. The MSW's organic fraction typically includes paper (34%), yard trimmings (13%) and food scraps (12%). Concomitantly food scrapes account for almost 31 million tonnes yearly for disposal in the United States (USEPA 2006b).

Landfilling is still the most common disposal method in the USA accounting for 55% of the MSW that must be managed. The organic fraction of municipal solid waste (OFMSW) has high moisture producing large amounts of leachate in landfills as it degrades. Additionally, anaerobic degradation of OFMSW in landfills has resulted in them being the largest human-related source of fugitive methane (CH_4), accounting for 34% of all anthropogenic CH_4 emissions (USEPA 2006a). Different technologies to treat OFMSW have been developed, such as incineration, composting and anaerobic digestion (AD). Direct incineration is often not possible due to the high moisture content of OFMSW and a supplemental fuel is needed. Consequently, potential energy contained in the waste is lost; and the bottom ash from incineration is considered a hazardous waste. Composting is a common method but produces odours, NH_3, flies and produces large amounts of residuals as 50% of the organic load is converted to biomass. Composting is also energy and labour intensive. In contrast, with anaerobic treatment of OFMSW, up to 80% of the organics can be degraded and transformed to CH_4 and CO_2 with a very small amount of sludge produced (Schober et al. 1999). The other advantage of AD is its positive energy balance. Accordingly, anaerobic treatment of OFMSW is superior in both reducing the organic matter and producing usable green energy.

In the first step of AD, hydrolysis transforms suspended organic solid reactants to a more readily biodegradable soluble form to be metabolized by micro-organisms. For high suspended solid substrates such as OFMSW, hydrolysis is the rate-limiting step in anaerobic biodegradation (Pavlostathis and Giraldogomez 1991). Various pretreatment methods have been used to improve hydrolysis and enhance the overall AD process. Methods including mechanical treatment (Mshandete et al. 2006), ultrasound (Akin 2008), chemical treatment

(Heo et al. 2003), thermal hydrolysis (Bougrier et al. 2007) and thermochemical pretreatment (Turker et al. 2008) have increased biodegradability of biomass and other organic solid wastes with varying degrees of success. In the case of OFMSW, conventional thermal pretreatment using high temperatures (160-175 °C) and pressure (6-8MPa) improved AD performance in terms of rate of reaction and extent of degradation.

Thermal pretreatment of food waste at 70 ºC for 2 hours and at 150 ºC for 1 hour was examined in a hybrid anaerobic solid–liquid system (Wang et al. 2006b). Thermally pretreated food waste halved the time to produce the same quantity of methane in comparison with AD of untreated food waste. Similarly, pretreatment using conventional heating between 160-200 ºC, pressures up to 4 MPa and residence times of up to 60 min significantly improved the rate and extent of AD of restaurant waste (Schieder et al. 2000). In both cases hydrolysis of the thermally pretreated waste was significantly faster, in comparison to untreated controls. Sawayama et al. (1997) liquidized kitchen waste at 175 ºC and 4 MPa (sodium carbonate catalyst) with 1 hour holding time and separated the mixture into a solid fraction and filtrate. Anaerobic treatment of the filtrate resulted in faster digestion compared with mechanically disrupted kitchen waste.

Microwaves (MW) are an electromagnetic radiation that can oscillate electric dipole molecules such as water when exposed to a MW field. Water molecules rotate as they try to align themselves with the alternating magnetic field which causes moisture in the material to heat up. The main difference between conventional and MW heating is that in the former, temperature increases from the outside to inside the body as energy transfers from the outer surface by convection and conduction but with MW irradiation the body temperature increases throughout and from within (Plazl et al. 1995). Dipole rotation (athermal effect) and subsequent heating effects can also break apart weak hydrogen bonds and has the potential to make complex organic molecules unfold and become smaller (Loupy 2002) potentially making them more readily biodegradable.

When municipal primary sludge (PS), waste activated sludge (WAS) and anaerobic digester sludge (ADS) were irradiated with MW to 70 ºC, the soluble chemical oxygen demand (SCOD) increased 16%, 25% and 45%, respectively compared to controls. PS microwaved to 85 ºC and 100 ºC resulted in 11.9% and 22.7% increases in biogas production, respectively while WAS irradiated to 85 ºC and 100 ºC produced 11.4% and 15% more gas, respectively (Hong et al. 2006). Eskicioglu et al. (2007b) investigated low temperature (96 ºC) MW

irradiation of WAS, taken from an activated sludge unit operating at 5d solids retention time (SRT). They reported 3.6 and 3.2 fold increase in SCOD/TCOD (total chemical oxygen demand) ratio and 13% and 17% increase in cumulative biogas production (CBP) at WAS concentrations of 1.4 and 3% total solids (TS), respectively, with similar improvement in volatile solids (VS) destruction compared to controls. Hu and Wen (2008) reported enhanced enzymatic digestibility of switch-grass by microwave-assisted alkali pretreatment followed by hydrolysis with cellulase enzymes. Total sugar yield from the combined chemical-MW pretreatment was 34.5 g/100 g biomass (58% of ultimate potential sugars) which was 53% higher compared to conventional heating of switch-grass.

This study demonstrates the applicability of MW heating as an emerging energy efficient technology that can be used to pretreat OFMSW. The main objectives of this study are to determine the single effects and interactive effects of high MW temperatures (>100 ^{o}C), MW intensities (temperature ramp times), and supplemental water addition (SWA) on solubilization of OFMSW in preparation to subsequent downstream AD.

3.3. Methodology

3.3.1. Organic waste

Since real OFMSW from domestic houses and food processing industries has variable characteristics, model OFMSW (M-OFMSW) was used to minimize effects due to compositional variation. M-OFMSW composition was based on the literature (Minowa et al. 1995; Sawayama et al. 1999; Wang et al. 2006a; Luostarinen and Rintala 2007) and was configured to have a similar composition of protein, hydrocarbon, vegetable and fat as the Canada Food Guide (CFG 2007) and be representative of Canadian kitchen waste. M-OFMSW contained cooked rice (18wt %), cooked pasta (18wt %), cabbage (11wt %), carrot (11wt %), apple (11wt %), banana (11wt %), corned ground beef (10wt %) and dog food (10wt %). Rice and pasta was cooked for 15 minutes then strained prior to MW pretreatment. Moisture content of M-OFMSW was 78.6±0.4%. To reduce the initial particle size and homogenize the M-OFMSW, 1Kg of M-OFMSW was placed in a Kitchen Aid food processor (PowerPro II, 500 Watts) for 30 seconds at high speed prior to MW irradiation. Additionally, M-OFMSW was supplemented with tap water depending on experimental conditions to

provide supplemental water addition of 20 and 30 % in the final M-OFMSW prior to MW pretreatment.

3.3.2. Microwave Pretreatment

A laboratory MW Accelerated Reaction System (Mars 5®) was used to pretreat the M-OFMSW. This system consists of the following:

- User selectable power settings (0-1200 Watts) and constant frequency of 2450 MHz.
- A programmable microcomputer that controls and monitors power delivered as well as temperature, and pressure within sealed reaction vessels.
- Explosion proof sealed reaction vessels that eliminate volatile losses and can operate up to 250ºC and 3.45 MPa.

Each of the 14 vessels and the control vessel was filled with 50 g of M-OFMSW. Samples were heated to temperatures of 115, 145 and 175 ^{o}C at three different MW intensities (low, medium, high) based on rates of temperature increase or ramps of 60, 40 and 20 minutes, respectively. Once final temperature was reached it was held for 1 minute. Samples were cooled to room temperature prior to opening to minimize volatilization losses.

3.3.3. Experimental Design

A statistical experimental method using a multilevel factorial design was applied (Berger and Maurer 2002) with the 3 variables being MW treatment temperature, supplement water addition to M-OFMSW and MW intensity (inversely proportional to ramp time). Table 3.1 shows the variables tested and their levels.

Table 3.1: Variable and their levels used in statistical design

Variables → Levels ↓	Temperature	Temperature Ramp	Supplemental Water Addition
1	115 ºC	20 min	20 %*
2	145 ºC	40 min	30 %**
3	175 ºC	60 min	

* 80 g M-OFMSW+ 20 g water
** 70 g M-OFMSW + 30 g water

3.3.4. Analytical Methods

pH was measured using a Fisher Accumet pH meter 750. Total solids (TS) and volatile solids (VS) were determined based on Standard Methods procedure 2540 G (APHA 1995). Alkalinity analysis was done by titration according to Standard method 2320B. SCOD measurements were conducted according to Standard Methods 5220C colorimetric method with a Perkin-Elmer spectrophotometer Model 295 at 600nm light absorbance. The SCOD was performed after samples were centrifuged and filtered through GN-6 Metricel S-Pack membrane disc filters with 0.45 μm pore size (Millipore). Volatile fatty acids (VFAs; acetic, propionic and butyric acids) were measured by injecting supernatants into a HP 5840A gas chromatograph with a flame ionization detector and Chromosorb 101 packed column. The concentration of soluble proteins and total soluble sugars were measured using a Beckman DU-40 spectrophotometer according to Frolund et al. (1995) and Benefield (1976), respectively. Bovine serum albumin (BSA) and glucose stock solutions were used as standards. Free water was determined by centrifuging 60 g of sample at 9000 relative centrifugal force (RCF) for 40 minutes and decanting and measuring the weight of the supernatant. Ultimate M-OFMSW solubilization was estimated using a severe chemical pretreatment (Bougrier et al. 2005). One gram of M-OFMSW was added to 1L of NaOH (1N) and mixed for 24 hours. After 24 hours SCOD was measured.

3.4. Results

Haug et al. (1978) observed that in thermal pretreatment, temperature has a significant effect on WAS biodegradability. Anaerobic biodegradability increased with temperature to an optimum near 175 ºC. At temperatures beyond 175 ºC biodegradability and concomitant biogas production decreased. Also a reaction temperature of 175 ºC was preferable for the solubilization of OFMSW prior to AD (Stuckey and McCarty 1984; Inoue et al. 2002). In preliminary MW tests not reported in this study, no measurable improvement was observed in solubility of M-OFMSW for temperatures lower than 100 ºC concomitantly the MW experiments were performed between 115 ºC and 175 ºC. MW Ramp (MW intensity) and SWA ranges were selected based on capabilities of the MARS microwave system and work of Toreci et al (2010) for high temperature WAS pretreatment. Water is the most significant

component in M-OFMSW that is effected by the MW field thus higher water content may increase the effectiveness of pretreatment. However there is a practical limit for water content and based on the literature, SWA of 20-30% has been used in solid waste AD processes.

M-OFMSW was microwaved at the different conditions to determine single and multiple parameter effects on solubilization and release of M-OFMSW bound water into the free water soluble phase. Results for M-OFMSW solubilization of samples before and after microwave treatment done in triplicate are presented in Table 3.2. The properties of high temperature MW treated M-OFMSW were compared with untreated controls in order to investigate the impact of MW irradiation on modifying the substrate for subsequent enhanced AD. In order to quantify the solubilized composition of organic matter liquefied during pretreatment before and after MW irradiation SCOD concentrations were used as the primary parameter for solubilization. Other parameters such as pH, HCO_3^- alkalinity, TS, VS, soluble protein and sugar were also determined before and after MW irradiation.

MW pretreatment at high, medium and low MW intensities and temperatures from 115-175 ^oC, resulted in SCOD increasing from 71 g/Kg for the control to 83-115 g/Kg for 30% SWA and from 92 g/Kg (control) to 101-127 for 20% SWA. The greatest increase in SCOD concentration was observed at 175 ºC and 1MPa pressure.

Microwave pretreatment to 175 ºC at high, medium and low MW intensities (20, 40, and 60 minute ramps), resulted in SCOD increasing from 71 g/Kg for the control to 112-115 g/Kg resulting in 1.61±0.05, 1.62±0.01, 1.58±0.03 fold increases SCOD depending on MW intensity with SWA of 30%. Similarly at 175 ^oC SCOD increased from 92 g/kg to 123-127 g/Kg or relative increases of 1.34±0.01, 1.38±0.03, 1.34±0.01 with SWA of 20% depending on high, medium and low MW intensities respectively. The relative increase in SCOD versus SCOD of controls for 20% and 30% SWA are illustrated in Figure 3.1. In addition to the increase in SCOD the free liquid fraction of samples after MW pretreatment also increased relative to the control by factors of 1.51±0.02, 1.61±0.03, 1.67±0.03 for SWA of 20% with increasing MW intensity at 175 ºC, respectively.

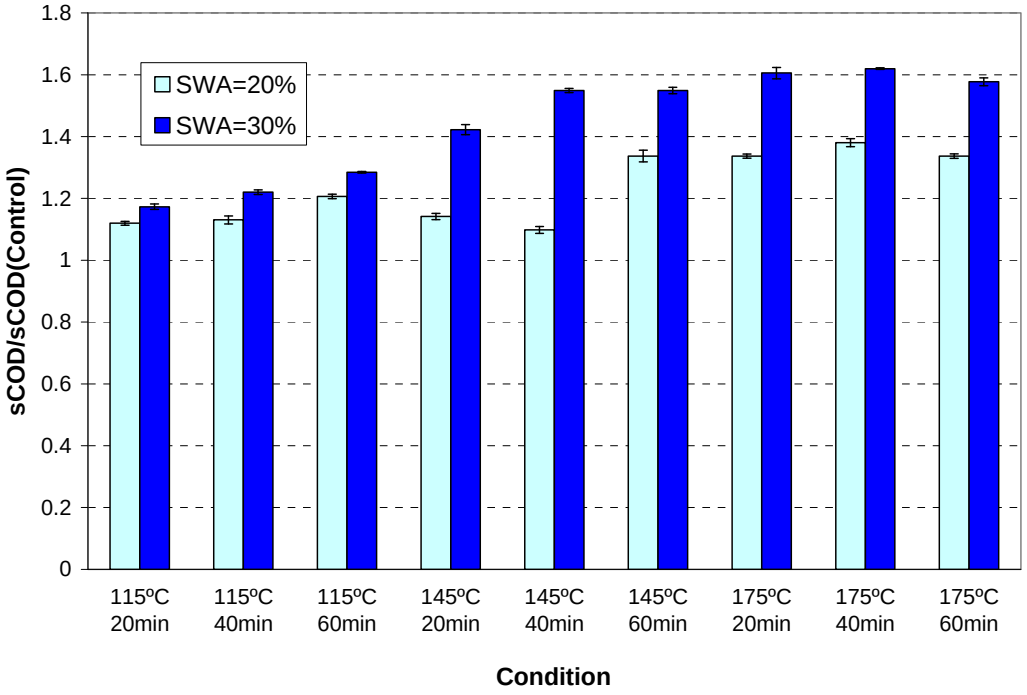


Figure 3.1: Effect of MW conditions on soluble COD

Free water increased by 1.37±0.01 and 1.67±0.02 versus the control for samples with SWA of 30% and 20% with 60 minutes ramp time, respectively. These results indicate significant transformation of organics and water from the solid and bound water phases into the free liquid phase with MW heating. Considering the combined effects of increased SCOD concentration and increased free water fraction after MW pretreatment, the total mass of SCOD available in the free water and readily available for AD biodegradation is the product of these 2 ratios. At 175 ^{o}C (60 minute ramp) this resulted in 2.23 and 2.16 fold increases in SCOD mass for 20% and 30% SWA respectively versus untreated controls.

Table 3.2: Organic waste properties before and after microwave treatment

Parameter	SWA	Untreated OFMSW	115 ºC			145 ºC			175 ºC		
			20 min	40 min	60 min	20 min	40 min	60 min	20 min	40 min	60 min
pH	20%	5.9	5.61	5.53	5.48	5.42	4.77	4.67	3.86	4.05	3.89
	30%	5.96	5.65	5.63	5.48	5.31	5.08	4.92	4.4	4.06	4.05
SCOD (g/Kg)	20%	92±1.3	103±1.2	104±2.4	111±1.3	105±1.9	101±2.1	123±3.5	123±1.2	127±2.4	123±1.3
	30%	71±1.4	83±3.4	87±0.5	91±2.3	101±3.0	110±1.2	110±1.9	114±1.6	115±1.4	112±0.5
TS (g/Kg)	20%	189±3.5	180±9.7	184±4.8	182±0.3	147±16.4	146±14.3	143±23.0	159±9.4	141±13.7	129*
	30%	167±28.4	151±29.0	156±2.0	157±0.3	134*	na**	125*	120±10.0	107±9.2	108±11
VS (g/Kg)	20%	182±3.9	173±9.4	177±4.4	175±0.3	141±12.8	140±0.3	138*	152±0.9	135±0.2	123*
	30%	160±0.9	145*	150±2.4	152±0.2	145*	154±1.7	136*	115±2.1	103±4.2	103±0.4
Alkalinity (mg CaCO3/Kg)	20%	462±17.7	650±0	850±70.7	650±35.4	663±17.7	0	0	0	0	0
	30%	413±17.7	600±35.4	550±35.4	588±17.7	375±0	325±0	0	0	0	0
TVFA* (mg/Kg)	20%	5	0	9	67	289	138	272	2028	1189	1451
	30%	4	0	7	9	155	250	198	647	1000	1275
Soluble Protein (g/Kg)	20%	8.0±1.4	9.7±2.0	10.4±3.2	14.2±3.1	13.5±2.0	14.5±2.0	21.3±1.5	42.9±2.0	43.0±1.6	44.2±1.3
	30%	6.6±0.9	9.4±2.7	10.2±3.2	11.6±3.3	13.3±1.9	18.2±0.3	22.9±0.9	20.3±0.1	32.2±1.5	32.8±3.3
Soluble Total Sugar (g/Kg)	20%	94.8±4.9	93.3±4.4	90.5±1.5	109.9±5.7	91.4±7.3	92.6±4.6	122.4±6.1	92.9±4.2	105.2±1.5	102.8±5.7
	30%	82.3±3.0	86.8±1.9	90.4±3.8	105.6±2.1	97.4±1.9	104.9±4.6	108.7±3.9	92.9±1.9	91.0±1.8	89.0±3.7

* Based on just one test result
** not available

Effect of temperature ramp times (MW intensity) on increasing waste solubilization was greatest for MW temperatures of 115 ºC and 145 ºC. The maximum increase in solublization was observed for pretreatment temperature of 145 ºC and SWA of 20%, when MW intensity was decreased from 20 to 60 minute temperature ramp times. The lowest MW intensity (60 minutes ramp) resulted in SCOD concentration and free water fraction increasing by 17% and 26%, respectively, over higher MW intensity (i.e., 20 minute ramp). At MW pretreatment temperature of 175 ºC and 20% SWA the SCOD concentration and free water fraction increased by 0% and 10% respectively, when MW intensity was decreased from 20 to 60 minutes temperature ramp times. These results suggest that for higher temperatures, MW intensity has less impact on M-OFMSW solubilisation compared with lower MW exposure temperatures.

Ultimate M-OFMSW solubilisation (NaOH chemical treatment) resulted in SCOD concentrations of 174 g/kg and 132 g/kg corresponding to a maximum ultimate SCOD ratio increase relative to the controls of 1.89±0.08 and 1.85±0.03 for SWA of 20% and 30%, respectively. Comparison of MW prereatment solubilisation results to ultimate chemical solubilisation gives a good indication of the percentage of sample disintegration (Schmitz et al. 2000) for a given pretreatment, with 100 % indicating a pretreatment solubilization methodology was equal to the ultimate achievable. For 175ºC and SWA of 20 and 30% for all MW ramp times (ramp time at 175ºC had negligible effect on solubilisation) the highest degree of solubilisation was found to be 43 and 72% of ultimate respectively. At 115 ºC and 145 ºC degree of solubilisation was significantly less and ranged between 14-33% and 11-65 % of ultimate solubilisation respectively, depending on MW intensity (ramp time) and SWA.

Results for soluble sugar concentration increased from the control value of 95 g/kg to a range of 90-122 g/kg depending on MW temperature and intensity (Figure 3.2) for 20% SWA. The highest soluble sugar concentration of 122 g/kg was achieved at 145 ^{o}C with the lowest MW intensity. Other temperatures and intensities had only a marginal effect on soluble total sugar concentrations. In general, SWA of 30% yielded slightly better overall increases in soluble sugar concentrations compared to the controls and increased from 82 g/kg for control to a range of 86-105 g/kg for 115 and 145 ^{o}C. Solubilization of sugars

tended to be marginally higher at lower MW intensity, possibly due to longer exposure time to the MW field. Soluble sugar concentration of samples with 30% SWA after MW tended higher for 115 ºC and 145 ºC versus the control but decreased at the highest temperature of 175 ºC. According to Stuckey and McCarty (1984), severe thermal pretreatment conditions results in the formation of refractory compounds. Some intermolecular reactions may occur between solubilized compounds (i.e. sugars and proteins) which lead to the formation of complex substances. As discussed above the increase in mass of soluble sugars is the product of increased sugar concentration and the increase in free water released from the M-OFMSW.

Soluble protein results indicated (Figure 3.3) that low to medium MW temperature pretreatment (175 ^{o}C) and lower MW intensity resulted in the greatest increase in soluble protein concentration. For example with 20% SWA soluble protein in the control of 8 g/Kg increased to 44 g/Kg at 175 ^{o}C at the lowest MW intensity. In general, protein solubilization was higher for samples with higher SWA. The change in soluble sugar and protein are in good agreement with the change in SCOD in most cases, except sugars for high temperature (175 ºC). In general longer irradiation time (lower MW intensity) and low and medium temperature treatments resulted in higher concentrations of proteins and sugars being liquefied from the solid phase into liquid phase. This result is in general agreement with the solubilization effect of MWs on WAS reported by Toreci et al. (2010). They found soluble protein and sugar concentrations had improvement at high-temperature MW (160 ^{o}C) treatment, greatest solubilization was reported for WAS sludge concentration of 6%, and with 11.8% WAS improvements in the soluble concentration was about a third of that for 6% sludge.

Table 3.2 provides data on VS after MW thermal pretreatment and VS of controls (VS made up > 95% of TS concomitantly TS follows the same trend). Loss of VS was observed at higher temperature treatment (even though sealed vessels were opened at room temperature) and SWA indicating that significant volatilization and loss ranging between 20-30% were occurring from high temperature pretreatment. One may conclude that MW thermal treatment, especially at high temperature, has to consider the impact of VS loss through volatilization on downstream processes and occupational health.

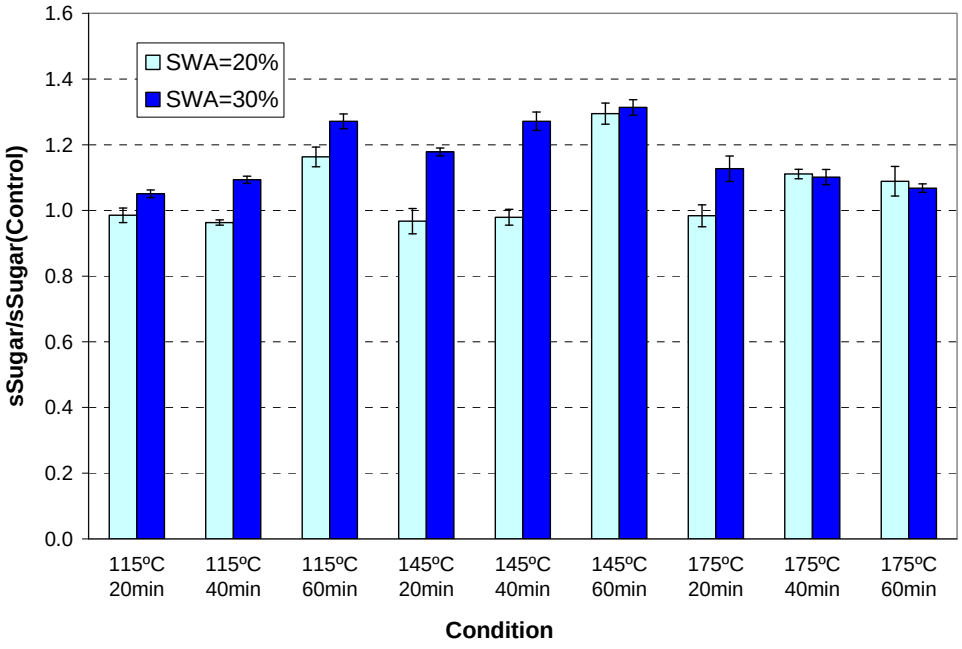


Figure 3.2: Effect of MW conditions on soluble sugar

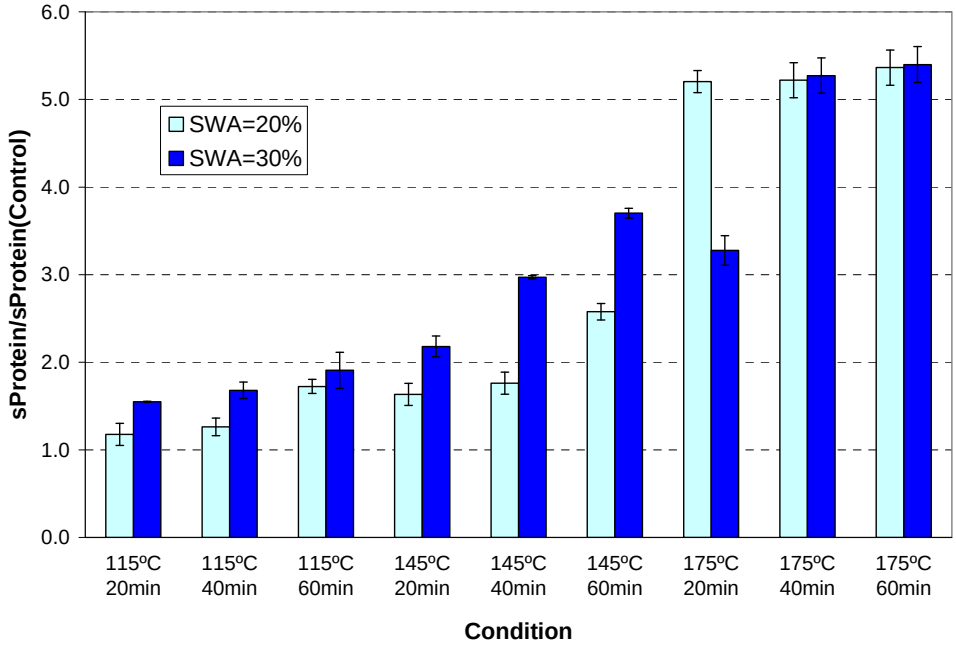


Figure 3.3: Effect of MW conditions on soluble protein

VFAs were measured in terms of acetic acid, butyric acid and propionic acid concentrations. Total VFAs (TVFAs) concentration increased during high temperature microwaving and ranged between 647-2028 mg/L in the case of 175 ºC. The effect of lower MW temperatures on VFA concentration is negligible and no other pattern in VFA production was observed.

Alkalinity increased for low and medium temperature MW pretreatment, while it was zero for high temperature. As temperature and ramp was increased the alkalinity and pH reduce as expected based on the higher VFA concentrations with high temperature MW pretreatment. As concentration of acids increase in the system alkalinity is consumed and pH drops. Toreci et al. (2010) observed exactly the same trend for VFA, alkalinity and pH after pretreatment.

3.4.1. Statistical Analysis

The statistical package S-Plus® 8.0 was used to evaluate the significance of pretreatment factors in a multilevel factorial design for organic waste solubilization by performing Analysis of Variance (ANOVA). Factorial ANOVA was used to evaluate the effects and inter-relationships of three independent pretreatment variables, temperature (T), MW intensity or ramp (R) and supplement water addition (SWA). Factorial ANOVA provides information on the relative importance of each parameter with respect to others and multiple interactions between parameters of concern. The response variable was the ratio of SCOD following MW pretreatment to control SCOD ($sCOD/sCOD_{Control}$) and the response surface is shown in Figure 3.4. The response surfaces for both SWA's tested shows the importance of high T and to a lesser extent the interactive effect of MW intensity on solubilising the waste. The results of ANOVA are summarized in Table 3.3.

In ANOVA analysis, the p-value is the α-error for the hypothesis that the parameter plays a significant role in the model. P-values of three variables (T, R and SWA) are less than 0.05; therefore all three factors independently have a significant effect on the waste solubilisation as determined by SCOD at a 95% confidence level. Between these parameters, the MW ramp effect is less significant than T and SWA on SCOD. Among the two-way and three-way parameter interactions only the T: SWA interaction had significant effect on COD

solubilization at the 95% confidence level and needed to be included in the empirical model. Microwave intensity was found to have only a minor effect and did not need to be incorporated as a significant variable in the model.

Table 3.3: Effect of MW pretreatment conditions on ANOVA for ($sCOD/sCOD_{Ctrl}$)

Parameter	DOF	Sum Of Squares	Mean of Squares	F Value	p-value
T	2	0.37818	0.18909	41.6	0.00000
R	2	0.10591	0.05295	11.7	0.00056
SWA	1	0.39059	0.39059	86.1	0.00000
T:R	4	0.04433	0.01108	2.4	0.08415
T:SWA	2	0.03526	0.01763	3.9	0.03955
R:SWA	2	0.00307	0.00153	0.3	0.71746
T:R:SWA	4	0.04395	0.01098	2.4	0.08612
Residuals	18	0.08168	0.00454		

S-Plus® 8.0 was also used to fit the best empirical model to SCOD measurements, and quality of fit was evaluated. Linear model parameter estimations were done with two or three factor interactions. In order to improve the precision of the models, variables were centralized by subtracting the average values. For example if a model is expressed as:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \varepsilon \tag{3.1}$$

where Y is the response (i.e., $sCOD/sCOD_{Control}$) , β_i are the estimated parameters, X_i are variables (i.e., T, R and SWA) and ε is the residual. Then the corresponding centralized variable model takes the form:

$$Y = \beta_0^* + \beta_1^* \left(X_1 - \overline{X}_1\right) + \beta_2^* \left(X_2 - \overline{X}_2\right) + \beta_3^* \left(X_3 - \overline{X}_3\right) + \varepsilon \tag{3.2}$$

in which β_i^* are the estimated parameters and $\overline{X}_i$ are the average of the variables (i.e., $\overline{T}$, $\overline{R}$ and $\overline{SWA}$).

The fit levels of models were compared together by using the coefficient of multiple determination or R^2 value. In order to compare different models with different number of parameters, the R^2 value has to be adjusted to take into account improvements due to introducing more parameters. Adjusted R^2 is defined as

$$R_a^2 = 1 - \frac{n-1}{n-(k+1)}(1-R^2) \tag{3.3}$$

where n is the number of experiments and k is the number of parameters in the model. Models with different structure were tested and the corresponding R^2 and R_a^2 shown in Table 3.4.

Table 3.4 shows that introducing more parameters into the models improves the overall fit based on R^2. Table 3.4 also verifies that the best linear model (i.e., the highest R_a^2) is the fifth model which has 6 coefficients. However the second model with 5 coefficients can provide an almost similar fit based on the similar R_a^2 for models 2 and 5. Although the fifth model provides a slightly better fit compared to the second model, this improvement is small while it is a more complicated model, concomitantly it was decided to select the second model as the best fit. This model describes the individual parameter effects as well as the interactive effects of T and SWA. Estimated coefficients for model two are shown in Table 3.5.

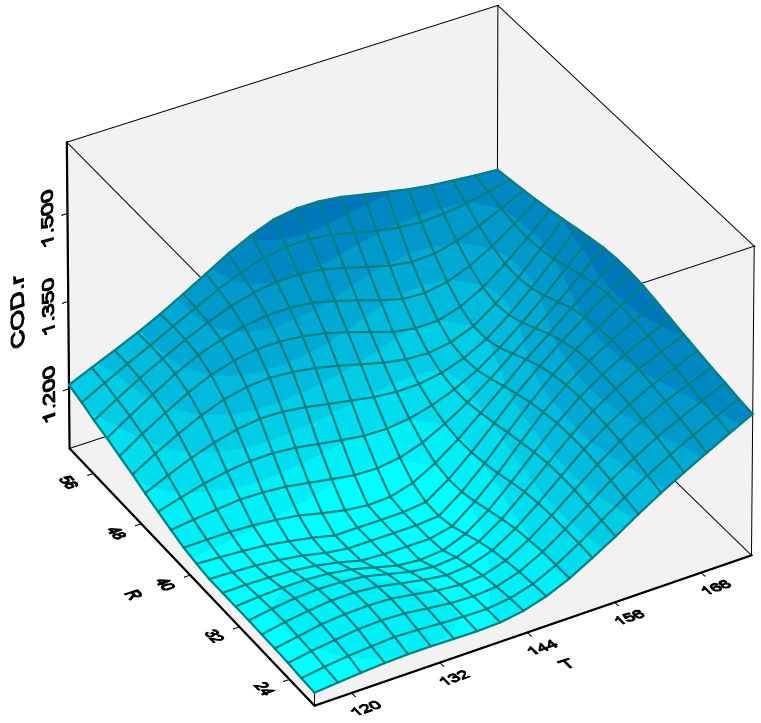
Values of $\mathrm{pr}(>|\mathrm{t}|)$ indicate that the level of confidence for β_0^*, β_1^* and β_3^* is very high (i.e., >99%) and close to 95% for β_2^* and β_4^*. In general, it can be said the model is representative of the response with 95% confidence. The proposed model #2 is written as

$$\begin{aligned} Y = {} & 1.3407 + 0.0048(T-145) + 0.0022(R-40) \\ & +0.0208(SWA-25) + 0.0003(T-145)(SWA-25) \end{aligned} \tag{3.4}$$

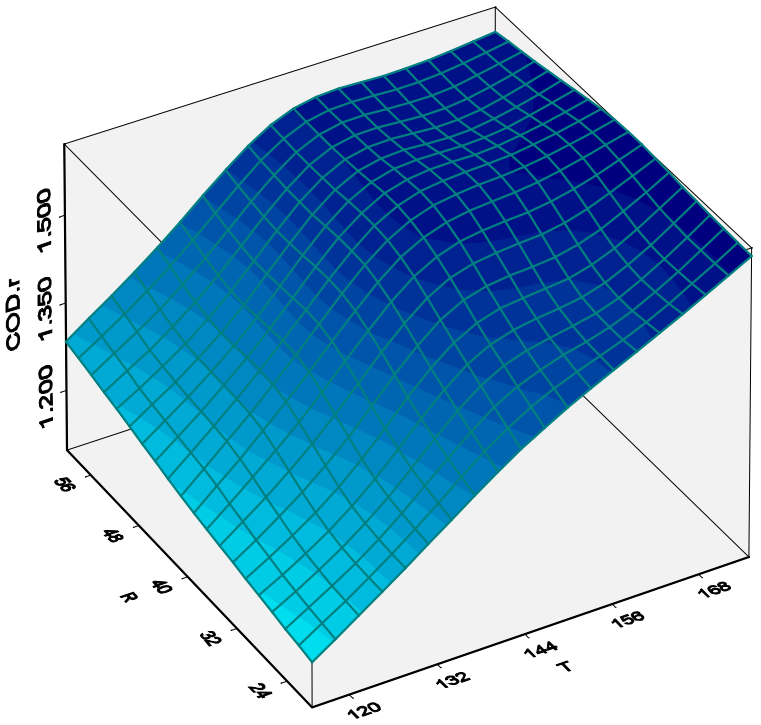
Equation 3.4 then simplifies into

$$Y = 1.1242 - 0.0027T + 0.0022R - 0.0227SWA + 0.0003T \times SWA \tag{3.5}$$

The residual versus fit graph for model two is depicted in Figure 3.5. This figure shows that model two's residuals are completely random and no trend can be seen. This assures that the model captures all trends in the response and that all the residuals are actually due to experimental errors.



(a)



(b)

Figure 3.4: Experimental response of SCOD changes, (a) SWA=20%, (b) SWA=30%

Table 3.4: Linear empirical models for COD solubilization ($sCOD/sCOD_{Ctrl}$)

No	Linear Model	No. of parameters	R^2	R_a^2
1	$Y = \beta_0^* + \beta_1^*(T-\overline{T}) + \beta_2^*(R-\overline{R}) + \beta_3^*(SWA-\overline{SWA})$	4	0.837	0.802
2	$Y = \beta_0^* + \beta_1^*(T-\overline{T}) + \beta_2^*(R-\overline{R}) + \beta_3^*(SWA-\overline{SWA}) + \beta_4^*(T-\overline{T})(SWA-\overline{SWA})$	5	0.878	0.841
3	$Y = \beta_0^* + \beta_1^*(T-\overline{T}) + \beta_2^*(R-\overline{R}) + \beta_3^*(SWA-\overline{SWA}) + \beta_4^*(R-\overline{R})(SWA-\overline{SWA}) + \beta_5^*(T-\overline{T})(R-\overline{R})$	6	0.850	0.788
4	$Y = \beta_0^* + \beta_1^*(T-\overline{T}) + \beta_2^*(R-\overline{R}) + \beta_3^*(SWA-\overline{SWA}) + \beta_4^*(T-\overline{T})(SWA-\overline{SWA}) + \beta_5^*(R-\overline{R})(SWA-\overline{SWA})$	6	0.880	0.831
5	$Y = \beta_0^* + \beta_1^*(T-\overline{T}) + \beta_2^*(R-\overline{R}) + \beta_3^*(SWA-\overline{SWA}) + \beta_4^*(T-\overline{T})(R-\overline{R}) + \beta_5^*(T-\overline{T})(SWA-\overline{SWA})$	6	0.890	0.844
6	$Y = \beta_0^* + \beta_1^*(T-\overline{T}) + \beta_2^*(R-\overline{R}) + \beta_3^*(SWA-\overline{SWA}) + \beta_4^*(T-\overline{T})(SWA-\overline{SWA}) + \beta_5^*(T-\overline{T})(R-\overline{R}) + \beta_6^*(R-\overline{R})(SWA-\overline{SWA})$	7	0.892	0.833
7	$Y = \beta_0^* + \beta_1^*(T-\overline{T}) + \beta_2^*(R-\overline{R}) + \beta_3^*(SWA-\overline{SWA}) + \beta_4^*(T-\overline{T})(SWA-\overline{SWA}) + \beta_5^*(T-\overline{T})(R-\overline{R}) + \beta_6^*(R-\overline{R})(SWA-\overline{SWA}) + \beta_7^*(T-\overline{T})(R-\overline{R})(SWA-\overline{SWA})$	8	0.893	0.818

Table 3.5: Estimated coefficients values for model 2

Coefficient	Value	Std Error	t value	pr(>|t|)
β_0^*	1.3407	0.0170	78.863	0.0000
β_1^*	0.0048	0.0007	6.894	0.0000
β_2^*	0.0022	0.0010	2.146	0.0503
β_3^*	0.0208	0.0034	6.116	0.0000
β_4^*	0.0003	0.0001	2.109	0.0529

The quantile - quantile plot of residuals is shown in Figure 3.6. As it can be seen all points fall close to the straight normal line and are about equally distributed on either side of it, which shows the data is normally distributed.

A comparison of the experimental data and the values predicted by the proposed model for solubilization is presented in Figure 3.7. This figure clearly shows a sudden increase in the response when SWA increases from 20% (runs 1 to 9) to 30% (runs 10 to 18) and increase in solubilization when MW pretreatment temperature increases to 175^{o}C.

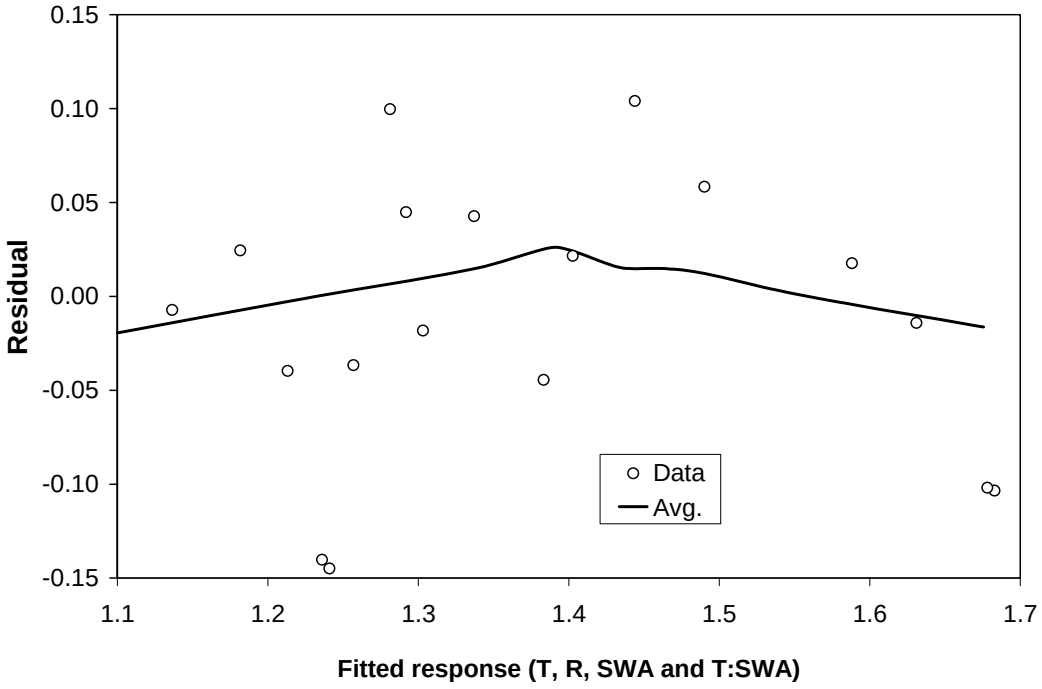


Figure 3.5: Residual QQ for model 2

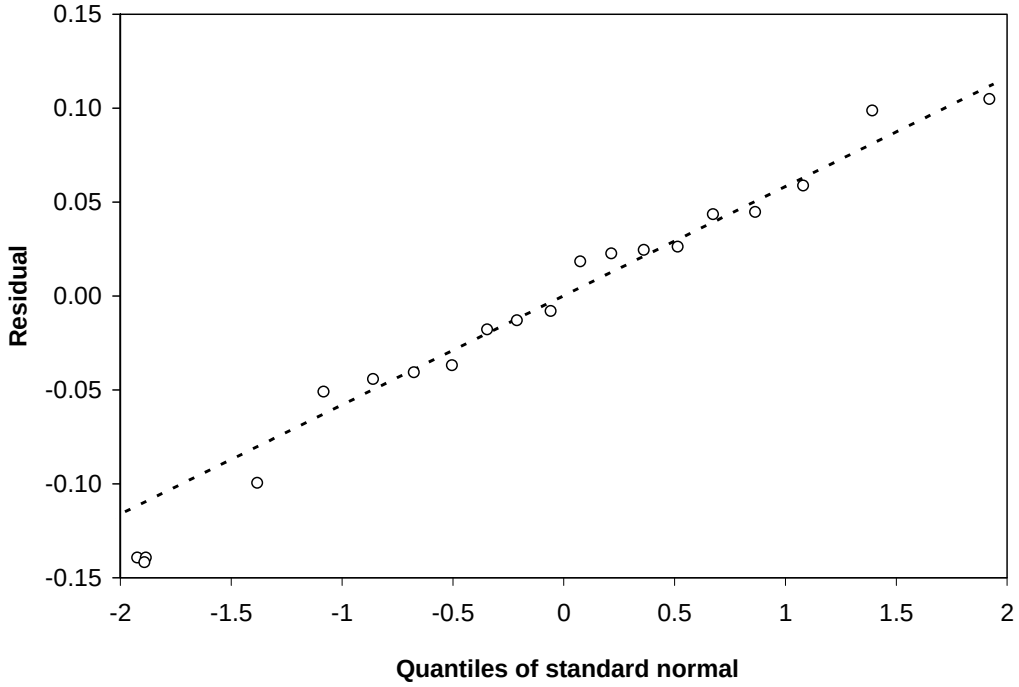


Figure 3.6: Residual normal QQ for model 2

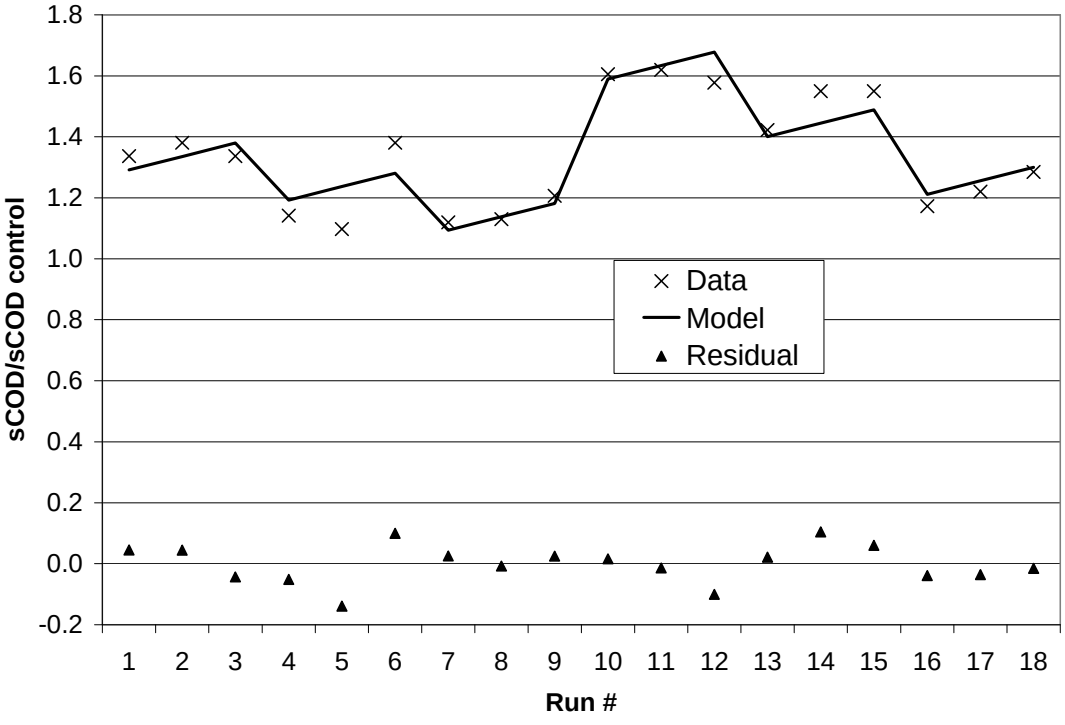


Figure 3.7: Comparison of experimental ($sCOD/sCOD_{Control}$) and model 2

3.5. Conclusion

The feasibility of using MW for pretreatment and solubilisation of OFMSW prior to final waste stabilization has been verified using different operating conditions. Different temperatures, MW intensities and supplemental water additions were investigated. Based on experimental data, the following conclusions are drawn.

The greatest increase in waste solublization based on SCOD was achieved at 175 ºC. MW pretreatment resulted in 1.61±0.05, 1.62±0.01 and 1.58±0.03 times higher SCOD with SWA of 30% for high, medium and low microwave intensity levels, respectively. For the same conditions, release of bound water of samples into the free liquid fraction was 1.39±0.01, 1.34±0.02 and 1.37±0.01 times greater than controls.

Changes in soluble total sugar did not show a specific trend, but it was slightly higher for 30% SWA and for longer MW ramp times. Soluble protein levels increased the greatest at higher temperature, lower MW intensity levels and higher SWA.

Three factor fixed effect ANOVA showed that independently all three variables tested (temperature, SWA and MW intensity) have significant effects on COD solubilisation for a 95% confidence interval. Evaluation of T, R and SWA interactions showed that only T and SWA interactions were significant for a 95% confidence interval. A simple empirical model describing single parameter effects and T and SWA interactions was determined that, can be used to describe COD solubilisation over the range of T, R and SWA evaluated.

It can be concluded that microwaving of M-OFMSW at high temperature (145 or 175 ^{o}C) with 30% supplemental water addition provides the best potentially beneficial conditions for M-OFMSW solubilisation in preparation for AD. Microwave intensity was found to have minor effect on COD solubilization. The actual effect of MW pretreatment on the AD process has yet to be determined.

CHAPTER 4

Anaerobic Digestion of Organic Fraction of Municipal Solid Waste Combining two Pretreatment Modalities, High Temperature Microwave and Hydrogen Peroxide

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4.1. Abstract

In order to enhance anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW), pretreatment combining two modalities, microwave (MW) heating in presence or absence of hydrogen peroxide (H2O2) were investigated. The main pretreatment variables affecting the characteristics of the OFMSW were temperature (T) via MW irradiation and supplemental water additions of 20% and 30% (SWA20 and SW30). Subsequently, the focus of this study was to evaluate mesophilic batch AD performance in terms of biogas production, as well as changes in the characteristics of the OFMSW post digestion. A high MW induced temperature range (115-175ºC) was applied, using sealed vessels and a bench scale MW unit equipped with temperature and pressure controls. Biochemical methane potential (BMP) tests were conducted on the whole OFMSW as well as the liquid fractions. The whole OFMSW pretreated at 115 and 145ºC showed 4 to 7% improvement in biogas production over untreated OFMSW (control). When pretreated at 175ºC, biogas production decreased due to formation of refractory compounds, inhibiting the digestion. For the liquid fraction of OFMSW, the effect of

pretreatment on the cumulative biogas production (CBP) was more pronounced for SWA20 at 145ºC, with a 26% increase in biogas production after 8 days of digestion, compared to the control. When considering the increased substrate availability in the liquid fraction after MW pretreatment, a 78% improvement in biogas production vs. the control was achieved. Combining MW and H2O2 modalities did not have a positive impact on OFMSW stabilization and enhanced biogas production. In general, all samples pretreated with H2O2 displayed a long lag phase and the CBP was usually lower than MW irradiated only samples. First order rate constant was calculated.

Keywords: Organic Solid Waste, Microwave pretreatment, Biochemical methane potential

4.2. Introduction

Municipal solid waste (MSW) is one of the largest sources of organic waste generated by our society. Almost 54% of the US's annual production of about 243 million tons (USEPA 2009) is still landfilled. Similarly in 2008, Canadians produced 34 million tons of MSW of which 76 % was disposed in landfills (Statistics Canada 2008). Conventional landfilling is not sustainable and leads to production of leachate and uncontrolled greenhouse gas emissions (e.g., methane). The organic fraction of MSW (OFMSW) is a large and renewable potential energy source that can be exploited on a sustained basis if treated under controlled conditions to reduce the environmental impact and recover energy.

Anaerobic digestion (AD) under controlled conditions is one appropriate technique for treatment of OFMSW and is currently employed mostly in Europe. Low biosolids production, low energy consumption and high rates of controlled biogas production are the main benefits of the process. The excess energy generated can be considered a renewable energy source.

AD of OFMSW can be divided into four main stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. During hydrolysis, suspended solid reactants are solublized so they can be converted into biogas by the anaerobic consortium and is the rate-limiting step for residuals containing suspended solids (Eastman and Ferguson 1981).

Concomitantly, AD of OFMSW usually requires a long retention time of more than 20 days in conventional digesters (Climent et al. 2007), with concomitant large reactor volume requirements.

Pretreatment of OFMSW to enhance hydrolysis can be used to solubilize organic matter prior to AD in order to improve the overall AD process in terms of faster rates and degree of OFMSW degradation, thus reducing AD retention time and increasing methane production (Mata-Alvarez 2003).

Most pretreatment studies have focused on single modalities with applications to waste activated sludge (WAS). Pretreatment methods proposed and evaluated to enhance AD, include, mechanical disintegration, ultrasound, thermal, chemical and thermochemical pretreatment methods (Sawayama et al. 1997; Lissens et al. 2004; Ardic and Taner 2005; Mshandete et al. 2006; Bougrier et al. 2007; Khanal et al. 2007; Akin 2008; He et al. 2008a). The majority of these studies have indicated that pretreatment tends to improve WAS digestion. However, conventional thermal pretreatment at high temperature (160-175ºC) and pressures (6-8 bar) has been demonstrated to produce better digestion results than other pretreatments in terms of increased volatile solids (VS) destruction as well as a surplus of energy gain due to higher biogas production (Abraham et al. 2003).

MW heating has a higher energy efficiency than conventional heating and has been evaluated at high temperature with thickened WAS (TWAS) by Toreci et al. (2010). MW heating to 175ºC resulted in 4.5±0.8 and 8.8±0.9 fold increases in soluble chemical oxygen demand (SCOD) concentration for 6 and 11.8% total solids (TS) concentrations vs. controls. Additionally TWAS with 3% TS concentration pretreated to 175ºC produced 31±6% more biogas by the 18th day of the mesophilic biochemical methane potential (BMP) assay compared with controls.

Zheng et al. (2009) studied the effect of MW heating on the characteristics and BMP of primary sludge (PS) which may better resemble OFMSW. The ratio of soluble to total chemical oxygen demand (SCOD/TCOD) increased almost 2.5 fold compared to controls with 4% TS and a MW pretreatment temperature of 90 °C, the BMP biogas production rate increased by 37%. They reported a 28% reduction in the digestion time to achieve 85% of the ultimate biogas production. Increased biogas production was also reported by

Eskicioglu (2007b) for TWAS. MW heating to 96ºC resulted in 3.6±0.6 and 3.2±0.1 fold increases in SCOD/TCOD at 5.4 and 1.4% TS concentrations, respectively. Subsequent mesophilic BMP assays resulted in 15±0.5% and 20±0.3% improvements over controls after 19 days of AD.

Recent studies have shown synergic solublization effects for TWAS when MW heating is combined with the oxidizing agent H_2O_2. Wong et al (2006b) reported that MW/H_2O_2 pretreatment of TWAS converted a larger fraction of TCOD into SCOD. TCOD was completely converted into SCOD at 80 ºC when 2 ml H_2O_2 (30%) was added to 30 ml TWAS (TS= 0.35-0.40%). Yin et al. (2007) reported the synergistic effects of H_2O_2 (29 ml TWAS (TS= 2.93%) + 1 ml H_2O_2 30%) and MW heating (100 ºC for 3 minutes) on TWAS solubilization. SCOD concentrations after pretreatment with H_2O_2, MW and MW/H_2O_2 were 2.6, 4.9 and 9.7 g/L, respectively.

Eskicioglu et al. (2008b) conducted BMP assays on TWAS after pretreatment by MW heating in presence of H_2O_2. SCOD/TCOD ratios for MW heating alone were 3±0, 12±0, 15±0, 16±0 and 15±1% for control, MW-60 ºC, MW-80 ºC, MW-100 ºC and MW-120 ºC, respectively. H_2O_2 and dual modality MW-60 ºC/H_2O_2, MW-80 ºC/H_2O_2, MW-100 ºC/H_2O_2 and MW-120 ºC/H_2O_2 samples achieved 17±2, 15±1, 18±0, 21±1 and 24±1% SCOD/TCOD ratios, respectively, indicating a synergic effect on solubilization when H_2O_2/MW modalities were combined. However, MW/H_2O_2 pretreatment resulted in slower biodegradation rates and lower methane yields compared to control and MW heated only samples. It was not reported if the lower rates and methane yields were an acute or chronic effect of the combined pretreatment. Combined modality pretreatment of this type has not been extended to OFMSW.

Shahriari et al. (2011c) studied the effect of MW on solubilization of model OFMSW (M-OFMSW). The greatest increase in waste solublization based on SCOD was achieved at 175 ºC. MW pretreatment resulted in 1.61±0.05, 1.62±0.01 and 1.58±0.03 times higher SCOD with supplemental water addition of 30% (SWA30) for temperature ramp rates of 2.5, 3.8 and 7.5 ^{o}C/minutes respectively. For the same conditions, release of bound water of samples into the free liquid fraction was 1.39±0.01, 1.34±0.02 and 1.37±0.01 times higher than control. It can be concluded that microwaving of M-OFMSW at high temperature

(175 ^{o}C) provides potentially beneficial conditions for waste solubilisation and subsequent enhanced AD. The actual effect of MW pretreatment on the AD process was not determined in their experiments.

The purpose of this study is to investigate the effects of single modality and combined MW/H_2O_2 pretreatment on mesophilic AD (MAD) of M-OFMSW. It is hypothesized that MW heating at high temperature and pressure when combined with H_2O_2 pretreatment will increase solubilization of organic solids, increasing bioavailability of biodegradable substrate resulting in increased rates and extent of OFMSW digestion compared with MW pretreatment only.

4.3. Methodology

4.3.1. Organic Waste

Real OFMSW has variable characteristics; therefore M-OFMSW was used to minimize compositional variation. M-OFMSW composition was based on experiments by Wang et al.(2006b) and, Luostarinen and Rintala (2007). It had a similar composition of protein, carbohydrates, vegetables and fat as the Canada Food Guide (CFG 2007), thus was representative of Canadian kitchen waste. M-OFMSW contained cooked rice (18wt %), cooked pasta (18wt %), cabbage (11wt %), carrot (11wt %), apple (11wt %), banana (11wt %), corned ground beef (10wt %) and dog food (10wt %). Rice and pasta was cooked for 15 minutes then strained prior to MW pretreatment. Moisture content of M-OFMSW was 80.7±0.3%. To reduce the particle size 1kg of M-OFMSW was placed in a Kitchen Aid food processor (PowerPro II, 500 Watts) for 30 seconds at high speed prior to any pretreatment. Additionally, supplemental tap water or H_2O_2 of 20 and 30 % was added to the M-OFMSW prior to pretreatment. Final moisture content of supplemental water addition of 20% (SWA20) or SWA20- H_2O_2, and SWA30 or SWA30- H_2O_2 mixtures were 80.7±0.3% or 84.9±0.3%, and 85.7±0.3% or 88.3±0.4%, respectively.

4.3.2. Microwave Pretreatment and Dual Modality Microwave

A laboratory MW Accelerated Reaction System (Mars 5®) was used to pretreat the M-OFMSW. This system consists of the following:

- User selectable power settings (0-1200 W) and constant frequency of 2450 MHz.
- A programmable microcomputer that controls and monitors power delivered as well as temperature, and pressure within sealed reaction vessels.
- Explosion proof sealed reaction vessels that eliminate volatile losses and can operate up to 250 ºC and 3.45 MPa.

Each reaction vessel was filled with 50 g of M-OFMSW. Samples were heated from room temperature to 115, 145 and 175 ^{o}C at a constant temperature ramp time of 40 min. Once final temperature was reached it was held for 1 minute. Samples were cooled to room temperature prior to opening to minimize volatilization losses.

For dual modality pretreatment M-OFMSW was placed in a volumetric flask and H_2O_2 (30% v/v) was added slowly (0.38 and 0.66 g H_2O_2/g TS to produce SWA20-H_2O_2 and SWA30-H_2O_2, respectively). SWA20- H_2O_2 and SWA30- H_2O_2 mixtures were reacted for 1 hour at room temperature. Subsequently, they underwent identical MW ramping as described above but only to a final temperature of 85 ^{o}C.

4.3.3. Biochemical Methane Potential Assay

BMP assays were used to evaluate the effect of single and dual modality pretreatments on ultimate methane production (i.e. biodegradability) of M-OFMSW as well as any potential AD inhibition effects (Davidsson et al. 2007; Neves et al. 2008; Angelidaki et al. 2009).

A multilevel factorial design was applied (Berger and Maurer 2002) with variables being MW treatment temperature (T) and supplemental water addition (SWA) to M-OFMSW. Factorial design makes it possible to determine correlations and interactions between dependent variables. Table 4.1 shows the variables and their respective levels. Experimental variables were selected based on Shahriari et al. (2011c), which showed that among T, SWA and temperature ramp (R) (i.e. MW intensity), the latter has minimal effect

on substrate solubilization concomitantly the temperature ramp time was kept constant at 40 minutes for the experiment.

Table 4.1: Variables and levels used in BMP test

Pretreatment	SWA	Fraction	Temperature ramp time (min)
Control	20%*	Whole	None
Control	20%	Free Liquid	None
Control	30%**	Whole	None
Control	30%	Free Liquid	None
115°C MW	20%	Whole	40
115°C MW	20%	Free Liquid	40
115°C MW	30%	Whole	40
115°C MW	30%	Free Liquid	40
145°C MW	20%	Whole	40
145°C MW	20%	Free Liquid	40
145°C MW	30%	Whole	40
145°C MW	30%	Free Liquid	40
175°C MW	20%	Whole	40
175°C MW	20%	Free Liquid	40
175°C MW	30%	Whole	40
175°C MW	30%	Free Liquid	40
H_2O_2	20%	Whole	None
H_2O_2	20%	Free Liquid	None
H_2O_2	30%	Whole	None
H_2O_2	30%	Free Liquid	None
H_2O_2 + 85°C MW	20%	Whole	40
H_2O_2 + 85°C MW	20%	Free Liquid	40
H_2O_2 + 85°C MW	30%	Whole	40
H_2O_2+ 85°C MW	30%	Free Liquid	40

* 80g M-OFMSW+ 20g water or H_2O_2
** 70g M-OFMSW + 30g water or H_2O_2

After single or dual modality pretreatment the M-OFMSW sample was divided in to (i) whole and (ii) free liquid fractions for separate BMP assays. Whole M-OFMSW was the sample as produced following pretreatment. The free liquid fraction was obtained by centrifuging the whole M-OFMSW sample at 9725 relative centrifugal force (RCF) for 40 minutes and decanting the liquid phase. BMP assays were performed in 250 mL Kimax bottles sealed with 45 mm screw caps and butyl rubber stoppers. In order to determine

variation in anaerobic biodegradability all samples were diluted with tap water to a standardized TCOD concentration of approximately 8.5 g/L. Each BMP assay contained 120 ml of standardized sample (controls and pretreated samples) and 35 ml of acclimated anaerobic biomass. Nitrogen was sparged through each bottle for 2 minutes prior to sealing the BMP bottles. BMP tests were performed at 33±1 ºC in an incubator shaker (PhycroTherm, New Brunswick Scientific Co. Inc, NB, Canada) rotating at 120 rpm. Biogas production was measured daily using a gas manometer. Total volatile fatty acid (TVFA) concentrations, pH and biogas composition was monitored weekly. TS and VS, pH, alkalinity, TCOD, SCOD, ammonia-N, total and soluble sugar, protein and humic acid (HA) analysis were performed on inoculum, untreated and pretreated M-OFMSW before and after BMP assays.

4.3.4. Analytical Methods

Ammonia and pH was measured using appropriate probes attached to a Fisher Accumet XL25 mV/pH meter. Ammonia analysis was conducted according to Standard Method 4500D (APHA 1995). Total solids (TS) and volatile solids (VS) were determined based on Standard Methods procedure 2540 G (APHA 1995). Alkalinity analysis was done by titration according to Standard method 2320B. SCOD measurements were conducted according to Standard Methods 5220C colorimetric method with a Perkin-Elmer spectrophotometer Model 295 at 600nm light absorbance. The SCOD was performed after samples were centrifuged and filtered through GN-6 Metricel S-Pack membrane disc filters with 0.45μm pore size (Millipore). Volatile fatty acids (VFAs; acetic, propionic and butyric acids) were measured by injecting supernatants into a HP 5840A gas chromatograph with a flame ionization detector and Chromosorb 101 packed column. The concentration of proteins, HA (Frolund et al. (1995)) and sugars (Benefield (1976)) were measured using a Beckman DU-40 spectrophotometer. Bovine serum albumin (BSA), HA sodium salt and glucose stock solutions were used as standards, respectively. Free water was determined by centrifuging 60g of sample at 9725 RCF for 40 minutes and decanting and measuring the weight of the supernatant. Biogas composition was determined with a HP 5710 GC with thermal conductivity detector and Chromosorb 101 packing.

4.4. Calculations

4.4.1. Post-digestion Parameter Calculation

Characteristics of M-OFMSW samples after AD are complex and contain the microbial consortia used in BMP assays. Consequently it is difficult to calculate characteristic changes of the sample alone. Eqn. 4.1 accounts for the initial inoculum biomass component in BMP assays.

Eqn. 4.1 for COD can be applied to other parameters such as protein, sugars, humic substance but not for alkalinity and pH.

$$\text{COD change (\%)} = \frac{COD_{W,I} - \frac{M_M COD_{M,F} - M_B COD_{B,F}}{M_W}}{COD_{W,I}} \times 100 \quad (4.1)$$

Where

$COD_{W,I}$ is the initial COD of waste at the beginning of BMP test;

$COD_{M,F}$ is the final COD of mixture includin waste, water and biomass at the end of test;

$COD_{B,F}$ is the final COD of biomass;

M_M is the weight of mixture (biomass, waste and water in the bottle);

M_B is the weight of biomass; and

M_W is the weight of waste.

4.5. Results and Discussion

4.5.1. Effects of Pretreatment on Characteristics of M-OFMSW

M-OFMSW was pretreated with high temperature MW irradiation, H_2O_2 and combined modalities at 24 different conditions (Table 4.1). The effects of the pretreatments on various parameters for the whole and free liquid fractions are summarized in Table 4.2 and Table 4.3.

Table 4.2: M-OFMSW characteristics

Parameter	Fraction	SWA	Control	115ºC	145ºC	175ºC	H_2O_2	H_2O_2+MW
COD (g/kg)	Whole	20%	208±0	227±2	261±2	199±4	230±6	227±4
		30%	183±2	193±8	189±6	196±4	187±0	207±4
	Free Liquid	20%	95±2	106±1	124±5	128±4	107±5	117±3
		30%	77±1	84±1	106±0	109±2	106±4	147±3
	Soluble	20%	79±1	92±1	95±1	114±1	94±8	107±2
		30%	67±0	81±5	73±1	102±2	97±12	112±5
Protein (g/kg)	Whole	20%	29.6±2.7	27.8±3.9	25.6±2.6	49.2±2.2	39.9±3.9	46.8±1.3
		30%	25.7±2.9	22.9±1.8	27.5±1.2	43.3±0.3	33.1±4.6	45.0±2.7
	Free Liquid	20%	14.1±3.1	16.7±1.4	18.0±0.7	31±2.3	27.7±1.2	24.2±3.0
		30%	9.5±0.8	14.5±0.6	18.9±2.3	27.7±1.8	15.8±0.8	22.1±3.7
	Soluble	20%	9.1±0.9	11.1±0.8	14.4±1.9	29.2±4.7	13.7±1.4	18.3±0.4
		30%	8.8±1.6	9.9±1.5	11.0±0.4	25.6±2.1	10.2±0.3	16.9±2.8
Humic Acid (g/kg)	Whole	20%	9.9±1.1	11.5±1.3	16.5±1.0	48.1±2.7	23.6±0.5	27.5±2.3
		30%	9.3±1.3	9.9±0.9	13.5±0.6	42.4±0.7	20.0±1.3	26.6±2.8
	Free Liquid	20%	1.9±0.5	2.8±0.2	9.2±0.7	31.0±0.6	9.3±0.7	11.7±2.6
		30%	1.7±0.0	2.5±0.1	5.4±0.5	26.0±0.7	10.6±0.5	20.9±0.2
Sugar (g/kg)	Whole	20%	104.7±4.1	126.7±17.8	120±10.2	155.5±35.8	62.2±7.8	75.4±3.0
		30%	73.5±8.5	122.4±3.0	115.0±5.3	136.6±23.1	31.7±8.5	43.8±1.4
	Free Liquid	20%	90.2±18.9	97.9±7.3	129.3±37.7	107.1±14.4	34.4±3.0	43.5±15.6
		30%	67.7±5.0	101.7±8.4	150.3±8.4	97.5±2.2	22.2±10.0	23.9±1.0
VS (g/kg)	Whole	20%	157.1±3.3	166.1±1.0	165.8±0.9	147.5±3.7	145.0±3.9	154.7±5.1
		30%	137.0±2.3	143.4±2.1	138.7±0.6	132.6±4.2	101.9±15.6	125.9±7.4
	Free Liquid	20%	95.7±13.5	99.9±15.6	115.8±4.0	107.7±0.6	62.0±30.9	102.5±8.6
		30%	86.0±11.9	91.5±3.8	92.0±0.0	96.6±1.8	81.4±14.6	68.1±1.9
VS/TS	Whole	20%	0.96	0.96	0.96	0.96	0.94	0.96
		30%	0.96	0.96	0.96	0.96	0.95	0.95
	Free Liquid	20%	0.95	0.94	0.95	0.94	0.91	0.95
		30%	0.95	0.95	0.95	0.95	0.94	0.93
Alkalinity (mg $CaCO_3$/kg)		20%	462±17.0	750±0.0	475±35.4	475±35.4	600±35.4	313±17.7
		30%	413±18.0	650±0.0	463±53.0	463±53.0	363±17.7	100±71
Ammonia (mg/L)		20%	197.0±5.8	117.6±13.8	96.6±22.5	156.7±0.0	274.5±8.1	214.0±6.3
		30%	201.1±0	147.6±13.0	90.5±18.5	170.3±0.0	232.5±6.8	201.1±0.0
pH		20%	5.9	5.5	4.9	4.2	5.2	4.8
		30%	6.0	5.5	4.9	4.2	4.9	4.6

Table 4.3: Free liquid fraction of samples (ratio of free liquid to total sample)

SWA	Control	115ºC	145ºC	175ºC	H_2O_2	H_2O_2+MW
20%	0.48±0.01	0.47±0.01	0.69±0.00	0.77±0.01	0.36±0.02	0.40±0.01
30%	0.52±0.03	0.54±0.04	0.73±0.01	0.82±0.00	0.43±0.02	0.42±0.02

All pretreatments improved the solubilization of the M-OFMSW to various extents. The greatest increase in waste solublization was achieved at two conditions, MW-175ºC and dual modality pretreatment of H_2O_2/MW-85ºC. MW pretreatment alone resulted in SCOD

increasing from 79 g/Kg for the control to 114 g/Kg for SWA20 and from 67 g/Kg to 102 g/Kg for SWA30 resulting in 1.44 and 1.52 times higher SCOD compared to controls, respectively. Similar increases to 107 g/Kg and 112 g/Kg resulting in ratios of 1.35 and 1.67 being obtained for SWA20-H_2O_2 and SWA30-H_2O_2, respectively. In addition to the specific increase in SCOD after MW to 175ºC the volume of free liquid fraction of samples after MW pretreatment also increased relative to the control by factors of 1.60 and 1.57 for SWA20 and SWA30, respectively (Table 4.3). On the other hand release of bound water from samples into the free liquid fraction decreased to 0.75 and 0.83 for dual modality SWA20-H_2O_2 and SWA30-H_2O_2, respectively. Review of Table 4.3 indicates that when only MW pretreatment was applied the free water faction compared to the controls generally increased in proportion to the increase in MW temperature. However, when H_2O_2 was used singularly or combined with MW the free water fraction decreased below control values. With combined H_2O_2/MW-85 ºC pretreatment, even after 90 minutes of centrifuging at RCF of 9725, a large amount of particles remained suspended. The effects of MW on solubilization of other parameters were discussed in detail by Shahriari et al. (2011c). The results indicate that dual modality H_2O_2/MW-85ºC pretreatment results in specific solubilization comparable to high temperature MW pretreatment but achieved at a lower MW temperature. Concomitantly, it is unknown if lower free water production resulting from combined H_2O_2/MW-85ºC pretreatment may adversely affect enhanced ultimate biogas production. The potential to enhance biogas production from M-OFMSW with potentially lower pretreatment energy input (H_2O_2/MW-85ºC) must be determined by BMP assays.

4.5.2. M-OFMSW BMP Assay

The effects of MW, H_2O_2 and combined modality H_2O_2/MW-85 ºC pretreatments on mesophilic AD of M-OFMSW were investigated using BMP assays. CBPs are shown in Figure 4.1 for whole samples and Figure 4.2 for free liquid samples. Results were compared based on their T, SWA level and M-OFMSW fraction (whole or free liquid). Change in COD, VS, humic acid and ammonia characteristics of the M-OFMSW at the end

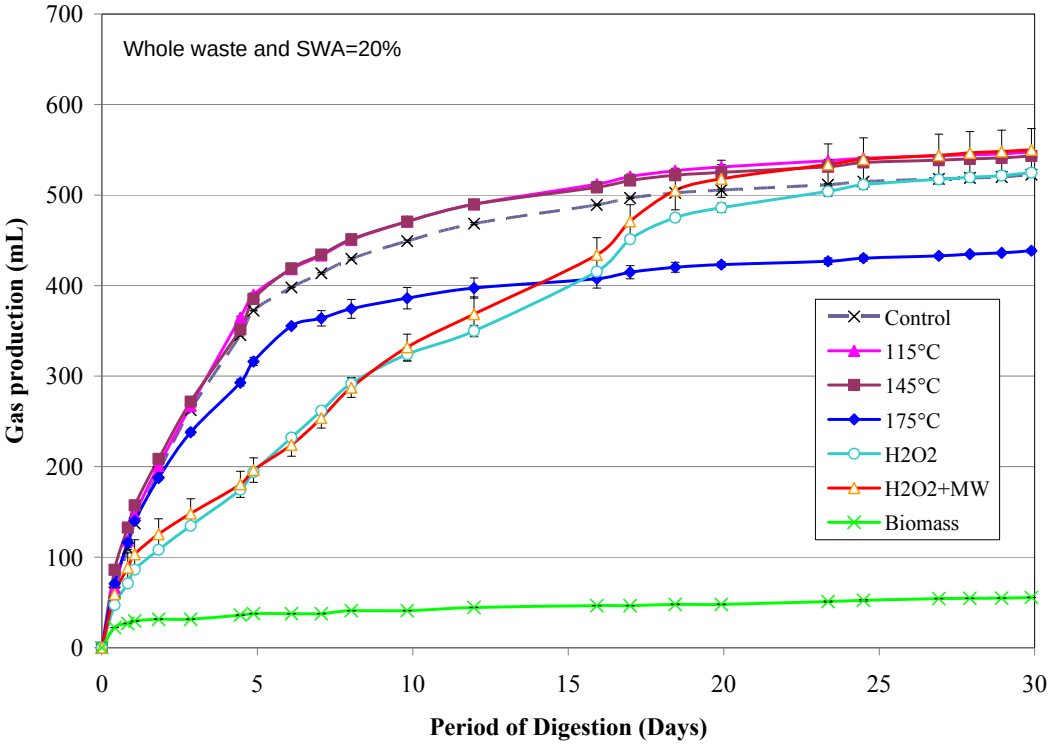
of the BMP assay are summarized in Table 4.5, while accounting for inoculm biomass components (Table 4.4) based on Eqn 4.1.

Table 4.4: Acclimated biomass properties

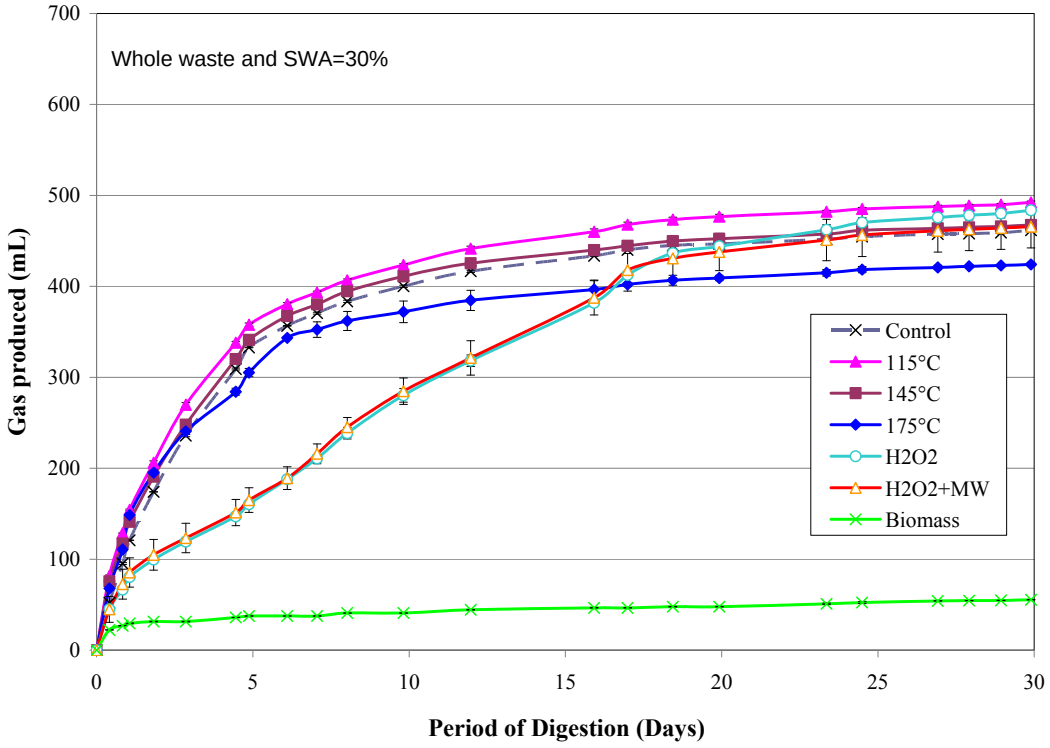
Parameter	Fraction	Biomass
COD	Total	10±0.0
(g/kg)	Soluble	2±0.27
Protein	Total	6±0.25
(g/kg)	Soluble	1±0.16
TS (g/kg)		18.92±1.27
VS (g/kg)		12.04±0.29
Ammonia (mg/L)		1197±88

Table 4.5: CBP (produced by waste not biomass) and associated removal efficiencies

Conditions	SWA	CBP(mL)		ΔCOD (g/kg)		Δ VS(g/kg)		Δ HA(g/kg)	
		Whole	Free Liquid	Whole	Free Liquid	Whole	Free Liquid	Whole	Free Liquid
Control	20%	469±1.8	433±29.2	6.5±0.13	5.6±0.04	4.5±0.02	6.0±0.17	0.28±0.1	0.13±0.0
	30%	408±10.4	438±35.1	5.7±0.22	4.7±0.08	4.2±0.01	5.7±0.01	0.31±0.0	0.11±0.0
115ºC	20%	494±2.1	458±.1	6.8±0.36	6.1±0.42	4.8±0.00	6.3±0.21	0.32±0.1	0.18±0.0
	30%	439±22.3	374±8.3	5.4±0.62	4.9±0.56	4.1±0.13	5.6±0.13	0.32±0.0	0.16±0.0
145ºC	20%	490±1.4	561±1.3	7.9±0.23	7.4±0.02	4.6±0.13	7.0±0.10	0.38±0.0	0.61±0.0
	30%	414±0.8	449±11.6	5.7±0.10	6.5±0.11	3.8±0.08	5.5±0.02	0.31±0.1	0.36±0.0
175ºC	20%	385±3.3	544±47.9	5.3±0.07	7.7±0.12	3.6±0.08	6.0±0.01	0.88±0.1	1.15±0.0
	30%	370±31.3	476±15.9	4.5±0.97	6.1±.49	3.1±0.08	5.4±0.01	0.79±0.0	1.06±0.1
H_2O_2	20%	471±6.4	494±15.9	7.4±0.40	7.0±0.03	4.4±0.10	3.5±0.81	0.80±0.0	0.61±0.0
	30%	430±7.1	406±24.9	5.9±0.35	6.5±0.2	2.9±0.21	5.2±0.14	0.68±0.0	0.70±0.0
H_2O_2+MW	20%	496±33.2	550±28.5	7.2±0.06	7.3±0.11	4.7±0.03	6.4±0.03	0.93±0.0	0.76±0.0
	30%	412±1.9	429±18.3	6.7±0.47	9.7±0.01	3.7±0.00	4.2±0.02	0.90±0.0	1.37±0.0

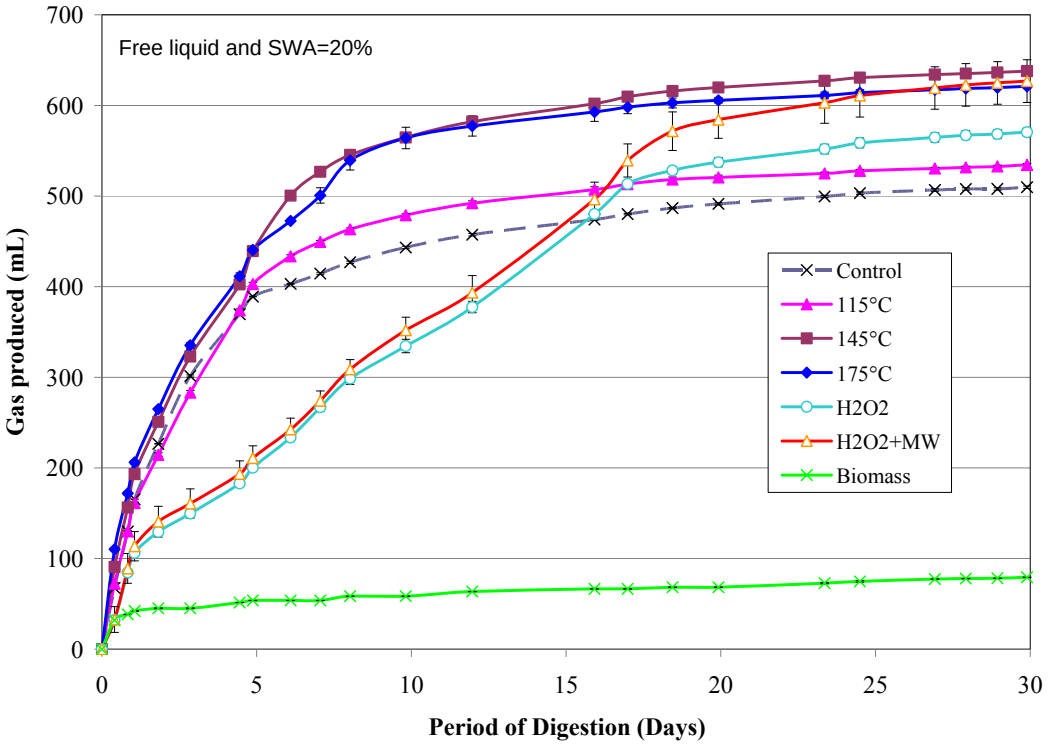


(a)

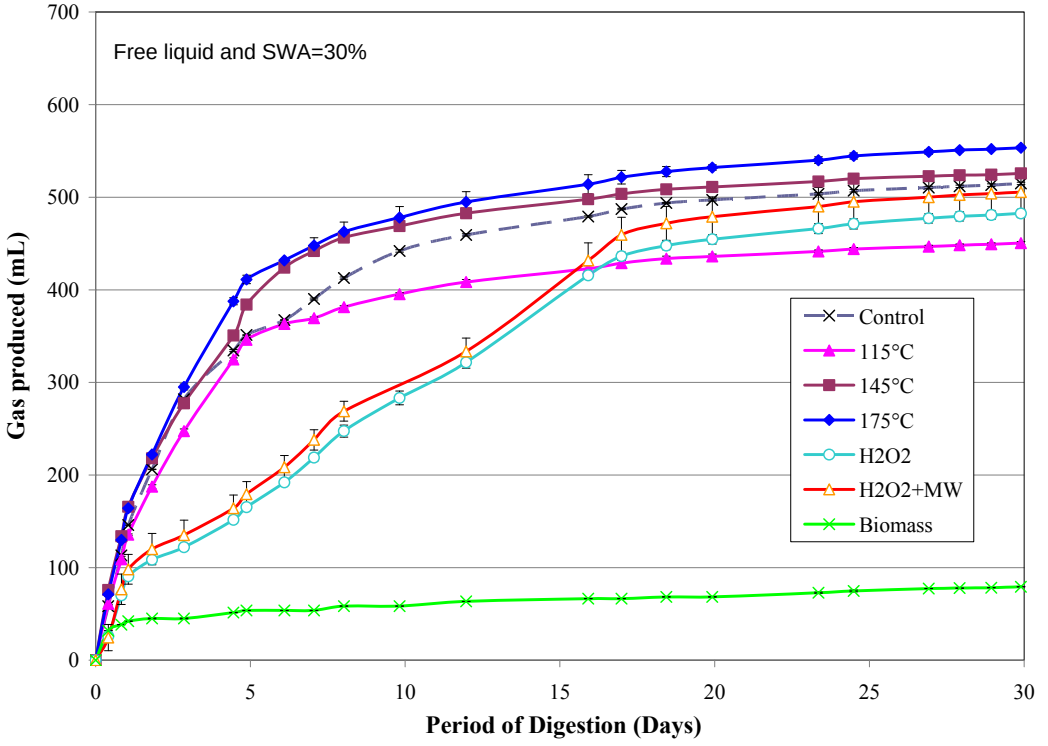


(b)

Figure 4.1: CBPs for whole waste, (a) SWA20 and (b) SWA30



(a)



(b)

Figure 4.2: CBPs for free liquid fraction, (a) SWA20 and (b) SWA30

4.5.3. Whole M-OFMSW

As discussed above significantly higher SCOD concentrations were observed following pretreatment (Table 4.2) with MW only to 175 ºC, H_2O_2 and H_2O_2/MW-85 ºC treated samples compared to the control (1.44, 1.19 and 1.35 fold increase for SWA20 and 1.52, 1.45 and 1.67 fold higher for SWA30, respectively). However, these three treatment conditions did not enhance the AD rate or extent of stabilization. These results are suggesting that M-OFMSW material that was solubilized and associated with the bound or free water fraction as soluble or colloidal material was either similar or less biodegradable than the controls.

For MW only pretreated samples, 85% of biodegradation was completed after almost 8 days. After three additional weeks no significant changes in biogas production rates were observed and the final 15% of biogas production accumulated. For samples pretreated with H_2O_2 and H_2O_2/MW-85 ºC, 85% biodegradation took longer and required about 20 days.

Normalized CBP for SWA20 and SWA30 (Figure 4.1) showed less biogas production for samples microwaved to 175ºC both in the short and long term compared to controls and samples pretreated with MW to lower temperatures (115 ºC and 145 ºC). H_2O_2 and H_2O_2/MW-85 ºC treated samples had a significantly lower biogas production rate for the first three weeks but their overall ultimate organic removal performance was similar to the controls and the lower temperature MW only samples. Based on a first order CBP model (Section 5) for SWA20 the reaction rate constants (k) for control and low temperature MW pretreatment only (115 ºC) were 0.252 and 0.251 per day respectively, while for H_2O_2 and H_2O_2/MW-85ºC the rate constants were significantly lower with values of 0.088 and 0.083 per day respectively. Ultimate CBP for controls, low temperature MW (115 ºC, 145 ºC), H_2O_2 and H_2O_2/MW-85 ºC for the standardized BMP assays with SWA20 were relatively constant between 523 and 550 mL (including biogas from biomass) while for MW-175 ºC the CBP was significantly lower at approximately 438 mL compared to the control and other pretreatment samples. Similar CBP values and trends were observed for SWA30. These results suggest that residual H_2O_2 or byproducts from chemical oxidation resulted in acute biomass inhibition decreasing specific activity and biogas production at the beginning of the assay. Another possibility could be insufficient time for the inoculum to acclimatize

to the presence of residual H_2O_2 in the sample or a material produced via the H_2O_2 pretreatment that is acutely inhibitory to the anaerobic consortia. This later explanation is plausible as discussed latter. The fact that the ultimate CBP of the H_2O_2 and dual modality pretreatment samples recovered (Figure 4.3) is an indicator that the anaerobic consortia adjusted to the materials produced by chemical oxidation or that residual H_2O_2 in the sample eventually decreased below inhibitory concentrations. Toreci (2008) working with TWAS also reported acute inhibition in BMP tests from inhibitory substances produced by high temperature MW pretreatment. Acute inhibition was overcome by acclimation of the microbial consortia.

In the case of SWA20 and SWA30 samples pretreated with MW to 175 ºC, mild acute inhibition was observed early in the assay and ultimate CBPs were about 10-20% lower compared with controls, lower MW temperatures, H_2O_2 or combined H_2O_2/MW-85 ºC. Since all samples were standardized to the same COD concentration, the results suggest that higher temperature MW pretreatment does not produce more readily degradable substrate. In fact a larger component of refractory material per g COD is produced. The absence of a lag phase in MW irradiated samples was expected since the inoculum had been acclimatized to this kind of substrate prior to the digestion. Figure 4.1 demonstrate that the ultimate biogas productions for pretreated whole samples at lower temperature (145 ºC and 115 ºC) are just slightly higher than the controls. Additionally, biogas production rates for controls and samples treated at 145 ºC and 115 ºC were approximately equal during the exponential phase, but the duration of this phase was a little shorter for MW pretreatment at 175 ºC. This further suggests that less readily biodegradable substrates were available at the higher MW temperature, likely due to conversion of biodegradable organics to refractory compounds and harder to digest materials. Hodge et al. (1953) observed the production of melanoidins (brown nitrogen copolymers) in food industry at moderate temperature. MW pretreated samples to 175 ºC displayed a dark brown colour, opposed to the lighter colour of controls and other pretreatment samples, which can be an indicator of the production of melanoidins. Humic acid was measured in all samples before and after pretreatment (Table 4.2). The concentration of total and soluble humic acid after pretreatment at 175 ºC with SWA20 increased more than 5 and 16 times, respectively

compared to the control and was 2-10 fold higher than the other pretreatments. In H_2O_2 pretreated samples, increase of humic acid was also observed compared to controls but were equal or less than half the concentration of 175 ºC samples. Similar comparable results were seen for the SWA30 samples microwaved to 175 ºC and the other pretreatments evaluated.

As both humic acid and melanoidins compounds are known to be refractory, their presence would explain the decrease of biodegradability of the COD in the standardized assay. They are likely to be a contributing factor for lower biogas production and lower COD and VS removal for the 175 ºC MW pretreatment vs lower MW temperatures, H_2O_2 or combined modality samples as indicated in Table 4.5. Under standardized testing this table shows the absolute value of COD, VS or HA removal per kg substrate in BMP assays accounting for the inoculum (i.e. Eqn. 4.1). The absolute change in COD and VS were compared with the cumulative biogas production for every condition (whole and free liquid fraction; SWA20 and SWA30). It was observed that there was good corroboration between increased biogas production and subsequent COD and VS removals. Samples pretreated at 145ºC and 115ºC had higher COD removal. For 175 ºC samples, COD and VS removal were 5.3 and 3.6 g/kg for SWA20; and 6.5 and 4.5 g/kg for control, respectively, the same trend was found in SWA30.

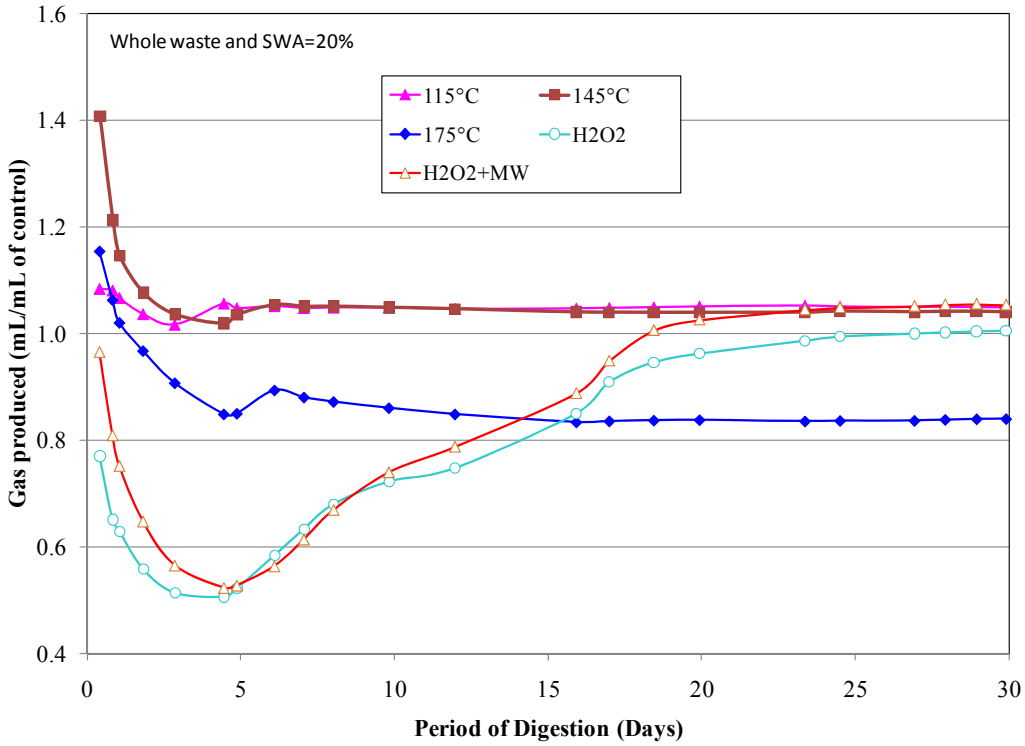
Figure 4.3 shows daily relative CBPs (CBP of pretreated sample/ CBP of control) for whole SWA20 and SWA30 samples and helps clarify the type of inhibition. These figures show that pretreated samples at 145 ºC and 115 ºC had slightly higher CBP compared to controls for the first 4-5 days. However, overall 4-7% improvement in biogas production was observed at 115 ºC and 145 ºC. 175 ºC irradiated samples were observed to produce consistently lower quantities of biogas compared to the control never catching up by the end of the experiment. This type of response suggests a refractory type waste rather than an acclimation issue. CBPs rate of samples pretreated with H_2O_2 or combined H_2O_2/MW-85 ºC decreased over the first 5-6 days before steadily improving with CBP equivalent to controls achieved after about 17 days. Initial temporal decrease in relative daily CBP followed by steady improvement is characteristic of acclimation type issues that are overcome by the microbial consortia given time.

Ammonia production for 175 ºC pretreated samples were not as high as H_2O_2 and H_2O_2/MW-85 ºC. It has been hypothesised by Stuckey and McCarty (1984) that nitrogenous organic materials become less biodegradable after pretreatment at high temperature. H_2O_2 and H_2O_2/MW-85 ºC samples produced more ammonia compared to other samples, meaning H_2O_2 might improve the digestion of protein. But concentrations observed were not inhibitory, the maximum ammonia concentration (ammonia of biomass and waste at the end of BMP test) for whole waste was less than 420 mg/L and for the free liquid less than 500 mg/L. Kayhanian (1994; 1999) observed ammonia inhibition occurred at ammonia concentration above 1000-1200 mg/L in high solids anaerobic digestion. Additionally, Hansen et al. (1998) digesting swine manure at pH 8 reported ammonia inhibition was insignificant at concentrations less than 1100 mg/L. which was twice the maximum concentration in the present study.

Based on the best whole sample results from this study (pretreatment at 145 ºC), 122 m^3 biogas/tonnes of M-OFMSW can be generated. Table 4.6 shows the range of biogas production for commercial AD of MSW. The results of this study are in general agreement with biogas yields for commercial digesters. Biogas composition was also observed to be close to commercial AD (Mata-Alvarez 2003), 55-60% methane.

Table 4.6: Biogas yield of commercial anaerobic digesters treating OFMSW (Ostrem 2004)

AD Design Firm	**Biogas Yield (m^3/tonne feedstock)**
BTA	80-120
Valorga	80-160
DRANCO	100-200
Kompogas	130
Present Study	122



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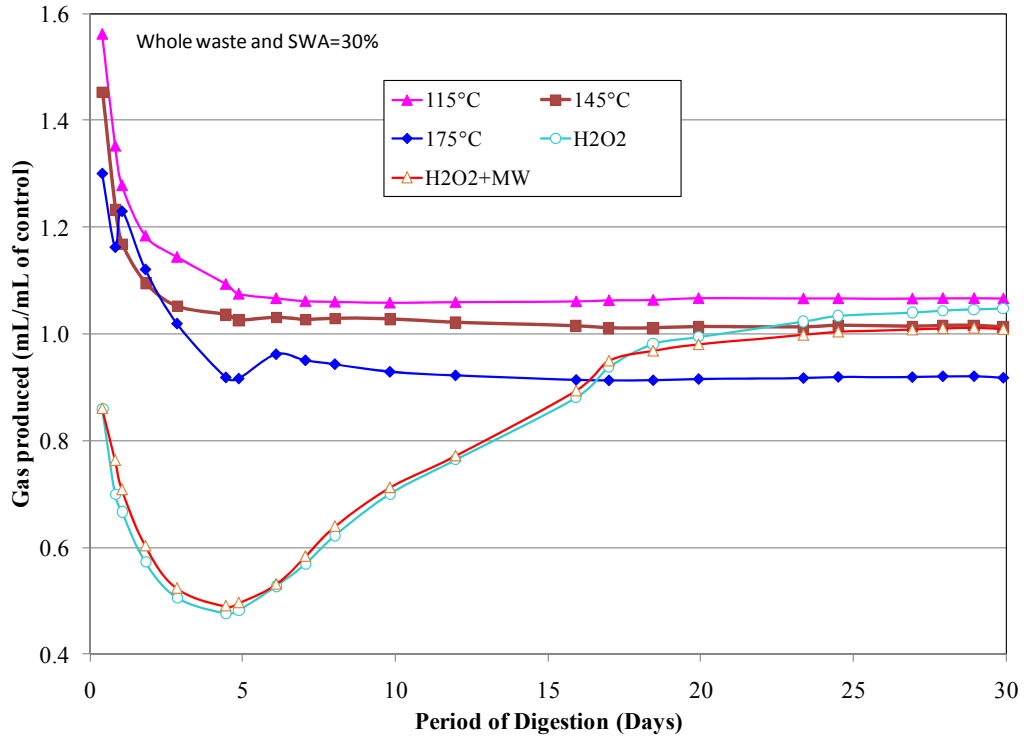


(b)

Figure 4.3: Relative CBPs for whole waste, (a) SWA20 and (b) SWA30

Most of the samples had low VFA concentrations at each weekly interval suggesting the anaerobic consortia were in balance and VFAs were consumed as generated. High VFA concentrations in the 1000-1300 mg/L range were observed in the first week for the 115ºC and H_2O_2/MW-85 ºC samples BMP assays. The predominate VFAs were propionic, acetic and butyric acid in order of concentration. This is an indicator of large concentrations of readily degradable substrate available after acidification and suggests an imbalance in the acetoclastic methanogenic consortia. However at the end of the third week VFA concentrations decreased as methanogenic activity increased and readily acidifying substrate was consumed. We do not have an explanation why the high VFA concentrations for the 115 ºC samples were observed. However for H_2O_2/MW-85 ºC samples presence of H_2O_2 inhibited methanogens resulting in accumulation of VFA. Why this did not occur for H_2O_2 only samples cannot be explained. In general VFA concentrations even in the cases where it was elevated in the first week were well within the range for stable AD operation.

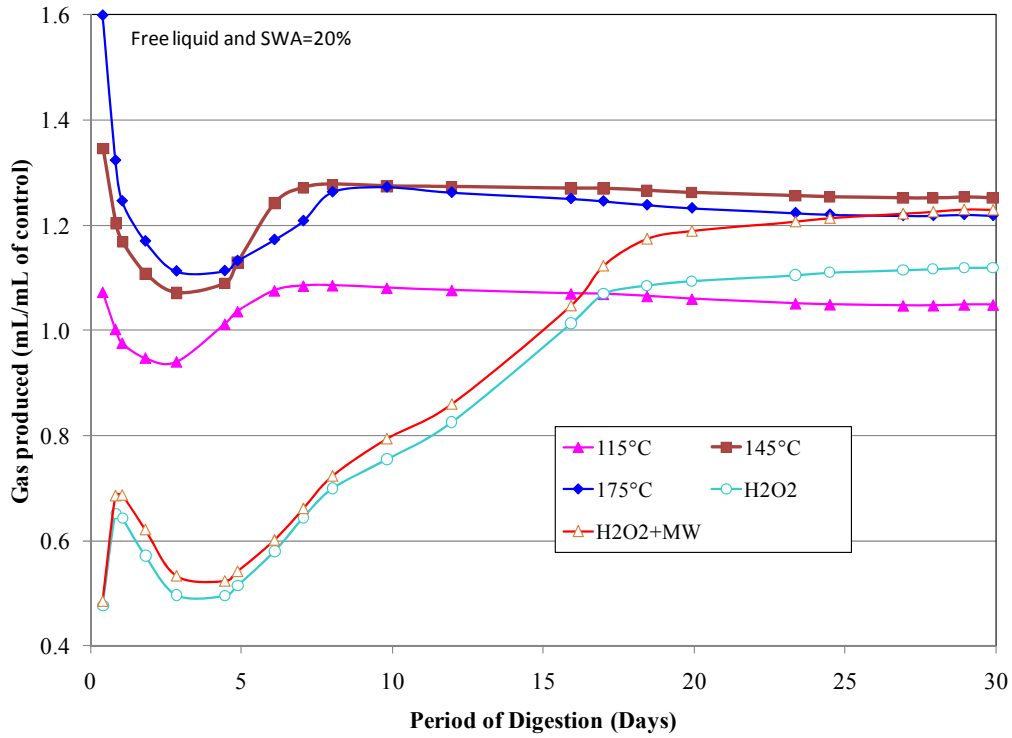
4.5.4. Free Liquid Fraction of M-OFMSW

For the free liquid fraction, the greatest improvement in CBP using initial standardized COD loadings was observed for MW samples pretreated at 145 ºC and 175 ºC (Figure 4.2). It was most significant for 145 ºC and 175 ºC for SWA20, which had a 26% and 25% increase in CBP after 8 days of digestion, when compared to controls. But, final CBP with MW 175 ºC and SWA20 was slightly lower than the 145 ºC sample. The H_2O_2/MW-85 ºC eventually produced approximately the same amount of biogas as MW 145 ºC samples (Figure 4.4). Dual modality samples preformed better than H_2O_2 only in terms of final CBP with SWA20 and SWA30, which was 23 and 8% greater than controls, respectively. Final CBP of SWA30 samples pretreated at 145 ºC and 175 ºC were 7% and 13% higher than the control. Even though the 175 ºC pretreatment had ultimately a better biogas production, it had similar performance to the 145 ºC pretreatment until the 8-12th day of digestion, when 90% of the cumulative biogas was produced. Incorporation of H_2O_2 alone or as a dual modality pretreatment again caused a long period of reduced rate of biogas production. Subsequently, both H_2O_2 and MW/H_2O_2-85 ºC samples produced little more biogas and

leveled off at a final CBP of 483 and 506 ml (including biomass), respectively. Dual modality SWA20 outperformed dual modality SWA30 resulting in 24% improvement.

MW heating with or without H_2O_2 solubilizes particulate organic carbon compounds. The free liquid fraction SCOD concentration increase over controls for SWA20-H_2O_2 and SWA30-H_2O_2 were 19% and 35%, respectively. These concentrations increased to 35% and 67% with dual modality H_2O_2/MW-85 ºC, respectively. MW alone to 175 ºC, showed similar results: 44% and 52% increase in SCOD over the control with SWA20 and SWA30 respectively. The enhanced release of COD into the soluble free liquid that occurred with dual modality pretreatment was slightly higher than achieved with MW to 175 ºC for SWA30. This is in agreement with findings of Wong et al. (2006b) who studied the efficacy of microwaving and H_2O_2 pretreatment of sewage sludge. MW heating to 80 ºC with H_2O_2 [2 ml (30 wt.%) H_2O_2 added to 30 ml sludge (TS=0.35-0.40%)] converted 100% of the COD into SCOD.

In the present study using standardized COD concentrations, increased solubilization (SCOD) in the presence of H_2O_2 decreased the rate of degradation of free liquid organics. Based on the BMP assay the initial rates (First 10 days) of CBP for H_2O_2 and H_2O_2/MW-85ºC pretreatment were 35 and 28 ml biogas/day for SWA20 and SWA30, respectively vs 45 ml biogas/day for the controls, indicating that the SCOD resulting from pretreatment using H_2O_2 was slower to biodegrade. In the free liquid fraction, a 23% increase in ultimate biogas production was observed for dual modality H_2O_2/MW-85 ºC and SWA20-H_2O_2 samples, but no enhancement over the control was observed for SWA30-H_2O_2. This could be due to inhibition from a higher percentage of H_2O_2 residuals in the SWA30- H_2O_2 sample.



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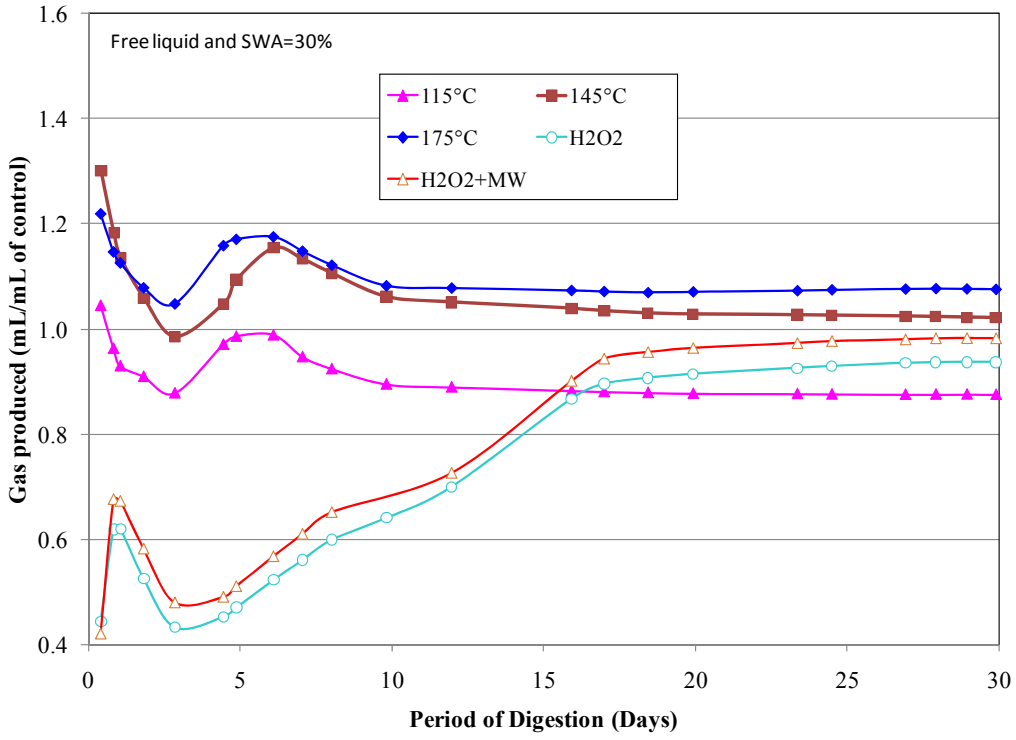


(b)

Figure 4.4: Relative CBPs for free liquid fraction, (a) SWA20 and (b) SWA30

Based on these results, it is suggested that a lower H_2O_2 dose should be used in future studies, in order to minimize the loss of methane potential due to advanced oxidation. Although the ultimate CBP was the same for pretreated sample at 145 ºC and H_2O_2/MW-85 ºC with SWA20, the former took 12 days to generate 91% of its ultimate biogas production, while for the latter it took 19 days to reach the same state. Normalized CBP curves (Figure 4.4) show the adaptation phase for samples including H_2O_2 pretreatment. For SWA20, final CBP results were promising since at the end of the digestion period, all pretreated samples reached superior biogas production than the control. For SWA30 however, only samples pretreated at 145 °C and 175 °C by MW obtained superior results, not with H_2O_2 or dual modality H_2O_2/MW-85 ºC.

Furthermore, taking into account that the volume of free water released (Table 4.3) from H_2O_2 pretreated samples was less than controls, it can be concluded that H_2O_2 is not the best pretreatment option for M-OFMSW prior to AD. Table 4.3 shows that the ratio of free liquid volume to whole sample mass with and without (control) pretreatment. With single or dual modality H_2O_2 pretreatment for SWA20 or SWA30 samples, the free liquid volume to whole sample mass ratio was 0.36-0.43 vs. the controls which were 0.48-0.52. This is significantly lower when compared to the ratios for 145^{o}C and 175^{o}C which were from 0.69-0.73 and 0.77-0.82, respectively.

These results are in good agreement with Eskicioglu et al. (2008b) who reported a 24% SCOD enhancement for waste activated sludge with H_2O_2 after 10 minutes MW heating to 120 ºC. However, for most conditions, MW/H_2O_2 treated samples had lower biodegradation rates and ultimate methane production potential. The exception was a 29% enhancement in biogas production observed with samples pretreated with MW/H_2O_2 at 100 ºC. No explanation was given explaining the sudden increase of biogas at this condition.

Trends regarding VFAs compositions and concentrations are similar to the whole waste as discussed in the previous section. The weekly monitored pH was 7.5±0.2, providing a good environment for the anaerobic consortia.

During batch AD of the free liquid fraction of M-OFMSW, sample pretreated at 145ºC and control (SWA20) generated 55.3 and 31.1 m^3 biogas/tonnes of M-OFMSW respectively. This translates into a 78% improvement in AD of liquid fraction of M-OFMSW after

pretreatment. These numbers were calculated based on the ratio of free liquid/whole sample mass (Table 4.3). When compared to the biogas production of the whole M-OFMSW, we can advance that digestion of only the free liquid fraction of M-OFMSW accounts for 48 % of the CBP of the whole waste. This implies that pretreatment does not release sufficient organics to the free liquid phase to justify treatment of the liquid phase only. However, if the digestion of the liquid fraction is desired, MW pretreatment to 145 ºC significantly increases biogas production from this fraction. Also, it is important to note that the volume of biogas produced in 7 days with MW pretreatment to 145 ºC (SWA20) is equivalent to 20 days when compared to AD results for the control.

4.5.5. Biogas Composition

Biogas composition (Table 4.7) for BMP assays was monitored weekly for all sample sets. In the first week assays for controls and MW samples contained 35-45% of CH_4, 35-45% of CO_2 and 25-35% of N_2 with similar average methane composition for the different conditions. On the other hand, samples treated with H_2O_2 showed different composition: 5-10% of CH_4, 45-50% of CO_2 and 40-45% of N_2 were detected in the first week. A higher production of N_2 and CO_2 may be caused by the existence of H_2O_2 in BMP bottles which resulted in acute oxygen toxicity of the microbial consortia particularyily the methanogens, In subsequent weeks methanogenic bacteria had sufficient time to adjust themselves to produce more methane displacing the other gases. By weeks 3 and 4 the composition of biogas in all samples was generally similar with average CH_4 in the range of 60%.

Table 4.7: Biogas composition in percentage during the BMP assay

	Week 1			**Week 2**			**Week 3**			**Week 4**		
Gas	N_2	CH_4	CO_2	N_2	CH_4	CO_2	N_2	CH_4	CO_2	N_2	CH_4	CO_2
Control& MW	25-35	35-45	25-35	10-15	50-55	30-35	5-10	55-60	30-40	5-10	55-60	35-40
H_2O_2& H_2O_2+MW	40-45	5-10	45-50	15-20	45-50	35-40	7-10	60-63	28-32	5-10	60-63	30-35

4.5.6. BMP Assays with Different COD Concentration

Another objective was to determine the effects of microorganisms (inoculum) to food (substrate) ratios (M:F ratios, based on VS) on CBP for SWA20 and SWA30 when pretreated with MW at 175 ^{o}C. This temperature was selected as it has been demonstrated in this study and by Toreci (2008) to produce compounds that inhibit methanogenesis. Table 4.8 summarizes the exact conditions for whole samples and free liquid sample in BMP assays used.

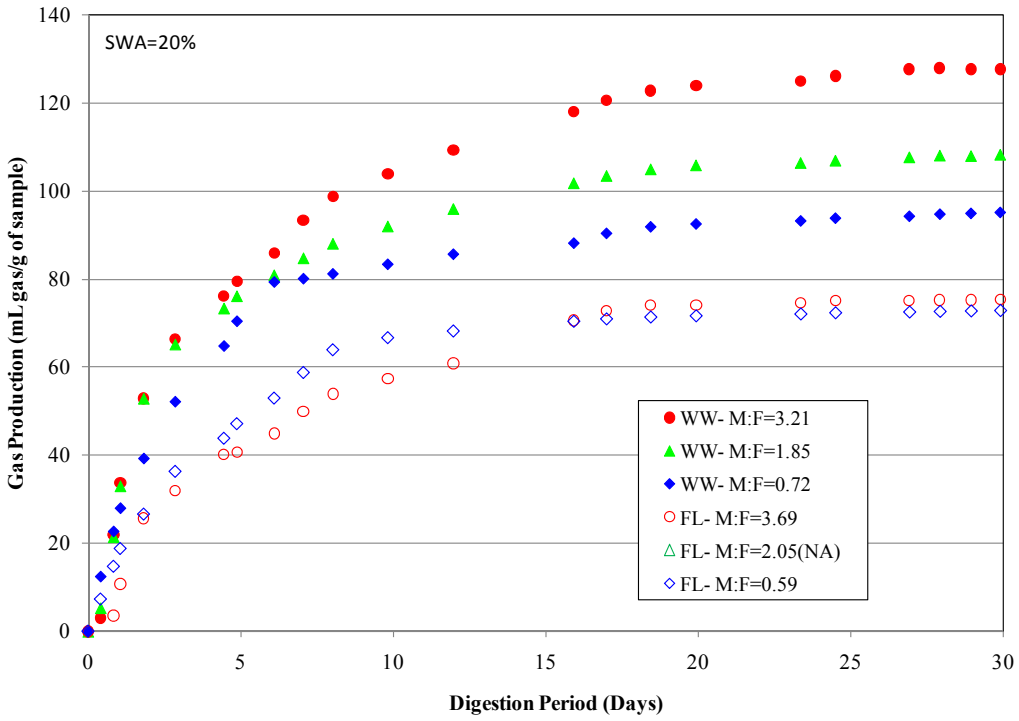
Table 4.8: Microorganism-Food ratio

SWA	Microorganism-Food ratio (based on VS)			
	20%		30%	
Sample	Whole Waste	Free Liquid	Whole Waste	Free Liquid fraction
A	0.72	0.59	0.80	0.65
B	1.85	2.05	2.12	2.30
C	3.21	3.69	3.28	4.10

As expected, CBPs from assays containing more dilute M-OFMSW were lower with both SWA20 and SWA30 sample assays. However, in order to better differentiate the effects of high temperature MW pretreated M-OFMSW concentration versus inoculum concentration, it is important to normalize biogas production. Concomitantly, biogas production attributed to endogenous decay was subtracted from all samples then CBP with different inoculum concentrations was divided by the initial mass of M-OFMSW in the sample. This now enables us to evaluate the biogas production per unit mass of waste for different M:F ratios. The resulting BMP trends for whole SWA20 and SWA30 samples are shown in Figure 4.5a and b. No lag phase was observed in biogas production indicating the anaerobic microbial consortia is acclimated to the waste at all M:F ratios and SWAs. Samples with lower initial OLR (i.e. higher M:F ratios) produced higher biogas per g of sample based on t-test evaluation at a 95% confidence interval. Moreno-Andrade and Buitron (2003) also reported similar results in wastes containing 4-chlorophenol potentially inhibitory materials, as may be present in our samples (i.e., high humic acid, melanoidins compounds). They concluded that as the M:F ratio increases the degree of inhibition decreases, it means that the

inhibition is not only dependent on toxic compounds concentration, but also on biomass concentration at which the test was conducted, but they did not offer an explanation. Chynoweth et al. (1993) also demonstrated that an M:F ratio of 2 gives maximum organic conversion rates compared to 1.5 and 0.92 with waste feedstocks. While no explanation was given we postulate that a higher inoculum concentration results in a higher inventory of enzymes available to metabolize difficult to degrade and/or mildly inhibitory compounds.

Figure 4.5 shows the effect of M:F ratio on CBP for the free liquid fraction, too. Results indicate that the refractory or mildly inhibitory materials in the pretreated M-OFMSW samples were associated for the most part with the suspended solid phase. There was no increase in CBP with increased M:F ratio. This observation is in agreement with results reported in Figures 1c and 1d. With free liquid assays was found that the inoculum size had little impact on the substrate specific CBP. This whole sample versus free liquid BMP inoculum assay indicates that the mildly inhibitory or recalcitrant materials are associated with the suspended phase and that the associated degradation of these materials can be increased by increasing the size of the microbial consortia treating the waste. When Toreci (2008) performed BMP toxicity assays for different concentrations with high temperature pretreated TWAS with unacclimated inoculum, a lag phase was observed and saw an improvement in biogas production only after 20 days of AD. They contended that a longer time was required for acclimation. Based on this study, it is also possible that the inhibition have been overcome by increasing the inoculum size. However, this was not considered or tested.



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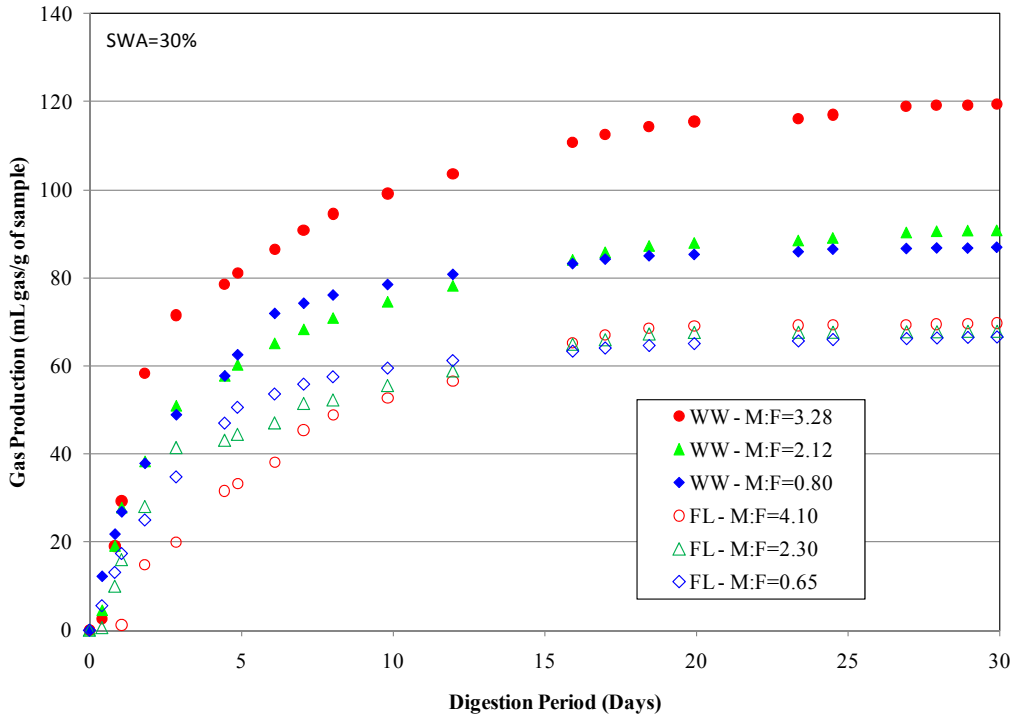


(b)

Figure 4.5: CBPs for different M:F ratios (175 ºC), (a) SWA20 and (b) SWA30

4.6. Kinetics for Anaerobic Biodegradation

AD kinetics of BMP assays were evaluated using mass balance of COD coupled with a first order model, which is widely accepted for complex wastes. In the study of Baccay and Hashimoto (1984) on fermentation of causticized straw, rates of acidogenesis and methanogenesis were determined using first order kinetics. In Anaerobic Digestion Model No.1 (ADM1) a first order model has been adopted to describe hydrolysis (IWA 2002). Angelidaki et al. (2009) also suggested using a first order model for estimating rate constant for batch assays of solid organic wastes.

The basic first order model yields a single kinetic constant that can be used when dealing with complex systems, like that involved in the fermentation of refuse. The basic equation is

$$r_s = dS/dt = -kS \tag{4.2}$$

where S is the substrate concentration (mg/L), k is the first order AD rate constant (day^{-1}) and r_s is substrate utilization rate (mg/L.day). For a batch process such as the BMP assay it is integrated between $t = t_0$ and $t = t$

$$S = S_0.e^{-k(t-t_0)} \tag{4.3}$$

In which S_0 is the substrate concentration (mg/L) at $t = t_0$ that is at the end of any lag phase and the rate of substrate utilization is directly proportional to its concentration. This model cannot differentiate between different degradation mechanisms of bacteria, but it reflects the overall combined effect.

Chowdhury and Fulford (1992) used a similar first order model to predict gas production for batch and semi continuous AD of cattle-dung. Their approach was used in this study with M-OFMSW and assumes that the CBP (G') is proportional to the concentration of feedstock consumed by microorganisms:

$$G' = C.f.V(S_0 - S) \tag{4.4}$$

where C is the biogas yield constant (volume of biogas or methane produced per unit mass of digestible feed stock degraded L/g), f is the digestible fraction in the total mass of feed stock and V is the working volume of reactor (L).

Substituting S from Eqn.4.3 into the above equation and assuming $t_0 = 0$ yields;

$$G' = C.f.VS_0\left[1 - e^{-kt}\right] \tag{4.5}$$

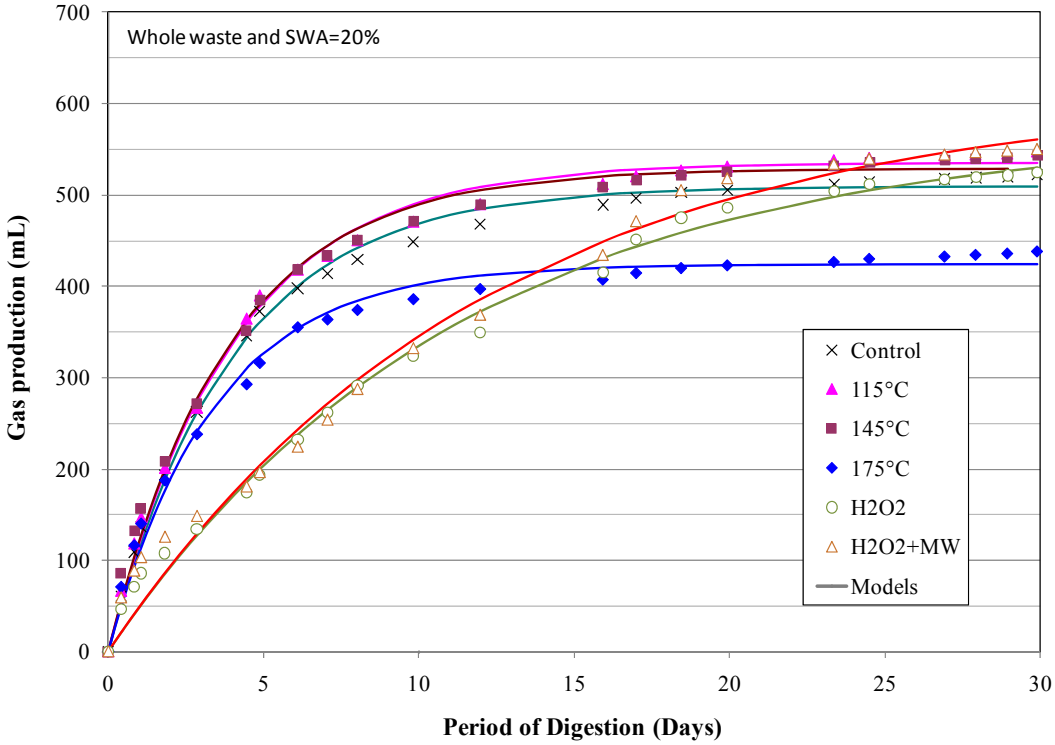
The digestible fraction of feed stock is not easy to measure, assuming all VS is degradable the ratio of VS/ TS was assumed to be the digestible fraction of M-OFMSW.

The criterion $\chi^2 = \sum_{i=1}^{n}\left[\left(y_i - \hat{y}_i\right)/\sigma\right]^2$ was used as the primary discriminator to evaluate the adequacy of fit (Table 4.9); parameters in the model were adjusted to achieve the minimum χ^2 value. The coefficient of determination, $R^2 = 1 - \sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2 \Big/ \sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2$, was also used ($\bar{y}$ is mean of observed values, y_i is measured value, $\hat{y}_i$ is the predicted value and, σ is the standard deviation of measured values), along with plots of predicted versus measured data, in making the final judgment of goodness of fit (Table 4.9).

Table 4.9: Predicted and measured values for first order model

		Whole Waste					Free Liquid				
Sample	SWA	K	C(L/g)	C*(L/g)	R^2	χ^2	K	C(L/g)	C*(L/g)	R^2	χ^2
Control	20%	0.252	0.534	0.520	0.996	0.083	0.280	0.584	0.577	0.990	0.229
115ºC		0.251	0.535	0.520	0.996	0.096	0.289	0.551	0.535	0.996	0.082
145ºC		0.261	0.461	0.449	0.992	0.166	0.262	0.574	0.546	0.993	0.149
175ºC		0.294	0.544	0.535	0.991	0.203	0.282	0.539	0.514	0.998	0.226
H_2O_2		0.088	0.531	0.463	0.993	0.155	0.082	0.614	0.521	0.987	0.281
H_2O_2+MW		0.083	0.548	0.493	0.986	0.316	0.074	0.660	0.545	0.987	0.293
Control	30%	0.258	0.541	0.526	0.997	0.066	0.249	0.714	0.699	0.990	0.212
115ºC		0.285	0.601	0.591	0.989	0.253	0.298	0.557	0.546	0.994	0.132
145ºC		0.282	0.545	0.532	0.993	0.159	0.285	0.546	0.521	0.994	0.135
175ºC		0.306	0.543	0.534	0.987	0.283	0.282	0.570	0.549	0.993	0.151
H_2O_2		0.075	0.637	0.530	0.99	0.228	0.081	0.565	0.476	0.986	0.305
H_2O_2+MW		0.085	0.531	0.453	0.987	0.285	0.082	0.394	0.334	0.983	0.382

C* Measured



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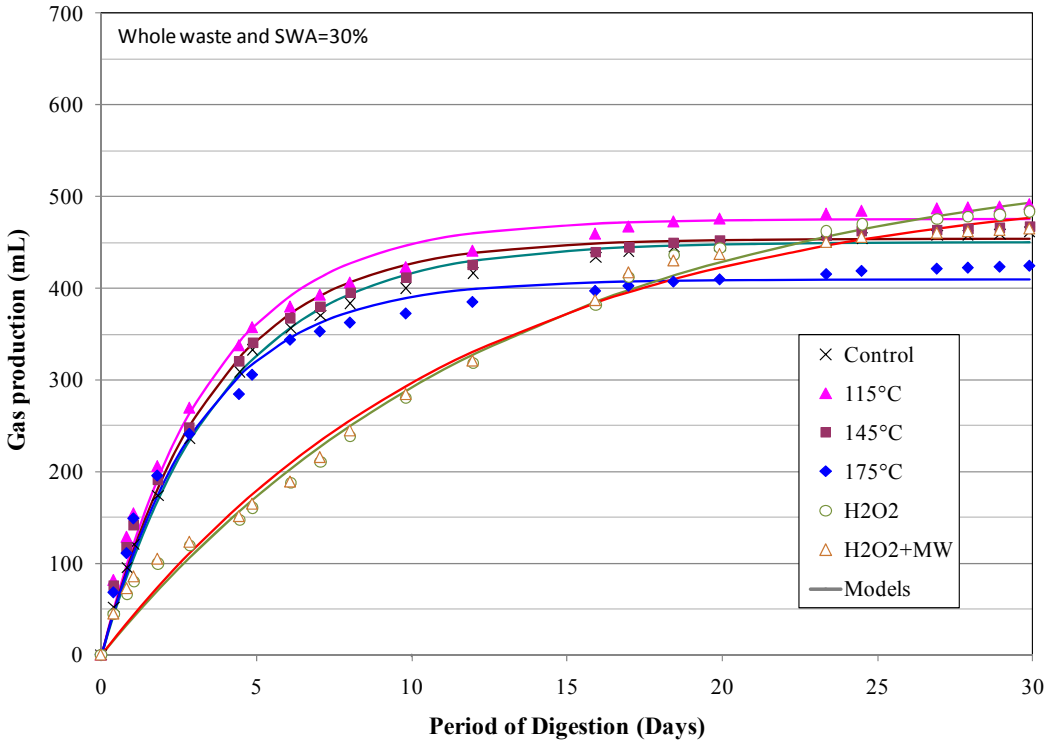
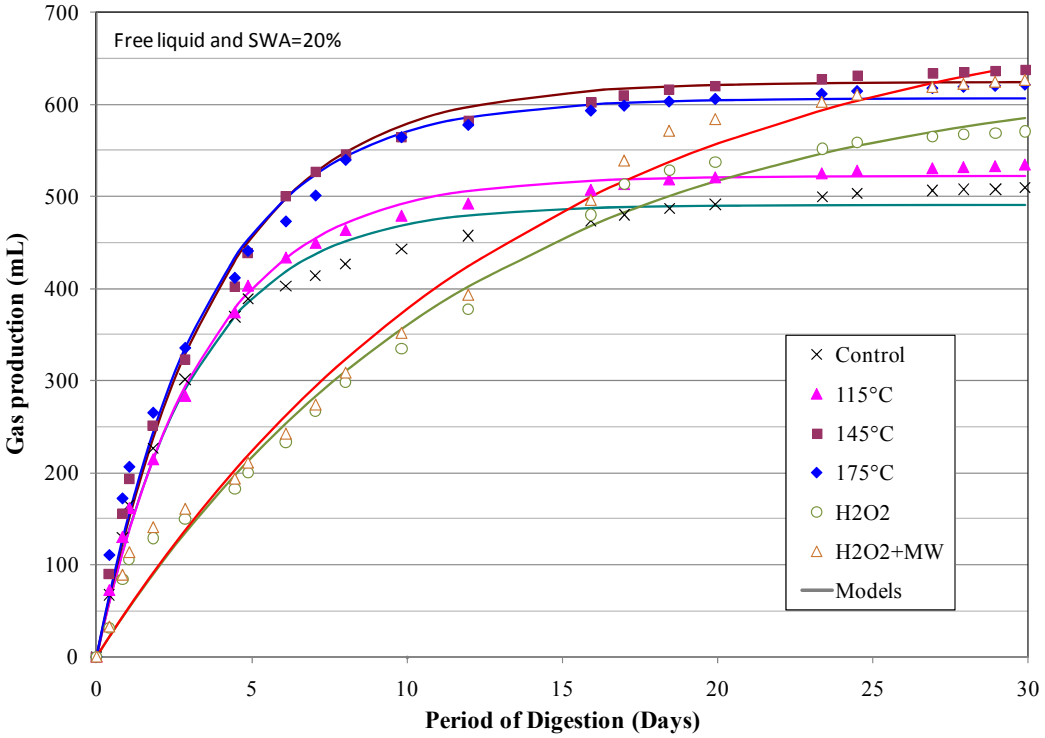


(b)

Figure 4.6: Model of CBPs for whole waste, (a) SWA20 and (b) SWA30



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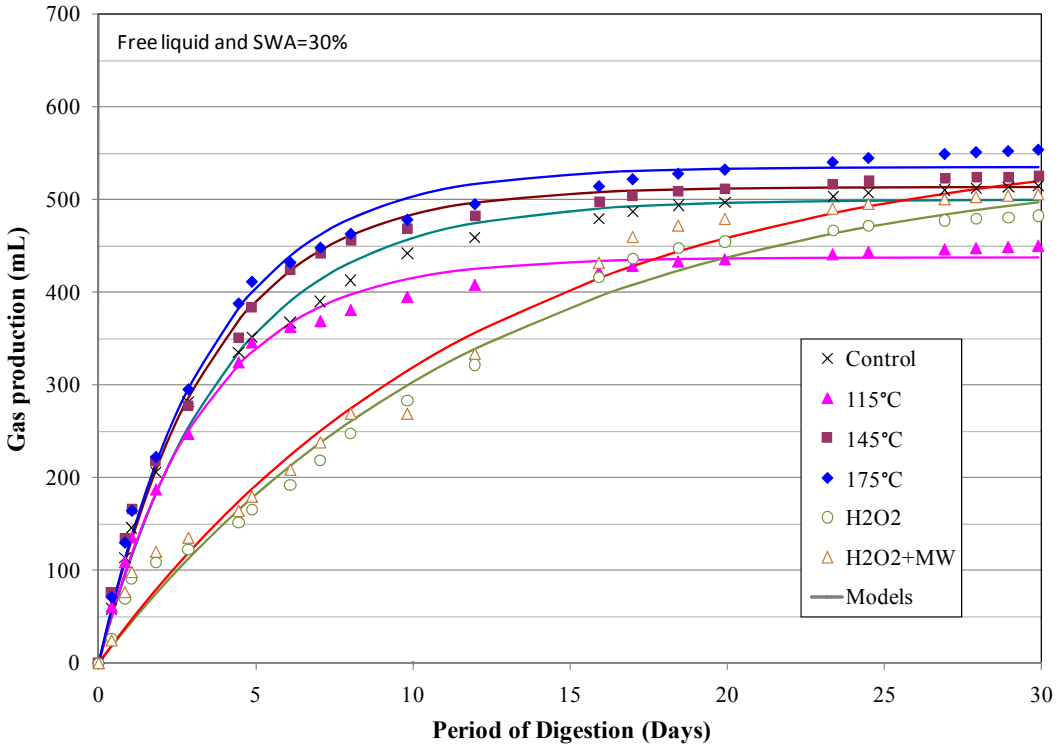

(b)

Figure 4.7: Model of CBPs for free liquid fraction, (a) SWA20 and (b) SWA30

Microsoft Excel solver was used to estimate *k* and *C (model calc)* values as well as experimental *C** for controls and different MW pretreated sample conditions of whole waste and free liquid. Values for *C* and *k* presented in Table 4.9 are estimated from the average of duplicate samples. Visual comparison between model and experimental data (Figure 4.6 and Figure 4.7) as well as χ^2 and R^2 indicate that the kinetics of gas production was satisfactory fitted with the first order model. The fit was more accurate for samples without H_2O_2 pretreatment.

The first order model was used twice. One time S_0 was assumed equal to the total initial COD and another time refractory COD (residual COD in the bottle at conclusion of BMP assay) was accounted, by subtraction from total initial COD and it was considered as the S_0. After comparing the *C* values calculated by the model based on lab results, it was found that by accounting for the refractory compound more accurate fit was obtained for *C* values. The results reported in Table 4.9 have been calculated by accounting for the residual refractory COD.

Estimated *k* values are close to the typical values for organic waste. Liebetrau et al. (2004) reported a *k* value of 0.34 day^{-1} for kitchen waste which was close to *k* value of 0.55 day^{-1} for food waste reported by Vavilin and Angelidaki. (2005). Comparing *k* values of whole M-OFMSW waste and free liquid before and after MW pretreatment under different conditions give similar results and were in the range of 0.25-0.30 day^{-1} for SWA20 and SWA30 with MW treatment only. A noticeable decrease in *k* values with H_2O_2 only or dual modality pretreatment was observed and was in the range of 0.075-0.09 day^{-1}. These *k* values for H_2O_2 and H_2O_2/MW-85 ºC are almost one third of the control and MW pretreated samples and show similar trends for both whole M-OFMSW waste and free liquid.

Lin et al. (1999) used NaOH chemically pretreatment of WAS prior to MAD and observed an increase in *k* for pretreated WAS which they stated was due to higher SCOD/TCOD ratios compared to controls. It is in contradiction with Eskicioglu et al. (2006) who found *k* values of WAS were the highest for controls followed by MW pretreated samples of at 96 ºC and conventional heating at 96 ºC. The first order model is good for describing of the amount and trend of gas production for MW pretreated samples, but does not fit the data as

well for samples pretreated with H_2O_2 or dual modalities, especially of the initial temporal portion of the BMP test when it is believed that residual H_2O_2 is inhibiting methanogenesis. By visually examination of (Figure 4.6 and Figure 4.7) one can conclude that MW pretreatment (without H_2O_2) does not significantly improve the degradation rate of whole M-OFMSW samples compared to controls. However, comparison of slopes for the first five days for free liquid shows that the biogas production rates increases with MW pretreatment. It can be concluded that MW pretreatment should decrease digestion time for free liquid in a continuous system since a large fraction of the potential biogas production should be produced at shorter HRTs. Based on results 145 ºC is a good condition for MW pretreatment of the M-OFMSW prior to whole waste or free liquid AD.

4.7. Conclusion

The results of this experiment showed that in general, the whole fraction of M-OFMSW SWA20 pretreated at 115 °C or 145 °C gave the best CBP results, when compared to controls and other whole samples. On the other hand, pretreatment to 145 °C and 175 °C were the best when considering only the free liquid fraction released from the whole M-OFMSW and the biogas potential of this fraction. Based on comparison to controls, SWA20 was more desirable than SWA30, especially when considering methane production rates and potential for the free liquid fraction of the M-OFMSW. Considering the increased availability of the free liquid fraction after MW pretreatment, a 78% improvement of the biogas production was achieved at 145 °C and SWA20 vs. controls. H_2O_2 pretreated samples generally had a respectable ultimate biogas production, but they took longer to reach this efficiency. They require on average 5 to 10 more days compared to controls or MW only pretreated samples.

More studies are necessary to evaluate the effect of MW pretreatment on enhancement of AD under more realistic conditions.

CHAPTER 5

Evaluation of Single versus Staged Mesophilic Anaerobic Digestion of Organic Fraction of Municipal Solid Waste with and without Microwave Pretreatment

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5.1. Abstract

The effects of microwave (MW) pretreatment on anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) in single and dual stage semi-continuous mesophilic digesters at hydraulic retention times (HRTs) of 20, 15, 12 and 9 days were investigated. Also the feasibility of digesting only the free liquid fraction of the OFMSW thermally liquidized by MW pretreatment was studied. MW pretreatment did not enhance the AD of the whole OFMSW; the dual stage AD system fed with untreated whole OFMSW had the best biogas production and stabilization efficiencies at the shortest HRT of 9 days. Conversely, for the free liquid resulting from MW pretreatment the two stage reactor at 20 day HRT produced triple the methane production compared with the untreated control free liquid. In most cases when the organic loading rate (OLR) was increased, the performance of the systems decreased, in terms of biogas yield, soluble chemical oxygen demand (SCOD), total COD (TCOD) and volatile solids (VS) removal. In general dual stage digesters out performed single stage reactors in terms of waste stabilization at shorter

HRT. Additionally, staging was a more important factor than MW pretreatment in increasing the rate of AD of OFMSW.

Keywords: Anaerobic digestion; Microwave pretreatment; Organic waste; Biogas production

5.2. Introduction

Solid waste management (SWM) has become a major issue in the last decade due to both environmental and economical concerns. Landfilling is still the main approach for solid waste disposal, and about 50% of the waste generated goes directly to landfill in the US. In 2009, only 2.5% of food scraps was recovered while the remaining was landfilled (USEPA 2009). The organic fraction of municipal solid waste (OFMSW) is a highly biodegradable moisture rich residual that is a potential source of environmental contamination, due to the fugitive green house gas (GHG) emissions and leachate generation within a landfill environment.

Biological processes such as anaerobic digestion (AD) offer sustainable methods to address the problems that may be caused by disposal of OFMSW in landfills and has great potential for controlled biogas and energy production. Life Cycle Assessment (LCA) of different waste disposal strategies by Cherubini et al. (2009) including landfilling, AD and waste incineration showed that landfilling is the least favourable option while AD was likely the best option for SWM. Comparing different studies related to composting and AD of OFMSW, Mata-Alvarez (2003) concluded that AD will gain more attention in the future for ecological reasons in particularly less fugitive GHG emissions and stabilized organic matter residue. Moreover, AD does not consume oxygen, has lower nutrient requirements and it generates methane gas that can be used as a source of energy. The rate limiting step in AD of solid wastes is the hydrolysis of particulate substrates (Eastman and Ferguson 1981). To accelerate hydrolysis and consequently the entire AD process, solid waste could be pretreated prior to AD, to potentially increase the biogas yield as well as reduce the reaction time and volume of residual solids for final disposal.

Several pretreatment techniques studied in the past (e.g. thermal, chemical, and mechanical) have been shown to effectively enhance AD. Microwave (MW) pretreatment is a novel technology that looks promising. Compared to conventional heating it is attractive due to its environmental and energy conservation properties (Decareau 1985; Kingston and Jassie 1988), since it eliminates heat losses that occur in energy transmission during normal heating. In microwave heating, direct vibration and rotation of dielectric molecules is possible so localized super heating maximizes heat transfer. Also the existence of the MW athermal effect on enhanced digestion of waste activated sludge (WAS) has been demonstrated by Coelho et al. (2011) and Eskicioglu et al. (2007c). So far, publications regarding the effect of MW pretreatment on waste solubilisation for enhancing AD have focused on WAS (Hong et al. 2006; Eskicioglu et al. 2008a).

Park et al. (2004) also reported that MW irradiation of WAS to 91ºC increased the ratio of soluble chemical oxygen demand (SCOD) to Total COD (TCOD) from 2% to 22% after microwaving. Mesophilic AD (MAD) of the control and MW pretreated sludge was reported for hydraulic retention times (HRTs) of 8, 10, 12 and 15 days. For an HRT of 10 days 43% higher COD removal and 37% higher methane production was reported with pretreated sludge. Additionally MW pretreated sludge could be successfully digested at an HRT of 8 days demonstrating high biogas production and volatile solids (VS) removal while the control reactor failed. Moreover the volatile fatty acid (VFA) concentration in the effluent from the 8 day HRT reactor was very low indicating that a healthy acetoclastic methanogenic consortia was present in the digester.

Eskicioglu et al. (2007a) performed similar comparative studies using thickened waste activated sludge (TWAS). TWAS characteristics and subsequent enhanced MAD were compared for MW and conventional heating (CH) at two final temperatures (50 and 96 ºC) and 3 HRTs (5, 10 and 20 days). The SCOD/TCOD ratio of TWAS pretreated to 96 ºC increased from 7% (control) to 15% and 20% for MW and CH pretreatments. Maximum improvements in biogas production and VS removal were observed for 96 ºC when the HRT was reduced to 5 days. MW and CH achieved 23 and 26% higher VS removal respectively compared to the control. Similar results for biogas production were achieved, 30 and 35% increases in biogas production over the control for MW and CH.

It has been reported by Mata-Alvarez et al. (1992) that problems will arise in one-step reactors digesting OFMSW that is readily degradable. The accumulation of VFA in a single reactor can cause imbalances between the methanogenic and acidogenic populations that can result in reduced methane production, thereby reducing the overall efficiency of the reactor. A two-stage acidogenic/methanogenic system may be a solution to overcome the microbial consortia imbalance discussed by different researchers. Mohan and Bindhu (2008) studied the AD of kitchen waste with single-phase and two-phase mesophilic digestion systems. The two-phase AD system was reported to perform well at an organic loading rate (OLR) of 8.0 kg VS/m^3.day and total HRT of 10 days, while the single phase AD process failed at an OLR of 4.5 kg VS/m^3.day and HRT of 15 days. Overall performance of the two stage system was also better than the single reactor. When compared at an HRT of 15 days the two stage AD reactor system had VS and COD removal efficiencies 94% and 92% vs. 79% and 81% for the one stage digester, respectively.

Coelho et al. (2011) investigated the effects of MW pretreatment to 96 ºC on AD of TWAS in one and two stages reactor under both thermophilic and mesophilic conditions at four HRTs (5, 10, 15, 20 days). The SCOD /TCOD ratio of the TWAS increased from 6% to 20% after MW pretreatment. In two steps AD reactors, with both stages operating under thermophilic condition and overall SRT of 5 days, a 106% enhancement in biogas production was observed compared to the one stage mesophilic control reactor (no MW pretreatment). The single stage mesophilic and thermophilic reactors that were fed with pretreated sludge had 44 and 83% higher biogas production compared to control at HRT of 20 days. In this study the MW pretreatment efficiency was reported to decrease with shortening HRTs for one stage reactors, but efficiency was maintained or increased for two stage reactors.

Toreci et al. (2009) performed similar MW pretreatment tests on TWAS but used a higher temperature of 175 ºC. Performance of single and dual stage mesophilic reactors with pretreatment were compared to a single stage control digesting untreated sludge. Pretreatment almost doubled the ratio of SCOD to TCOD compared with the control. Single stage reactors had similar performance with two stage digesters at HRT of 20 days,

indicating that given sufficient reaction time pretreatment did not increase the biogas yield or VS removal. However, when the HRT was shortened, reactors that were fed with pretreated sludge started to produce more biogas and have higher VS removcal efficiencies. The enhancements in biogas production and VS removal were more pronounced for the dual stage reactor system treating non pretreated TWAS and the single stage reactor fed with MW pretreated feed. Under the best conditions, biogas production was 83% higher than the control at an HRT of 5 days in the single stage reactor. It was reported that high MW temperature pretreatment produced compounds that may have been inhibitory or more recalcitrant. In this research, dual stage reactors did not show enhancement in AD when digesting high temperature pretreated TWAS compared to single stage reactors. Observations of Raynal et al. (1998), Schober et al. (1999), Pavan et al. (2000a), Bouallagui et al. (2004), Wang et al. (2005) and Liu et al. (2008) confirm that the two-stage anaerobic process for complex wastes is potentially superior to a one-stage process. Most of these studies used strictly anaerobic conditions and WAS without pretreatment. However, biological hydrolysis of solids can be conducted under aerobic as well as anaerobic conditions. Botheju (2009) observed that hydrolysis rates were higher under aerobic conditions and attributed this to higher enzyme production rates using oxygen as the final electon acceptor. Similarly Johansen and Bakke (2006) also reported that addition of very small amounts of air (microaeration) in to an acidogenic reactor can enhance the hydrolysis rate.

MW pretreatment studies of OFMSW in continuous reactors have not yet been addressed. It is hypothesized that combining MW pretreatment with 2 stage AD will enhance the rate and extent of M-OFMSW stabilization. Semi-continuous digestion tests will be carried out to obtain a better understanding of the effect of MW pretreatment of OFMSW on the performance of single and dual stage AD reactors. Additionally the study will evaluate the effect of MW pretreatment on the solubilisation of OFMSW and the digestion of the free liquid portion only as an alternative to digestion of the whole OFMSW mixture. The secondary objective is to further increase the rate of hydrolysis and acidification by bioaugmentation with WAS and microaerophilic conditions in the first reactor in dual stage digesters.

5.3. Methods

5.3.1. Organic waste and Microwave

Model-OFMSW (M-OFMSW) simulating kitchen waste was used. Components of M-OFMSW were cooked rice (18 wt %), cooked pasta (18 wt %), cabbage (11 wt %), carrot (11 wt %), apple (11 wt %), banana (11 wt %), cooked ground beef (10 wt %), wet dog food (10 wt %). Supplemental water addition of 20% (SWA20) was used (Shahriari et al. 2011a).

A MW Accelerated Reaction System (Mars 5®, CEM Corporation, 0-1200 Watts and 2450 MHz frequency) was used to irradiate the M-OFMSW. The Mars 5 controls and monitors the power, temperature, and pressure within each reaction vessel up to 250 ºC and 3.45 MPa. MW intensity was controlled by adjusting the temperature ramp time to achieve the set temperature (145 ^{o}C with a ramp of 2.7 ^{o}C/min).

5.3.2. Acidogenic Fermentation

One of the goals of this research was to increase the rate of hydrolysis and acidification in a two step reactor process by bioaugmentation with TWAS using either an anaerobic or microaerophilic acidification stage. For this purpose initial acidification batch experiments (duplicate) were performed in 0. 25/0.50 L serum bottles (0.15/0.40 L working volume) at 35 ºC using a New Brunswick orbital shaker (100rpm). Serum bottles contained 22.5% (v/v) acclimatized inoculum, diluted M-OFMSW with or without pretreatment and varying amounts of TWAS. Original inoculum was obtained from a mesophilic anaerobic digester at ROPEC municipal wastewater treatment plant (Gloucester, ON, Canada), which treats combined primary and secondary sludge (5 day SRT). Inoculum was acclimatized to MW pretreatment over a period of 1.5 years in an mesophilic complete mixed digester, using M-OFMSW pretreated to 145 ºC with a ramp of 2.7 ^{o}C/min operated at a HRT of 33-40 days. TWAS was supplemented in the serum bottles at 0, 15, and 30% based on VS (w/w) without any additional buffer and the F/M ratio was in the same range as previously reported by Shahriari et al. (2011a). For microaerophilic acidification, oxygen

concentrations were maintained between 0.5-1 mg/L by bubbling air at 0.008 vvm at 35 ºC through the serum bottles. All assays were monitored daily for VFA accumulation, pH and biogas (where applicable).

5.3.3. Semi- Continuous Reactors

A total of 12 mesophilic single and dual stage reactors (Figure 5.1) were used to evaluate the effects of MW pretreatment, staging and HRT on the stabilization of the whole M-OFMSW waste (6 reactors) and free liquid extracted from whole M-OFMSW (6 reactors).

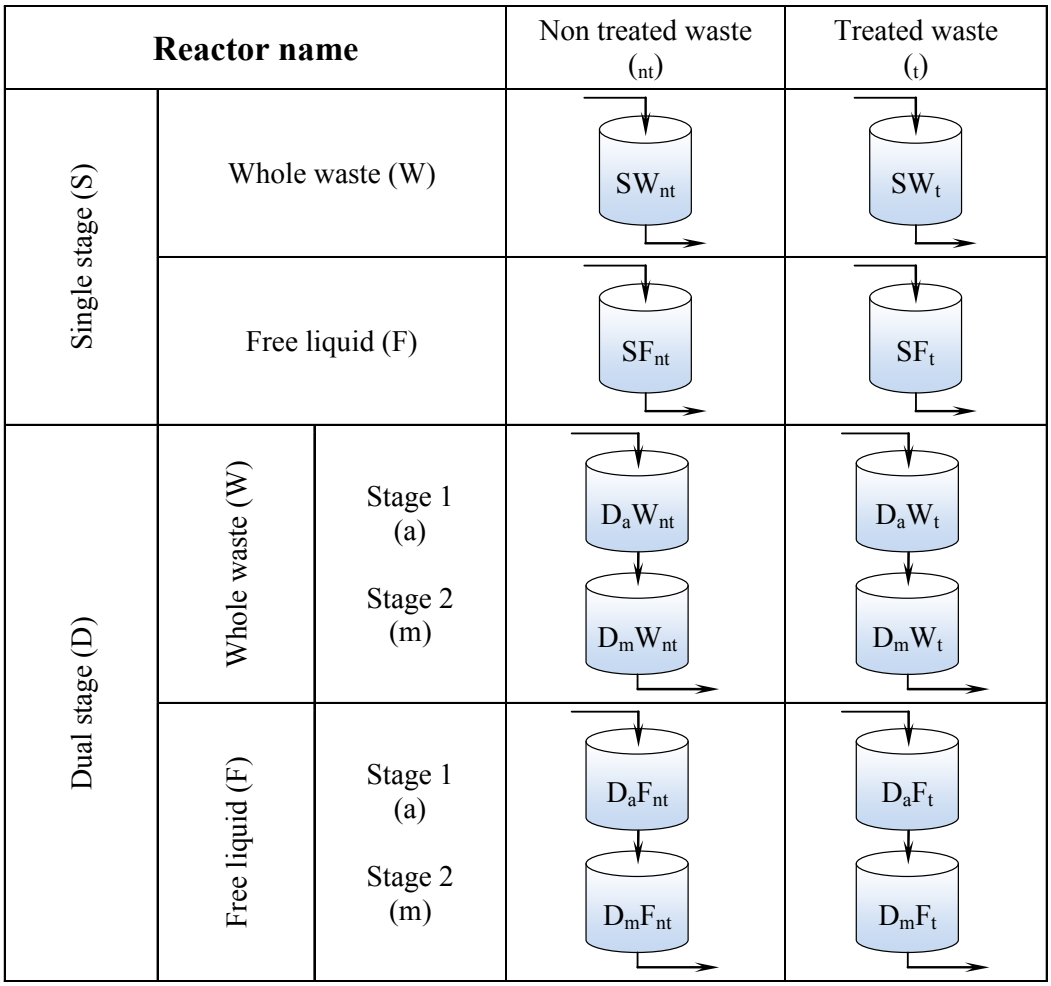


Figure 5.1: Semi-continuous reactors

The liquid fraction of M-OFMSW was evaluated to determine the feasibility of MAD of supernatant only. Free liquid was obtained by centrifuging whole M-OFMSW at 9725 RCF for 45 min followed by decantation of the liquid phase. Each group of 6 reactors was evaluated at HRTs of 20, 15, 12 and 9 days. Acidogenic reactors were operated at a fixed HRT of 2 days hence a 20 day HRT for a two stage system was 2 days/18 days for acidogenic (a) and methanogenic (m) phases respectively. HRT of 2 days for the first stage was based on the findings of the acidogenic fermentation assay described above.

Semi-continuous studies were performed using 0.5 L and 1.0 L Kimax bottles (0.4/0.6 L working volume) for acid and methane phases respectively and sealed with butyl rubber stoppers. Ports in the rubber stoppers with glass tubes were used to collect biogas and withdraw/add substrate once per day. Tedlar bags (Chromatographic Specialties Inc., ON, Canada) were used to collect biogas which was then released and measured using a manometer. A combination (50:50 V/V) of biomass from ROPEC (Shahriari et al. 2011a) and granular biomass from Lake Utopia Paper (a chemical thermal pulp treatment plant located in St. George New Brunswick, Canada) was used as inoculum.

This latter biomass was used previously in anaerobic baffled reactors to treat aircraft de-icing fluid (Kennedy and Barriault 2005). The properties of the granular biomass are listed in Table 5.1. The reactors were kept on a shaker at 35±1 ºC and 90 rpm (PhycroTherm, New Brunswick Scientific Co. Inc., NB) and were started at an HRT of 20 days (2 days/18 days for the two-stage reactors) and were operated until they reached steady state (SS). Fluctuations of less than 10% in daily biogas production and completion of 2-3 HRTs was considered as SS. Reduction of HRT and concomitant increase in volumetric OLRs were done slowly over a period of approximately 1 week in order to allow the microbial consortia to adapt to new conditions. Performance of semi-continuous reactors was assessed by monitoring pH, VFA, alkalinity, total solids (TS), VS, TCOD, SCOD and ammonia-N. Standard methods (APHA 1995) and techniques given in Shahriari et al. (2011c) were used for all analysis.

Table 5.1: Properties of granular biomass

Parameter	Unit	Quantity
TCOD	mg/L	29.01±0.38
SCOD	mg/L	0.84±0.00
TS	%	20.75±0.09
VS	%	16.01±0.19
Alkalinity	mg $CaCO_3$/L	2108±12
Ammonia	(NH_3-N)mg/L	212±10
pH	-	8.27
TVFA	mg/L	50±2

5.4. Results

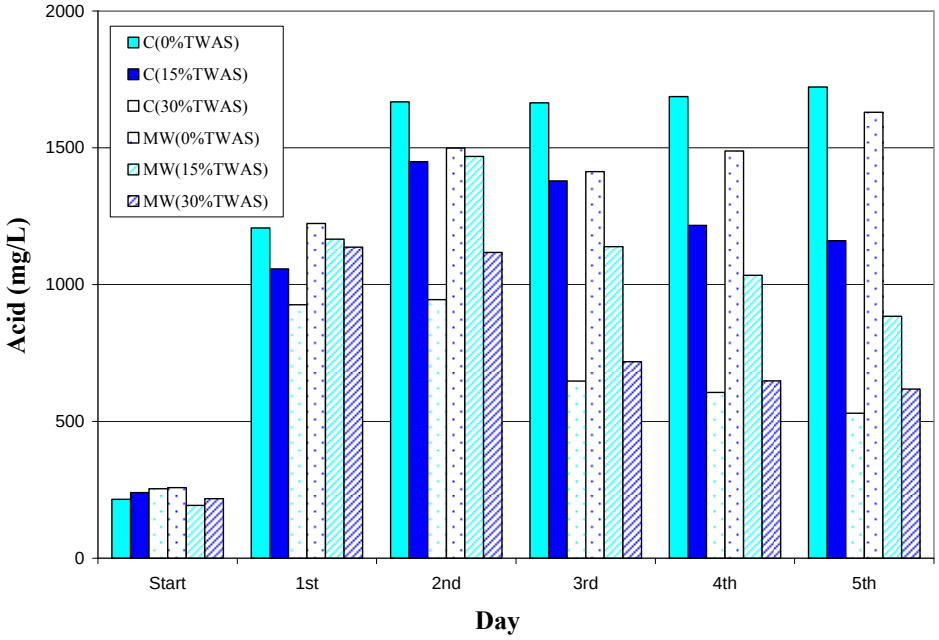
5.4.1. Acidogenic Fermentation

Acidification was evaluated based on VFA accumulation (acetic, AA, propionic, PA and butyric acids, BA) over a period of 6 days. Average daily VFA accumulations as a measure of acidification are shown in Figure 5.2a and b for anaerobic and microaerophilic conditions, respectively.

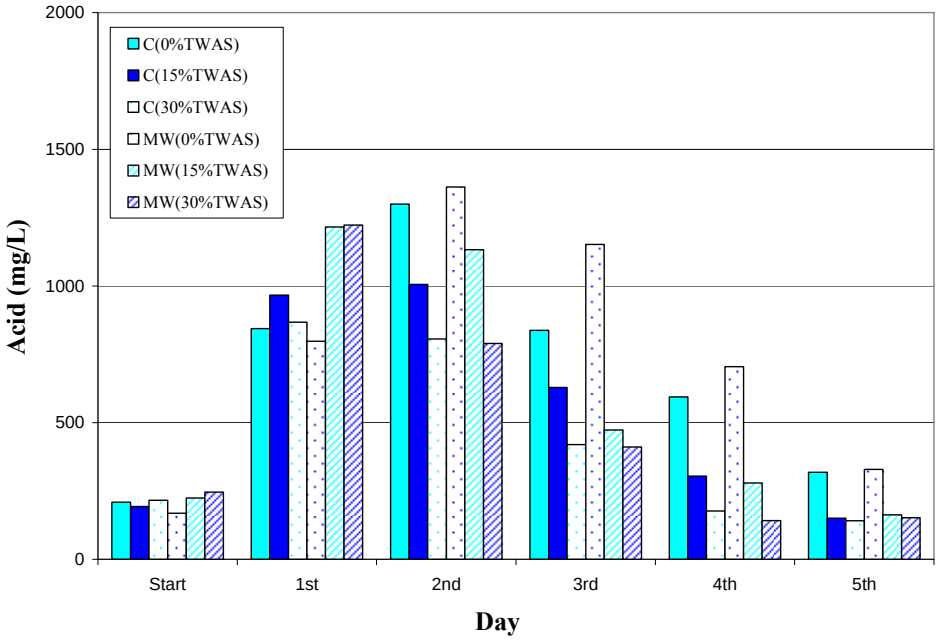
For both anaerobic and microaerophilic acidification maximum VFA accumulation occurred after approximately 2 days and were 1700 and 1300 mg/L, respectively while the pH in the bottles decreased from 7.0 to about 6.0. No attempt to control/lower the pH was used in this evaluation of acidification. The pH values were slightly higher than desired for acidification especially with the assays supplemented with TWAS and this may be attributed to the higher alkalinity associated with the TWAS as well as microbial consumption of the VFAs. Additionally, pH values in the microaerophilic reactors were likely higher (6.1-7.1) due to the bicarbonate buffering capacity caused by the formation of carbon dioxide during aerobic metabolism of substrate by facultative bacteria. Anaerobic acidification both had the highest VFA accumulation as well as the lowest pH values (6.0).

Jagadabhi et al. (2010) applied microaerophilic acidification for grass-silage at a micro-aeration rate of 0.0023 vvm and reported a 4 fold increase in VFAs production (2200 to 9300 mg/L) without any significant increase in cumulative SCOD in the effluent. VFA concentrations tended to decrease if microaeration was increased. Decreased VFA

concentrations with increased microaerophilic condition were attributed to an increased rate of aerobic metabolism by facultative microbes.



(a)



(b)

Figure 5.2: VFA accumulation under (a) anaerobic (b) microaerophilic condition

In the present study under microaerophilic conditions VFAs were consumed in days 3-6 (consumption exsided VFA production) and were less than 400 mg/L by day 6. In terms of TWAS addition the greater the percentage of TWAS the greater the consumption of VFAs. Additionally, microwaving of the M-OFMSW had negligible impact on acidification when compared to the controls. It would seem the combination of microaerophilic conditions and additional TWAS actually had a negative effect on acidification.

Anaerobic acidification in terms of acid accumulation was superior compared to microaerophilic acidification and produced VFAs concentration 6.8 times higher compared to initial controls. Unlike the microaerophilic conditions VFAs that accumulated were generally not consumed after day 2 and remained high till the end of the assay (day 6). It was noted that when TWAS was added there was some decrease in the concentration of accumulated VFAs from day 3-6 but not to the same extend as under microaerophilic conditions. When MW pretreatment was applied the VFA accumulation was high but slightly less (Day 2, 1499 mg/L) than without MW pretreatment and without TWAS addition. VFA accumulation coincided with maximum COD solubilisation (SCOD) which was also observed after two days for anaerobic acidification (without TWAS supplementation and MW pretreatment) which increased by 31% from 2.0 g/L to 2.6 g/L. It should be kept in mind that in this batch acidification assay both acidification and metabolism can occur simultaneously and that the increased accumulation of VFAs (and/or SCOD) is a strong indicator of the potential improvements that are possible in acidification. In comparison to a previous study (Shahriari et al. 2011a) with the same conditions but with buffered media (pH= 7.0-8.0) cumulative biogas production (CBPs) after 5 days in this study was less than 30% of the biogas produced in their study, indicating that some waste stabilization was still occurring during the assay, but at a slower rate. It had been hoped that pH adjustment could be avoided, as it has been reported that pH during acidogenesis can decrease towards a pH value in the range of 5–6.5 (Wu-Haan et al. ; Guerrero et al. 1999; Jagadabhi et al. 2010) depending on the nature of the substrate and organic load. Unfortunately, for the specific waste being evaluated this was not the case. This result indicates that in future acidification tests lower pH conditions may be established to increase acidification and inhibit methanogenesis.

The fact that greater VFA accumulation occurred under anaerobic conditions is favourable for two stages AD, since the mixed liquor/effluent has a low oxidation reduction potential (ORP) and VFAs can be transferred directly to the methanogenic stage. Based on the evaluation of acidification of the specific waste to be treated (M-OFMSW with and without MW pretreatment) it was decided that for 2 stage digestion anaerobic acidification at an HRT of 2 days with initial pH adjustment to 5.0-6.0 would be used.

5.4.2. AD of Microwaved M-OFMSW

Shahriari et al. (2011c) have previously demonstrated that MW pretreatment increases solubilisation of M-OFMSW, which resulted in enhanced biogas production based on batch mesophilic BMP assays (Shahriari et al. 2011a). This study evaluates the effects of pretreatment, reactor staging and HRT on semi-continious waste stabilization and biogas production from whole M-OFMSW and free liquid extract from M-OFMSW. Over the duration of this study small changes in the characteristics of the SCOD/TCOD ratio of M-OFMSW (Table 5.2) were observed.

Table 5.2: Properties of feed at the different HRTs tested

SRT	**20 days**		**15 days**		**12 days**		**9 days**	
Prop.	**Control**	**MW**	**Control**	**MW**	**Control**	**MW**	**Control**	**MW**
Whole Waste								
TS (%)	3.21±0.22	3.33±0.20	3.26±0.27	3.39±0.21	3.09±0.07	3.31±0.10	3.11±0.02	3.42±0.06
VS (%)	3.06±0.21	3.19±0.19	3.12±0.26	3.27±0.21	2.96±0.06	3.18±0.11	2.97±0.03	3.28±0.06
VS/TS	0.95±0.00	0.96±0.00	0.96±0.00	0.96±0.00	0.96±0.00	0.96±0.00	0.96±0.00	0.96±0.00
TCOD (g/L)	39.3±2.3	40.6±2.0	37.5±0.7	40.5±0.7	37.1±1.9	38.8±1.2	38.6±0.4	39.6±0.5
SCOD (g/L)	14.9±0.6	17.1±0.8	14.6±0.1	18.4±1.2	16.2±1.8	19.2±1.1	17.0±0.15	20.3±0.8
SCOD/TCOD	0.38±0.01	0.42±0.00	0.39±0.01	0.45±0.02	0.44±0.03	0.49±0.02	0.44±0.02	0.51±0.01
Liquid Fraction								
TS (%)	2.38±0.12	3.32±0.04	2.52±0.16	3.24±0.16	2.43±0.06	3.08±0.02	2.23±0.23	3.04±0.18
VS (%)	2.20±0.12	3.13±0.04	2.34±0.16	3.06±0.15	2.23±0.10	2.89±0.01	2.01±0.20	2.87±0.17
VS/TS	0.93±0.00	0.94±0.00	0.93±0.01	0.94±0.00	0.92±0.02	0.94±0.00	0.90±0.00	0.94±0.00
TCOD (g/L)	27.5±0.7	37.0±2.8	28.1±1.0	36.1±2.0	30.8±0.4	33.3±0.3	26.2±1.2	34.8±0.3
SCOD (g/L)	23.0±1.6	31.5±1.9	25.8±1.3	32.4±1.9	28.7±0.0	32.2±0.3	21.3±2.8	28.2±2.5
SCOD/TCOD	0.84±0.04	0.85±0.01	0.92±0.02	0.90±0.00	0.93±0.01	0.97±0.00	0.81±0.07	0.81±0.08

Small changes were likely related to differences in the nature of the raw materials used for sample preparation. SCOD/TCOD ratios were in the range of 0.38-0.44 and 0.42-0.51 for untreated and after MW pretreatment of M-OFMSW, respectively. Generally, SCOD of the

M-OFMSW after MW pretreatment was approximately 15-26% and 12-37% greater than the controls for whole M-OFMSW and free liquid extract from M-OFMSW, respectively. For all test conditions prior to digestion the whole M-OFMSW and free liquid extract from M-OFMSW had ammonia-N (NH_3-N) below 40mg/L; alkalinity of approximately 300mg $CaCO_3$/L and VFAs of less than 300mg/L.

Semi-continuous tests were conducted in sequence from the longest HRT (20 days) to the minimum HRT of 9 days. This sequence was implemented to maximize acclimation of the anaerobic biomass and minimize risks of reactor instability due to high organic loads. It should be noted that the combined HRT of staged systems was the sum of the HRT of the methanogenic stage and the HRT of acidification reactor which was maintained constant at 2 days for the study. Initially, pH in the acidification stage reactors decreased to approximately 4.0. This was attributed to a combination of semi-continuous operation, high organic load and readily degradable substrate that resulted in accelerated acidification. In order to circumvent the low pH problem buffer was added daily to maintain a pH between 5.0- 6.0 in the acidification stage which is the optimal pH range for acidogenic bacteria (Jash and Ghosh 1996; Raynal et al. 1998). Once adjusted the VFAs in the acidification stage (2 day HRT) were in the range of 6000-14000 mg/L based on the type of feed with an average AA/PA/BA distribution ratio of 25/10/65. Whole M-OFMSW had lower VFA's in the range of 6000-10,000 while for free liquid M-OFMSW concentrations were higher in the 7000-14,000 mg/L range. It was noted that VFA concentrations for MW pretreated samples of M-OFMSW were generally 1000-1500 mg/L greater than samples without MW pretreatment.

Solubilization of M-OFMSW can occur as a result of MW pretreatment or as a result of acidification in a single reactor or in the primary staging reactor. The question to be answered is, does pretreatment increase acidification or is it not required for M-OFMSW if staging is used. Comparison of effluent quality from primary stage acidification reactors indicated that maximum solubilisation occurred in reactor D_aW_{nt} which was fed untreated whole M-OFMSW. With a 2 day HRT the SCOD concentrations of the acid phase reactors with and without pretreatment were fairly similar suggesting that staging had the same impact as MW pretreatment in terms of solubilization. Over the course of the experiment

(145 days) SCOD concentration increases in the acid phase reactor treating non pretreated whole M-OFMSW ranged from 11 to 26% which was comparable to the 15-26% improvement as a result of microwaving of the whole M-OFMSW. This range of solubilizations is not unexpected based on the variation in characteristics of the M-OFMSW over the course of the experiment. It should be emphazised that the combination of MW pretreatment and primary acidification of the M-OFMSW resulted in no further improvement in SCOD concentration although the VFA concentrations were slightly higher in the acid phase reactor with MW pretreatment. This initial finding suggests that MW pretreatment of M-OFMSW does not improve solubilisation when compared to no pretreatment and staging and only a marginal improvement in acidification based on VFA concentrations. It should be noted that this finding is related to M-OFMSW which is readily biodegradable and may or may not apply for real OFMSW which may have a larger component of less readily biodegradable material.

While MW pretreatment did not seem to have a significant positive impact on acidification it is possible that its benefits may be realized during methanogenesis in either the single or dual stage systems. It has been reported that MW pretreatment not only increases solubilisation of TWAS as a whole but the degree of pretreatment can influence the distribution of mass fractions of various sizes for both the soluble and suspended components. Eskcioglu et al. (2006) and Toreci et al. (2010), both noted an increase in the colloidal component of TWAS suspended solids after MW pretreatment that would be generally characterized as suspended solids but would likely be more easily biodegradable than larger suspended solid TWAS components. Similar size distribution results were also reported for soluble fractions some of which showed higher and others lower rates of degradation and that in general had a positive overall effect on TWAS digestion performance. Depending on the degree of MW pretreatment the nature of the soluble and suspended particle distributions can impact the overall AD performance, potentially leading to improved waste stabilization during methanogenesis which is best observed at high organic loading rates and short HRTs. Concomitantly, single and dual stage (phase separated) continuous mesophilic digesters were operated with and without MW

pretreatment at increased loading rates at decreasing HRT of 20, 15, 12 and 9 days to assess the benefits of MW pretreatment and/or reactor configuration. Table 5.3 to

Table 5.6 summarize the steady state (SS) characteristics of the digester effluents at different HRTs when fed with MW pretreated and untreated M-OFMSW. In order to evaluate the effects of pretreatment and reactor staging, results are compared to the single stage mesophilic digesters treating whole M-OFMSW without pretreatment (SW_{nt}) and the free liquid fraction of M-OFMSW without pretreatment (SF_{nt}). It should be noted that approximately 90% of full scale AD plants treating OFMSW in Europe are single stage digester controls (De Baere 2000). Results are compared and discussed in two sections (whole waste and free liquid fraction) to prevent confusion.

Table 5.3: Steady state characterization of reactors at HRT of 20 days

HRT= 20 days		Reactor							
Parameters	Units	SWnt	SWt	DmWnt	DmWt	SFnt	SFt	DmFnt	DmFt
OLR	g VS/L.d	1.53±0.10	1.60±0.09	1.24±0.01	1.31±0.14	1.01±0.10	1.43±0.09	1.01±0.03	1.39±0.00
OLR	g TCOD/L.d	1.96±0.11	2.03±0.10	1.86±0.14	1.90±0.07	1.31±0.06	1.74±0.01	1.45±0.09	1.80±0.04
TCOD removal	%	72.9±2.5	71.3±1.5	90.5±0.2	86.5±0.7	76.4±4.1	74.6±0.8	87.2±1.7	84.4±0.8
	g/L.d	1.43±0.03	1.45±0.10	1.70±0.13	1.67±0.06	0.99±0.10	1.30±0.03	1.28±0.11	1.54±0.06
VS removal	%	74.7±3.8	78.5±3.4	87.3±1.7	83.5±1.7	70.9±4.6	79.3±3.2	80.6±2.6	80.9±4.3
	g/L.d	1.13±0.02	1.25±0.02	1.07±0.02	1.09±0.11	0.72±0.12	1.13±0.02	0.80±0.02	1.09±0.04
Gas production	L/L.d	1.20±0.02	1.22±0.07	1.02±0.04	1.06±0.04	0.78±0.00	1.18±0.02	0.80±0.04	1.07±0.09
Methane production	L CH_4 /L.d	0.53±0.02	0.55±0.03	0.65±0.02	0.69±0.02	0.35±0.00	0.53±0.02	0.52±0.02	0.70±0.07
	L/L .gVS add.d	0.55±0.00	0.55±0.03	1.00±0.00	0.98±0.11	0.55±0.02	0.58±0.02	0.96±0.04	0.98±0.04
	L/L.gVS rem.d	0.78±0.03	0.77±0.02	1.11±0.02	1.15±0.11	0.83±0.17	0.78±0.02	1.17±0.04	1.09±0.06
SCOD removal	%	92.1±5.1	93.6±0.3	97.1±1.3	95.3±1.0	97.5±2.3	98.2±1.9	95.2±0.9	93.1±0.9
Effluent SCOD	g/L	1.20±0.81	1.10±0.11	0.47±0.25	0.77±0.23	0.51±0.42	0.53±0.58	0.71±0.27	1.47±0.37
TVFA	mg/L	649±828	126±110	497±68	485±181	68±45	46±27	882±175	1481±74
Alkalinity	mg $CaCO_3$ / L	5025±530	4925±389	8050±354	8525±35	4650±283	4525±530	8625±389	10000±283
pH	-	8.23±0.16	8.16±0.15	8.38±0.08	8.41±0.17	8.18±0.15	8.22±0.11	8.44±0.15	8.50±0.18
Ammonia	NH_4-N mg/L	508±116	407±92	761±72	518±54	162±42	137±14	425±65	439±43

Table 5.4: Steady state characterization of reactors at HRT of 15 days

HRT= 15 days		Reactor							
Parameters	Units	SWnt	SWt	DmWnt	DmWt	SFnt	SFt	DmFnt	DmFt
OLR	g VS/L.d	2.08±0.18	2.18±0.14	1.66±0.01	1.90±0.02	1.47±0.08	2.09±0.03	1.33±0.20	2.06±0.00
OLR	g TCOD/L.d	2.52±0.02	2.72±0.02	2.80±0.02	2.79±0.03	1.85±0.02	2.53±0.09	1.90±0.03	2.78±0.03
COD removal	%	69.8±2.7	67.0±5.1	80.0±0.0	77.9±2.6	75.2±1.0	67.2±4.4	78.9±1.6	77.4±1.5
	g/L.d	1.75±0.03	1.82±0.10	2.12±0.17	2.00±0.35	1.38±0.05	1.65±0.02	1.44±0.10	2.10±0.06
VS removal	%	69.7±1.3	68.5±1.2	72.0±7.6	78.9±5.0	72.2±7.4	64.2±1.2	70.5±0.77	69.9±3.4
	g/L.d	1.45±0.15	1.50±0.12	1.19±0.13	1.50±0.10	1.07±0.17	1.33±0.00	0.94±0.13	1.44±0.06
Gas production	L/L.d	1.42±0.08	1.42±0.03	1.25±0.13	1.27±0.08	1.12±0.02	1.35±0.08	1.10±0.08	1.29±0.02
Methane production	L CH_4 /L.d	0.63±0.03	0.63±0.02	0.81±0.08	0.83±0.06	0.50±0.02	0.60±0.03	0.71±0.04	0.85±0.02
	L/L .gVS add.d	0.52±0.07	0.48±0.03	0.81±0.10	0.75±0.06	0.58±0.03	0.50±0.00	0.98±0.15	0.77±0.00
	L/L.gVS rem.d	0.73±0.12	0.72±0.07	1.48±0.04	1.17±0.02	0.80±0.13	0.72±0.00	1.52±0.21	1.13±0.06
SCOD removal	%	78.2±0.5	85.5±1.3	84.1±1.7	90.5±2.1	96.5±1.9	86.6±2.2	88.9±3.7	86.8±2.7
Effluent SCOD	g/L	2.99±0.20	2.66±0.07	2.58±0.28	1.60±0.27	0.78±0.37	4.25±0.94	1.70±0.58	2.98±0.46
TVFA	mg/L	2204±36	1740±130	2286±65	1631±166	664±362	2888±375	1683±541	3243±881
Alkalinity	mg $CaCO_3$ / L	7575±530	7381±592	8469±44	8638±230	7188±124	7450±389	6031±2148	10313±513
pH	-	8.12±0.44	8.06±0.28	8.21±0.14	8.30±0.14	8.02±0.41	8.02±0.30	8.33±0.22	8.34±0.25
Ammonia	NH_4-N mg/L	453±47	216±40	437±22	332±61	163±22	46±1	315±64	331±77

Table 5.5: Steady state characterization of reactors at HRT of 12 days

HRT= 12 days		Reactor							
Parameters	Units	SWnt	SWt	DmWnt	DmWt	SFnt	SFt	DmFnt	DmFt
OLR	g VS/L.d	2.46±0.05	2.65±0.09	2.29±0.17	2.34±0.15	1.95±0.14	2.55±0.13	2.19±0.03	2.80±0.21
OLR	g TCOD/L.d	3.09±0.16	3.24±0.10	3.41±0.16	3.40±0.11	2.34±0.08	3.01±0.17	2.76±0.04	3.43±0.09
COD removal	%	59.2±2.7	61.2±3.9	73.7±1.6	67.0±1.5	70.3±3.4	59.4±2.2	63.6±2.2	65.7±1.8
	g/L.d	1.83±0.03	1.98±0.08	2.52±0.16	2.28±0.06	1.63±0.10	1.82±0.12	1.74±0.06	2.24±0.08
VS removal	%	55.5±2.2	61.0±3.5	61.9±3.9	55.1±3.7	57.6±6.5	53.5±4.1	49.0±3.9	53.0±3.4
	g/L.d	1.35±0.07	1.62±0.12	1.42±0.14	1.30±0.18	1.13±0.20	1.37±0.17	1.08±0.08	1.48±0.20
Gas production	L/L.d	1.63±0.05	1.63±0.07	1.50±0.08	1.32±0.08	1.33±0.02	1.57±0.02	1.10±0.04	1.42±0.10
Methane production	L CH_4 /L.d	0.73±0.03	0.73±0.03	0.98±0.06	0.86±0.04	0.60±0.00	0.70±0.00	0.72±0.02	0.92±0.06
	L/L .gVS add.d	0.50±0.03	0.47±0.02	0.86±0.02	0.74±0.06	0.52±0.03	0.47±0.02	0.64±0.02	0.66±0.04
	L/L.gVS rem.d	0.90±0.08	0.75±0.03	1.40±0.06	1.34±0.20	0.90±0.17	0.87±0.12	1.32±0.14	1.24±0.14
SCOD removal	%	65.7±3.4	82.8±1.7	76.1±0.8	71.1±0.9	88.3±3.5	75.5±0.4	69.7±1.9	76.6±6.4
Effluent SCOD	g/L	5.53±0.16	3.84±0.75	4.08±0.08	5.69±0.58	3.75±0.38	7.68±0.24	6.14±0.01	7.79±1.52
TVFA	mg/L	3453±185	2288±202	3151±628	3953±141	2443±642	4490±394	4872±557	6357±212
Alkalinity	mg $CaCO_3$ / L	8417±797	8033±247	8467±451	8467±301	7850±87	8467±293	8933±153	10150±522
pH	-	8.14±0.02	8.10±0.15	8.22±0.10	8.20±0.06	8.28±0.10	8.17±0.08	8.27±0.06	8.22±0.05
Ammonia	NH_4-N mg/L	558±100	319±14	639±35	394±46	139±14	127±16	419±17	487±12

Table 5.6: Steady state characterization of reactors at HRT of 9 days

HRT= 9 days		Reactor							
Parameters	Units	SWnt	SWt	DmWnt	DmWt	SFnt	SFt	DmFnt	DmFt
OLR	g VS/L.d	3.32±0.04	3.67±0.06	3.42±0.09	3.26±0.10	2.49±0.11	3.23±0.01	2.66±0.01	4.09±0.01
OLR	g TCOD/L.d	4.31±0.12	4.43±0.06	4.90±0.16	4.78±0.00	3.45±0.05	3.72±0.03	3.97±0.00	4.62±0.11
COD removal	%	49.3±1.2	47.8±0.2	67.2±0.7	56.1±3.2	63.6±1.5	54.5±0.8	61.1±0.2	49.9±1.4
	g/L.d	2.13±0.05	2.12±0.03	3.23±0.05	2.68±0.15	2.17±.10	2.25±0.07	2.44±0.05	2.23±0.02
VS removal	%	42.6±0.7	45.4±1.1	61.7±0.5	42.1±0.4	44.9±1.5	45.3±0.8	43.6±0.7	32.1±1.2
	g/L.d	1.42±0.02	1.65±0.04	2.12±0.02	1.37±0.02	1.15±0.05	1.47±0.04	1.16±0.02	1.31±0.05
Gas production	L/L.d	1.72±0.02	1.62±0.01	1.97±0.01	1.50±0.00	1.58±0.02	1.78±0.03	1.56±0.02	1.24±0.03
Methane production	L CH_4 /L.d	0.78±0.01	0.73±0.00	1.28±0.01	0.96±0.00	0.72±0.02	0.80±0.02	1.01±0.00	0.79±0.02
	L/L .gVS add.d	0.40±0.05	0.33±0.03	0.81±0.02	0.62±0.05	0.47±0.04	0.42±0.02	0.81±0.02	0.43±0.01
	L/L.gVS rem.d	0.92±0.04	0.73±0.02	1.31±0.02	1.50±0.06	1.03±0.04	0.92±0.01	1.86±0.02	1.31±0.00
SCOD removal	%	45.8±0.5	58.9±1.1	72.2±0.7	58.2±1.6	84.6±0.5	73.8±0.8	79.0±1.5	57.6±0.9
Effluent SCOD	g/L	9.29±0.42	8.12±0.33	4.77±0.27	8.26±0.55	4.42±0.32	8.82±0.10	6.03±0.05	14.26±1.04
TVFA	mg/L	5720	5228	3366	5485	3332	5735	4177	9761
Alkalinity	mg $CaCO_3$ / L	8950±524	8200±218	8900±328	8500±156	7950±324	8800±159	9100±410	10400±286
pH	-	8.15	7.96	8.31	8.18	8.36	8.26	8.33	8.24
Ammonia	NH_4-N mg/L	319±37	172±11	562±3	423±3	83±3	83±2	365±2	459±21

5.4.3. Biogas Production of the Whole Waste

Daily biogas production data obtained from reactors fed with whole M-OFMSW with and without MW pretreatment through out the experiment at the various HRTs are shown in Figure 5.3a and the average SS data are given in Figure 5.5. MW pretreatment did not show a positive effect on methane production of the whole waste, when comparing single or two stage processes to each other with and without MW pretreatment. However, dual stage reactors performed significantly better in term of methane production and waste stabilization when compared to single stage digesters at similar HRTs both with and without MW pretreatment. The greatest relative increase in performance for the staged process without pretreatment (D_mW_{nt}) occurred at the shortest HRT of 9 days with methane production 60% greater compared to the single reactor control or single reactor with pretreatment as illustrated in Figure 5.6. The staged reactor combination achieved higher biogas production and organic removal efficiencies at all HRTs even at high OLR's when compared to the single stage systems. Additionally, the biogas yield (gas production per mass VS added) for D_mW_{nt} compared to the control (SWnt) was approximately 1.5 greater for all HRTs tested (Figure 5.7). Results are also in agreement with TCOD removal. Figure 5.4a shows TCOD removal efficiencies for all conditions and clearly indicates the superior performance of the dual stage process without pretreatment (D_mW_{nt}) which tended to be about 10-35% greater than the single stage control system at similar HRTs. Similar improvements in biogas production and COD removal were not realized for SW_t and D_mW_t, especially at the shortest HRT and concomitant highest OLR. At an HRT of 9 days both single stage systems and the dual stage system with MW pretreatment had a COD removal efficiency of approximately 50% and 60% respectively, compared with about 70% for D_mW_{nt}. It should be noted that at HRTs of 20, 15 and 12 days, D_mW_t always had COD removal efficiencies greater than the single stage reactor but were always slightly less than what was determined for D_mW_{nt} (Figure 5.4a). MAD staging without MW pretreatment of M-OFMSW was deemed to be the best and most economical configuration (D_mW_{nt}) to achieve the greatest biogas production, biogas yield as well as TCOD and VS removals over the OLRs and HRTs evaluated. Similar findings for the relative importance of AD

staging vs. pretreatment has also been reported by Coelho et al. (2011) for TWAS digestion. It should be noted that for AD of TWAS improved COD removal and biogas production has been reported with high temperature MW pretreatment compared to controls in single stage digesters (Toreci et al. 2009), which is not the case in this study using M-OFMSW. However they had similar results when comparing dual stage reactors to each other and single stage digestion, with and without pretreatment. It should be clarified; MW pretreatment of M-OFMSW did not improve the digestion of whole waste when comparing single or dual stage reactors to their counterpart especially at high OLRs. One reason can be the nature of the waste, M-OFMSW is highly biodegradable and there is little material that is difficult to hydrolyse and digest. Palmowski and Muller (2000) had similar findings to the present study when they investigated the effect of comminution of an organic waste on its anaerobic biodegradability, finding no improvement in biogas production after comminution pretreatment. In single stage systems operated at high OLR the M-OFMSW rapidly accumulates VFAs since methanogens grow slower than the acidogenic bacteria, which can cause an imbalance in the anaerobic consortia and eventual reduction in methane production. Separation of the different AD populations and growth under more favourable conditions, has potential applications for OFMSW (Mohan and Bindhu 2008).

Another possible reason for reduced waste stabilization after high temperature MW pretreatment is the formation of complex by products which may be refractory or inhibitory to methanogenesi. These compounds tend to have a greater negative impact at higher organic loadings and concomitant low HRTs (i.e. short contact times). Marin et al. (2010) pretreated kitchen waste (KW) with MW at high temperature (175 ºC) and reported decreased biogas production at heating rates of 3.9 and 1.9 ºC/min. It was reported that decreased biogas production was likely related to complex compounds that were being produced at the high temperature. In another study (Shahriari et al. 2011a), whole M-OFMSW pretreated at 115 ºC and 145 ºC showed 4 to 7% improvement in biogas production over untreated M-OFMSW (control) using batch mesophilic BMP assays. However, at 175 ºC, biogas production decreased due to the formation of refractory compounds that inhibited digestion. In the present study, continuous AD treatment with MW temperature of 145 ºC was implemented at progressively decreasing HRTs. At the

long HRTs concentrations of refractory and/or inhibitory compounds in the reactor such as humic substances resulting from MW pretreatment are low and sufficient time is available such that little negative impact on digestion is observed. However, as HRTs are reduced (i.e. OLR increased) accumulation of humic and like compounds in the system increases while contact time for digestion decreases resulting in higher specific loading rates. Concomitantly the positive or negative impact of pretreatment on biogas production and waste stabilization becomes more evident as HRT is decreased and loading is increased. With decreasing HRTs there was a decrease in biogas production with MW pretreated waste compared to untreated waste. In this study (Shahriari et al. 2011a) higher concentrations of humic acid (HA) were observed after MW pretreatment (the concentration of total HA after pretreatment at 145 ºC increased almost 2 times compared to the control), which were believed to have decreased biogas production compared to the untreated controls. At short HRTs and after microwaving there was sufficient substrate available but the microbial consortia were unable to metabolize the substrate rapidly which is indicative of non-competitive inhibition. In non competitive inhibition, the inhibitor binds to the enzyme at a site other than the enzyme's active site. This affects the rate of the reaction catalyzed by the enzyme because the inhibitor causes a change in the structure and shape of the enzyme, preventing it from being able to bind with the substrate correctly. Increasing the concentration of the substrate still does not allow the maximum enzyme activity rate to be reached which we speculate is happening in both the single and dual stage AD reactors.

5.4.4. Biogas Production of the Free Liquid

Daily biogas production data obtained from semi-continuous reactors fed with the free liquid extracted from MW pretreated or untreated M-OFMSW throughout the experiment at the various HRTs are shown in Figure 5.3b and the average SS data are provided in Figure 5.5. Details pertaining to the concentration of the organics extracted into the free liquid per unit mass of whole M-OFMSW are found in Table 5.2. It should be noted that SCOD concentrations of the free liquid extracted from MW pretreated whole M-OFMSW are 12-37 % greater than free liquid obtained from untreated whole M-OFMSW. The volume of

free liquid extracted per unit mass of MW pretreated whole M-OFMSW was also approximately 40% higher than the volume of free liquid obtained from controls. Since the free liquid extracted is based on per unit mass of whole M-OFMSW the semi-continuous reactors were operated at the various HRTs with the free liquid as produced. Figure 5.3b indicates that per unit volume of free liquid treated, MW pretreatment results in higher biogas production compared to single and dual stage controls. Additionally, staging of reactors has a significant benefit in relation to the amount of biogas produced per unit volume of free liquid when compared to either of the single stage systems with or without MW pretreatment. The relative improvement for the 4 reactor configurations evaluated is best shown in Figure 5.6.

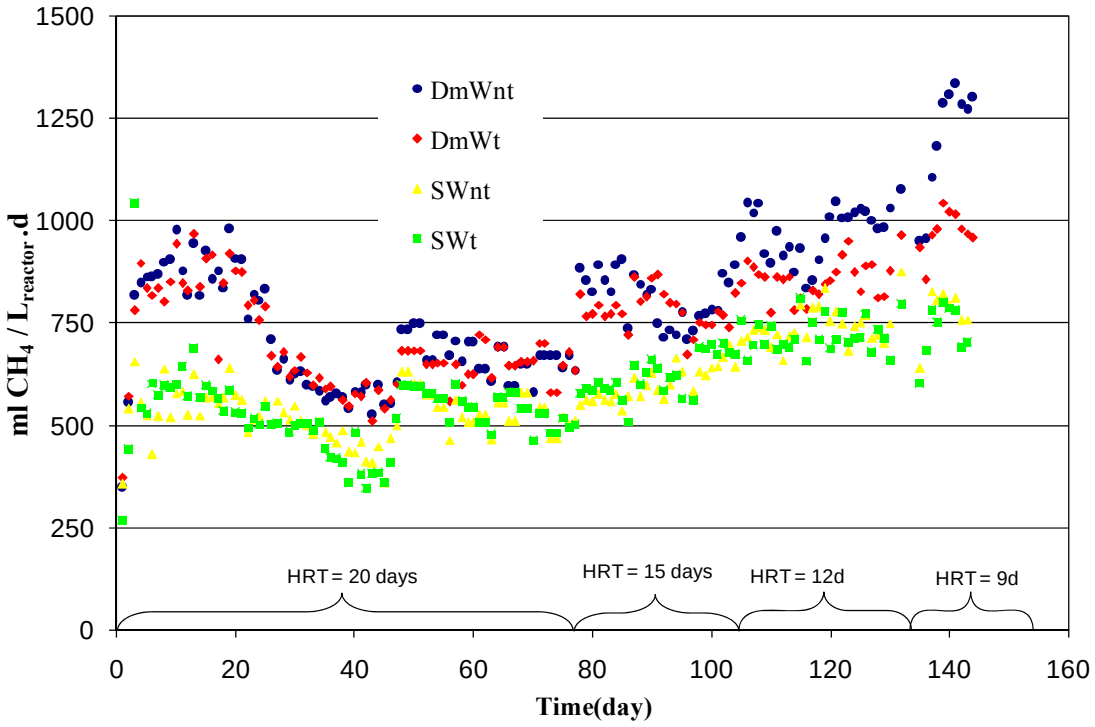
Maximum enhancement in relative CH_4 production when comparing SF_{nt} (354 ml/L/d) to the other systems occurred at an HRT of 20 days and was 1.50, 1.46 and 1.97 fold greater in SF_t, D_mF_{nt} and D_mF_t respectively. While CH_4 production increased with decreasing HRT the relative change vs. the control reactor SF_{nt} tended to decrease. The staged process without pretreatment (D_mF_{nt}) produced biogas at approximately the same rate or slightly higher as the single reactor with pretreatment (SF_t) at all HRTs (9-20 days). The fact that greater waste stabilization and CH_4 production occurred in D_mF_{nt} compared to SF_t is significant when considering that the organic loading to SF_t was about 30-40% higher at each HRT evaluated (due to increased COD and VS concentrations in the free liquid extracted after MW pretreatment). This finding with regard to the benefit of staging vs. pretreatment alone is similar to what was reported above for the whole waste. Biogas results were also supported based on the COD removal data (Figure 5.4b). When the HRT was decreased to 9 days (OLR increased) COD removal without pretreatment remained high (>60%), however for the single reactor with MW pretreatment COD efficiency decreased. It can also be noted that the COD removal efficiency also trended downward in D_mF_t tending to indicate that in this reactor as the HRT decreased there was some level of inhibition or increased recalcitrance of the free liquid as a result of MW pretreatment (discussed later). It should be reemphasized that the rates of biogas production were always greater than the control however the relative improvement decreased to 1.12 for SF_t and D_mF_t at an HRT of 9 days, compared to 1.50 and 1.97 at 20 days.

It may be difficult to clearly separate and understand the advantages of pretreatment and staging based on the volumetric parameters discussed above. However, Figure 5.7 which is based on CH_4 production per unit mass of organics added clearly differentiates any advantages of either process. If one compares the yield of methane for single stage reactors with and without pretreatment over the 4 HRTs evaluated there is very little difference in the two systems. Similarly if one compares the dual stage systems with each other they are also fairly similar to each other except for the HRT of 9 days when D_mF_t began to fail and biogas production plummeted. The most important aspect of Figure 5.7 supports the discussion above that when single reactors are compared to their dual stage counterparts at similar HRTs and loading rates there is a clear improvement in the yield of CH_4 production per unit mass of organics added for the dual stage system. On average the range of improvement over the HRTs evaluated when comparing like single and dual stage treatments were in the range of 25 - 75% (except D_mF_t at HRT of 9 days). This again indicates the advantages of staging on improving the digestion process for M-OFMSW. Additionally, the results also support the conclusion that staging provides more benefits than MW pretreatment. It should be remembered that MW pretreatment not only increased the concentration of organics in the free liquid but also the quantity of free liquid per mass of M-OFMSW treated. This will have an impact on the process if a mass balance approach is utilized.

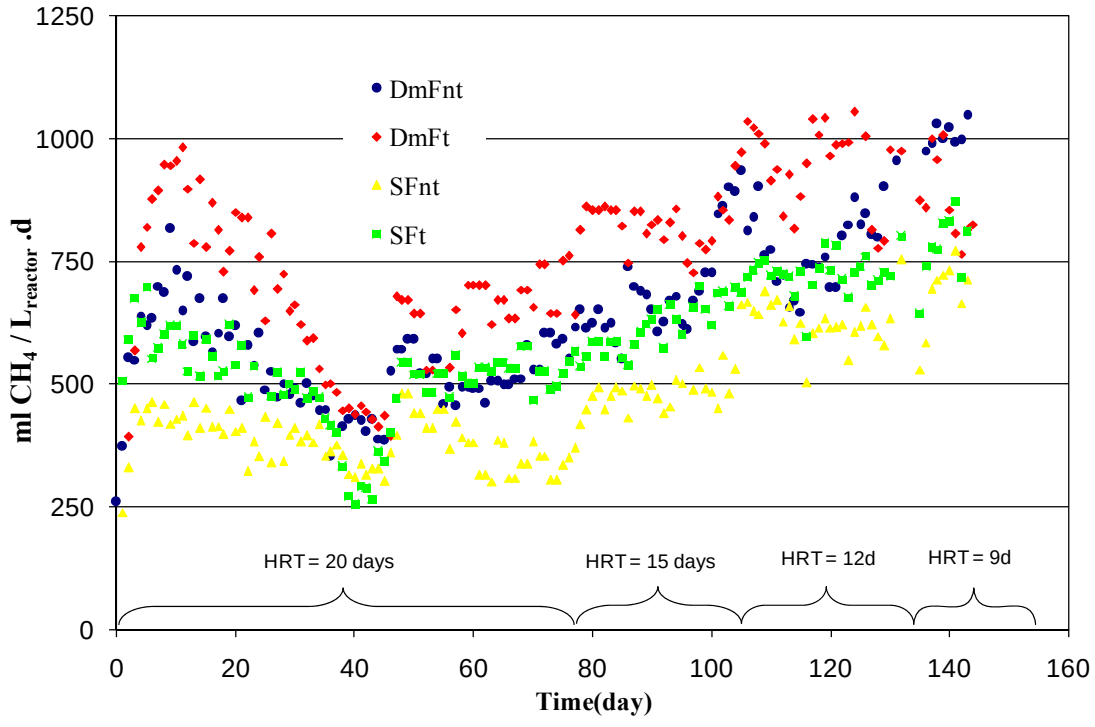
Reduced methane production relative to SF_{nt} (control) at the shortest HRTs may be due to VFA accumulation possibly related to inhibition of methanogens. VFA of 1481 mg/L at an HRT of 20 days in D_mF_t increased to 9761 mg/L at an HRT of 9 days. Table 5.3 to Table 5.6 show higher VFA accumulation in reactors with MW pretreated whole M-OFMSW and free liquid extracted from MW pretreated whole M-OFMSW compared to the controls in most cases. Approximately 65% of the VFAs produced in and transferred from stage one to the second stage was butyric acid. Among VFAs, propionic and butyric acid have been found to be the most inhibitory to methanogensis (Mata-Alvarez 2003; Warith et al. 2005). Callaghan et al. (2002) reported that with a VFA/alkalinity ratio of less than 0.4, AD is usually stable. For HRTs of 15 and 20 days this condition was met, but at an HRT of 12 days the ratios were 0.53, 0.47, 0.55 and 0.63 for reactors SF_t, D_mW_t, D_mF_{nt} and D_mF_t,

respectively. At an HRT of 9 days D_mW_{nt} was the only process configuration with a ratio below 0.4, the rest were in the unfavourable range. The low VFA/alkalinity ratio is one likely reason for superior performance of D_mW_{nt} at short the HRT (9 days). D_mF_t failed at an HRT of 9 days and had a VFA/alkalinity ratio of 0.94. SCOD results indicated that although increasing the OLR (shortening HRT) will provide a surplus of biodegradable substrate for methanogenesis, the microbial consortia in the two step reactor were not in equilibrium when treating the free liquid which resulted in VFA accumulation in the second reactor with concomitant reduced methane production.

The methane production has an inverse relationship with respect to the OLR (Figure 5.7). In general CH_4 produced /VS added decreased with decreasing HRT. SCOD results showed that although increasing the OLR provides an abundance of organic substrate, the system is unable to use it as efficiently. At the 20 day HRT the maximum SCOD concentration (D_mF_t) was below 1500 mg/L, but it increased as HRT was shortened, and SCOD removal was 48% at an HRT of 9 days (majority of SCOD was VFAs). These results are in agreement with other similar studies which were summarized by Hartmann and Ahring (2006). Coelho et al. (2011) used MW pretreatment of TWAS to 96 ^oC and reported that gas production/ mass VS added decreased with decreasing HRT with or without pretreatment. Toreci et al. (2009) also evaluated MW pretreatment of TWAS at temperatures above 100 ^oC and found that biogas production/mass VS added for controls decreased with shorter HRTs but with optimum MW pretreatment it remained relatively constant for an HRT of 10 days suggesting that pretreatment increased biodegradability of the TWAS. Mohan and Bindhu (2008) worked with kitchen waste and reported similar biogas yields/mass VS added at different OLRs. However, in that study the HRT was 15 days suggesting that the systems were not stressed and more than sufficient time was provided for ultimate waste stabilization. This is not the case in our work where shorter HRTs were evaluated.

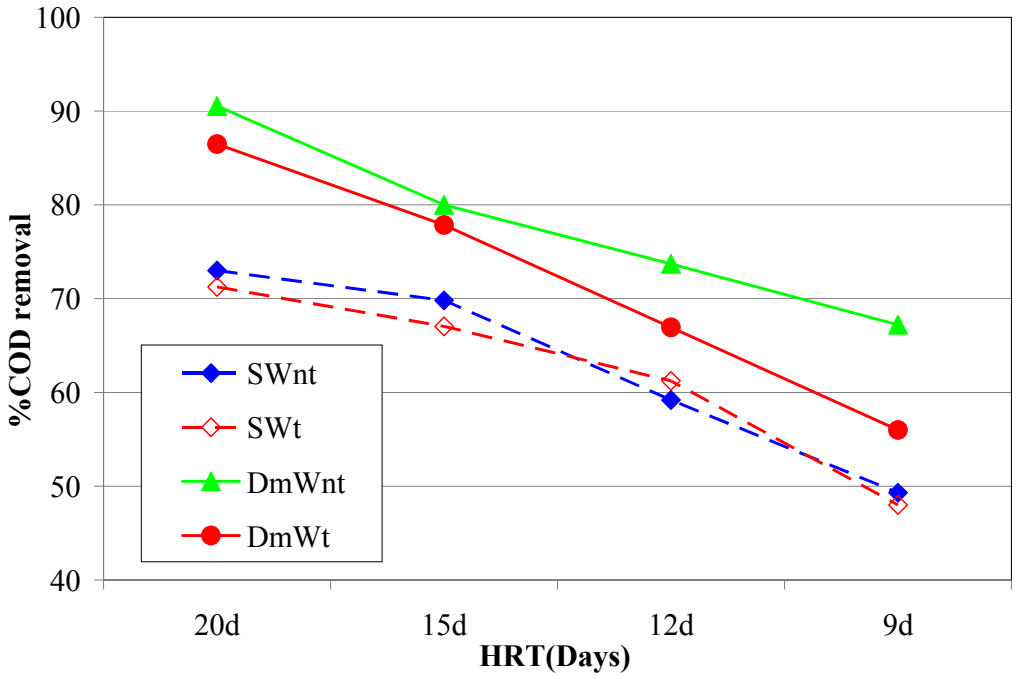


(a)



(b)

Figure 5.3: Daily CH_4 Production for a) Whole waste, b) Free liquid



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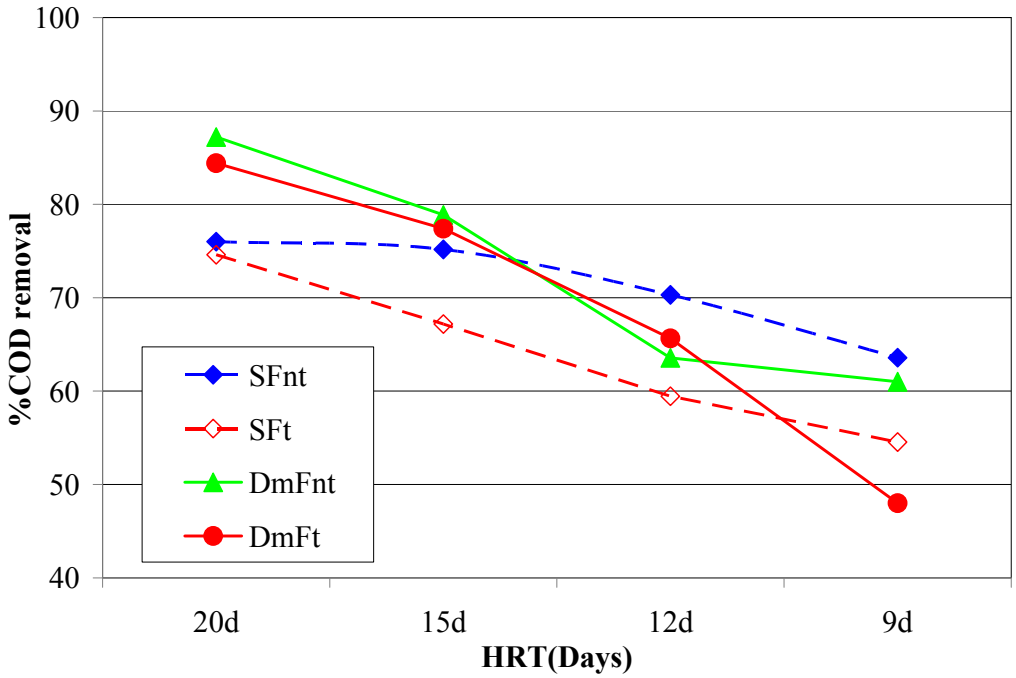

(b)

Figure 5.4: Percentage of COD removal a) Whole waste, b) Free liquid

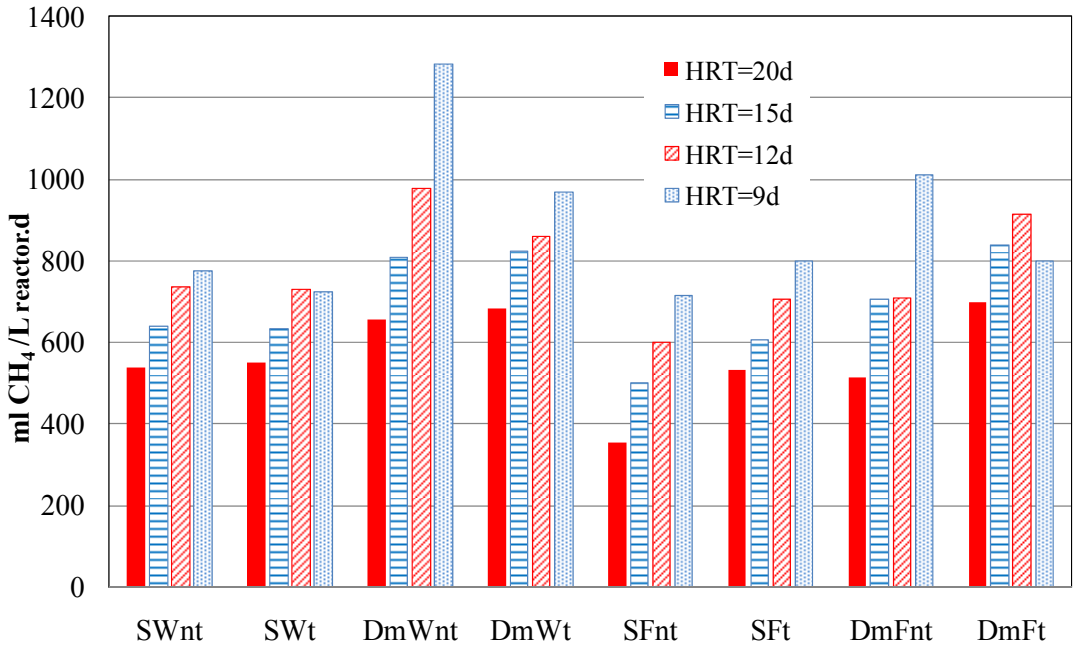

Figure 5.5: Average of daily methane production

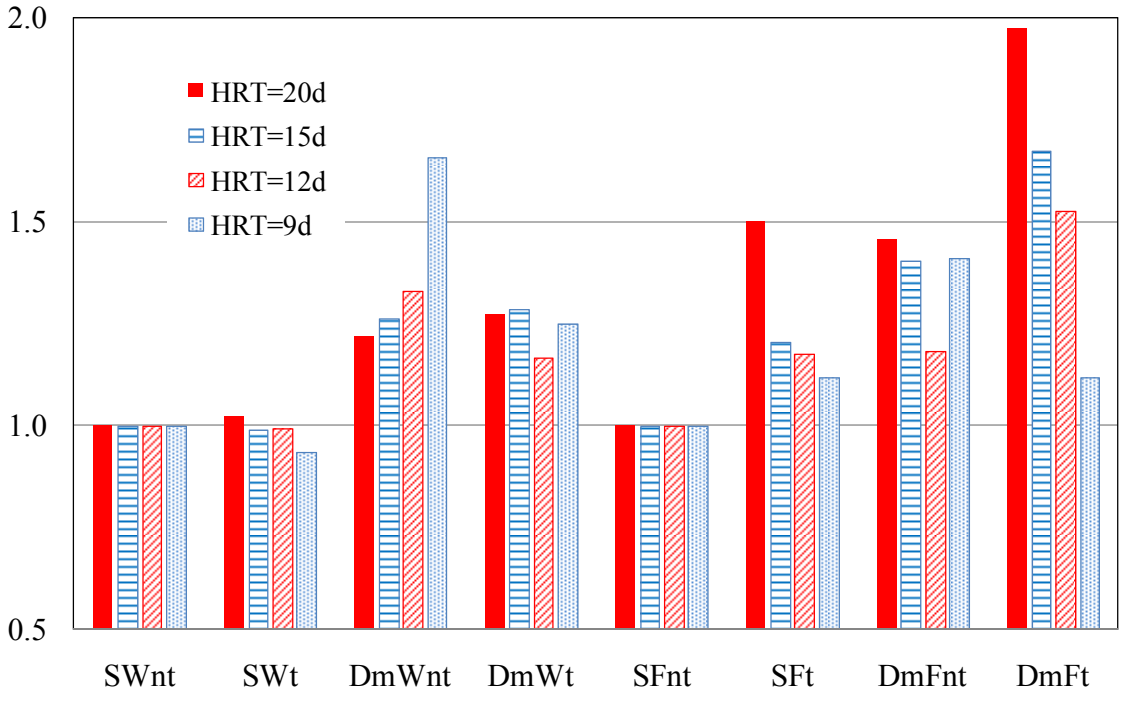

Figure 5.6: Relative methane production compared to controls

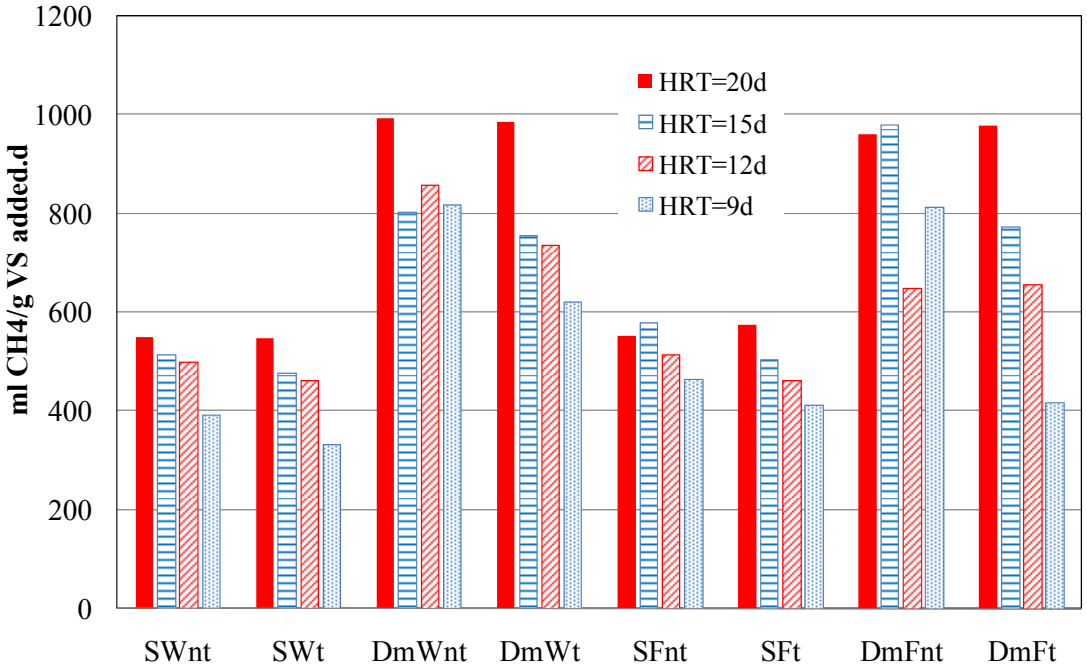

Figure 5.7: Methane per g VS per day

5.4.5. Mass Balance

To evaluate the overall performance of the single and dual stage systems with and without MW pretreatment a COD mass balance was completed. COD conversion to methane was based on the theoretical conversion of 1g COD removed per 350ml methane produced (Speece 1996). The daily conversion of COD is known (ΔCOD), so CH_4 production can be calculated and compared with the observed values (Table 5.7). While most of the calculated results are in agreement with the experimental observations it could be argued that the observed values were slightly higher than predicted. However based on daily fluctuations in feed concentration, experimental determination of COD values and errors in measurement of gas the data comparison shows a very close correlation and gives us added confidence in our evaluation of the various processes and MW pretreatment and the conclusions we have drawn.

Under what was deemed to be the best condition (HRT of 20 days) for AD of M-OFMSW, volumetric methane production yields were determined for the various pretreatment and

reactor configurations and are shown in Table 5.8. The best condition was selected based on the highest methane yield per mass of M-OFMSW volatile solids added as well as reactor stability and taking into account provincial regulations for treatment of municipal sludge which are set at 15 days.

Table 5.7: Observed and calculated values for methane production (L methane/day)

HRT	20 days		15 days		12 days		9 days	
Reactor	observed	predicted	observed	predicted	observed	predicted	observed	predicted
SW_{nt}	0.32±0.01	0.29±0.01	0.38±0.02	0.38±0.03	0.44±0.02	0.38±0.01	0.47	0.45
SW_t	0.33±0.02	0.30±0.02	0.38±0.10	0.38±0.02	0.44±0.02	0.42±0.02	0.44	0.45
SF_{nt}	0.21±0.00	0.20±0.02	0.30±0.01	0.29±0.01	0.36±0.00	0.34±0.02	0.43	0.46
SF_t	0.32±0.01	0.27±0.01	0.36±0.02	0.35±0.00	0.42±0.00	0.38±0.03	0.48	0.43
D_mW_{nt}	0.35±0.01	0.32±0.02	0.42±0.04	0.39±0.03	0.49±0.03	0.44±0.03	0.60	0.54
D_mW_t	0.37±0.01	0.31±0.01	0.43±0.03	0.36±0.06	0.43±0.02	0.40±0.01	0.45	0.44
D_mF_{nt}	0.28±0.01	0.24±0.02	0.37±0.02	0.26±0.02	0.36±0.01	0.30±0.01	0.47	0.40
D_mF_t	0.38±0.04	0.29±0.01	0.44±0.01	0.38±0.01	0.46±0.03	0.39±0.02	0.37	0.37

Biogas production values were determined per mass of M-OFMSW treated (approximately 16% solids) and also considering the mass and concentration of free liquid extracted from whole M-OFMSW. For semi-continuous AD the most economical combination to enhance biogas production from M-OFMSW is digestion of whole waste M-OFMSW in a two stage configuration without pretreatment which had a 22% improvement vs. the control (HRT of 20 days). The expenditure of energy for pretreatment would not justify the application of D_mW_t which had a 27% improvement vs. the control but only 5% improvement vs. D_mW_{nt}. Treatment of the free liquid only is not a practical option as in the best case scenario (D_mF_t) it only accounted for 59% of the methane production of the whole waste compared to control (SW_{nt}). Concomitantly, pretreatment of M-OFMSW does not release sufficient organics in to the free liquid phase to justify treatment of the liquid phase only. However, if digestion of the liquid fraction is desired, pretreatment at 145 ºC and staging significantly increases biogas production from this fraction. However, methane produced from the free liquid in SF_t (single reactor after MW pretreatment) and D_mF_t (dual state after MW pretreatment) were approximately two and three fold greater than the control reactor (SF_{nt}). Additionally, both single and dual stage systems treating free liquid produced more methane than the dual system without pretreatment (D_mF_{nt}) which can be attributed to the higher concentration of organics and volume of free liquid released from the whole M-

OFMSW after MW pretreatment. If one just looks at the impact of staging vs. single reactors (SW_{nt} vs D_mW_{nt} or SF_{nt} vs D_mF_{nt}) a 22% and 45% improvement respectively can be obtained by selection of an alternate 2 stage reactor configuration.

Table 5.8. Methane production comparison (HRT of 20 days)

HRT= 20 days	Reactor							
	SWnt	SWt	DmWnt	DmWt	SFnt	SFt	DmFnt	DmFt
L Methane/L reactor per tonne of waste	89.7	91.8	109.1	114.0	18.8	40.7	24.5	53.5
Improvement relative to SWnt	-	2%	22%	27%	-21%	-45%	-27%	-59%
Improvement relative to SFnt	477%	488%	580%	606%	-	116%	46%	185%

5.5. Conclusion

Maximum acidification of M-OFMSW was determined to be 2 days under anaerobic conditions based on a modified BMP assay which was selected for the HRT of the acidification stage of the dual digestion system, this condition was found to be appropriate.

MW pretreatment increased the solubilization and volume of free liquid from M-OFMSW. However, pretreatment and digestion of the free liquid fraction only, is not a sustainable option.

For digestion of the whole M-OFMSW or the free liquid obtained from M-OFMSW, staging of the AD process had a greater positive impact on waste stabilization and improved methane yield compared to single stage reactors or MW pretreatment. For M-OFMSW which was deemed to be composed of readily biodegradable components it is recommended that staging be utilized without MW pretreatment as being the most economical mode for AD. This conclusion may be challenged if the OFMSW has a greater proportion of more difficult or less biodegradable components which would justify MW pretreatment. However, in both cases (M-OFMSW or OFMSW) dual stage AD should be considered.

CHAPTER 6

Effect of Leachate Recirculation on Mesophilic Anaerobic Digestion of Organic Fraction of Municipal Solid Waste

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6.1. Abstract

The effects of using untreated leachate for supplemental water addition and liquid recirculation on anaerobic digestion of organic fraction of municipal solid waste (OFMSW) was evaluated by combining cyclic water recycle operations with batch mesophilic biochemical methane potential (BMP) assays. Cyclic BMP assays indicated that using an appropriate fraction of recycled leachate and fresh make up water can stimulate methanogenic activity and enhance biogas production. Conversely increasing the percentage of recycled leachate in the make up water eventually causes methanogenic inhibition and decrease in the rate of OFMSW stabilization. The decrease in activity is exacerbated as the number cycles increases. Inhibition is possibly attributed to accumulation and elevated concentrations of ammonia as well as other waste by products in the recycled leachate that inhibit methnogenesis.

Keywords: Anaerobic digestion, BMP, Organic waste, Effluent recycling, Water reuse

6.2. Introduction

Anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) for solids reduction and biogas production has become a reliable technology in recent years with a number of processes available. Variations in OFMSW digestion are often characterized by the level of moisture used in the process. In general three categories of moisture and solid content exist: a) low-solids or "wet" process with total solids (TS) less than 20%, b) high-solids or "dry" process with TS greater than 20%, and c) "semi-dry" process with TS of about 20%.

One of the main advantages claimed for the dry fermentation of OFMSW is high volumetric organic loading rates. However there are a number of disadvantages: complete mixing of the waste is extremely difficult and in practice is not possible; accordingly the optimal performance and interactions of the various microbial consortia in the AD process is believed not to be achieved. Moreover, expensive pumps or augers with high maintenance requirements are needed to move the denser material caused by the higher TS concentration in the reactors (Nichols 2004).

Wet digestion of OFMSW can be performed in conventional reactor systems by incorporating OFMSW dilution either by addition of fresh and/or recycled leachate (De Laclos et al. 1997; Hamzavi et al. 1999) or by co-digestion with a more liquid waste if available (Bujoczek et al. 2002; Agdag and Sponza 2007). In some cases tap water (Pavan et al. 2000b) and in other cases (such as BTA) fresh make up water is mixed with untreated leachate. Using fresh water for dilution is not a sustainable or feasible option both environmentally and/or economically. Recycling of leachate is a good solution but there are restrictions and limits for water reuse. Accumulation of microbial waste products, recalcitrant components from treated OFMSW as well as intermediate breakdown components such as ammonia in the leachate with its reuse can eventually produce environmental conditions that inhibit the microbial consortia responsible for digestion. Unfortunately information in the literature pertaining to water reuse for digestion of OFMSW is very limited. Nordberg (1992) reported on the use of water and leachate to dilute alfalfa silage to 6% TS for subsequent AD. While limited in its scope they reported that AD could not be sustained if 100% leachate was used for dilution. They indicated that the process failed due to the accumulation of inhibitory concentrations of ammonium in the

system. Unfortunately they did not provide any information on water/leachate mixtures or potential operational scenarios to reduce fresh water consumption.

The objective of this study is to provide insight in to the use of leachate for process make up water and investigate the impact of leachate/fresh water mixtures on the biogas production and stabilization of a wet OFMSW treatment process. The study uses batch biochemical methane potential (BMP) assays various water/leachate mixtures and multiple cycles to evaluate the impact on the digestion of OFMSW.

6.3. Methods

Initial base line BMP assays referred to as Cycle 0 were performed at 35 ± 1°C in 250 mL (150 ml working volume) Kimax bottles sealed with 45mm screw caps and butyl rubber stoppers. In order to determine variation in anaerobic biodegradability, each BMP assay contained 120 ml of COD standardized sample and 30 ml of acclimated anaerobic biomass acclimated to OFMSW over a period of 1 year. The biomass has characterized by Shahriari et al. (2011a). Model OFMSW (M-OFMSW) was first diluted with fresh water to TCOD concentrations of ~7g/L (Shahriari et al. 2011a) . M-OFMSW contained cooked rice (18wt %), cooked pasta (18wt %), cabbage (11wt %), carrot (11wt %), apple (11wt %), banana (11wt %), corned ground beef (10wt %) and dog food (10wt %). An initial M/F ratio of approximately 0.75 gVS inoculum/g VS of M-OFMSW feed was used with equal parts of $NaHCO_3$ and $KHCO_3$ for an alkalinity 4000-6000 mg/L as $CaCO_3$ to minimize pH effects. BMP bottles were placed on a rotary shaker (PhycroTherm, New Brunswick Scientific Co. Inc, NB, Canada) at 100 rpm and biogas production was monitored daily. After almost 15 days bottles were allowed to stand for 24 hours which resulted in a relatively clarified leachate. Concentrations of VS and COD in the leachate recovered from the bottles for the next BMP assay were considered in all subsequent calculations. The biomass was then mixed with fresh M-OFMSW diluted with different combinations of leachate and fresh water: 0, 30, 60 or 100%. This procedure was repeated and BMP assay bottles were run through five sequential assay cycles designated C_1, C_2, C_3, C_4 and C_5 respectively. Reactors R_0, R_{30}, R_{60} and R_{100} refer to 0, 30, 60 and 100 % recycled leachate, respectively.

Biogas production, pH, VFA, COD and ammonium concentration were monitored to establish the number of times leachate can be recycled without decreasing the efficiency of the system. Analytical methods are the same as Shahriari et al. (2011c).

6.4. Results

Cycle 0 was run for 20 days and at the end all BMP assay bottles produced very similar amounts of biogas. Cycle 0 results suggests that all assays had a healthy anaerobic microbial consortia able to stabilize the M-OFMSW and subsequent assays could be compared to each other to evaluate the impact of leachate recycle. Cycle 0 results were also used to estimate the maximum biogas yield and set a practical assay time (15d) for subsequent cycles that would tend to maximize biogas production from the M-OFMSW while minimizing biogas production carryover. While some biogas carryover does occur it was considered in all calculations and discussion. The cumulative biogas productions (CBPs) for cycles 1, 3, 4 and 5 are shown in Figure 6.1 to Figure 6.5, respectively.

Figure 6.1 shows that all four C_1 reactors were acclimated to the waste and there was no evidence of a lag phase indicating little advantage or disadvantage for any of the leachate combinations. Around day 4, CBPs differences between R_0 and R_{100} was 30%, but by day 12 the difference decreased to 6% and by the end of the assay there was no statistical difference in the biogas production between any of the bottles. It is possible that with the higher proportion of leachate used for dilution in R_{60} and R_{100} resulted in a greater carryover of anaerobic biomass that stimulated biogas production early in the assay. It was also noted that use of leachate for dilution increased alkalinity of R_{30}, R_{60} and R_{100} proportionally (Table 6.1), which resulted in a proportional increase in the sample pH.

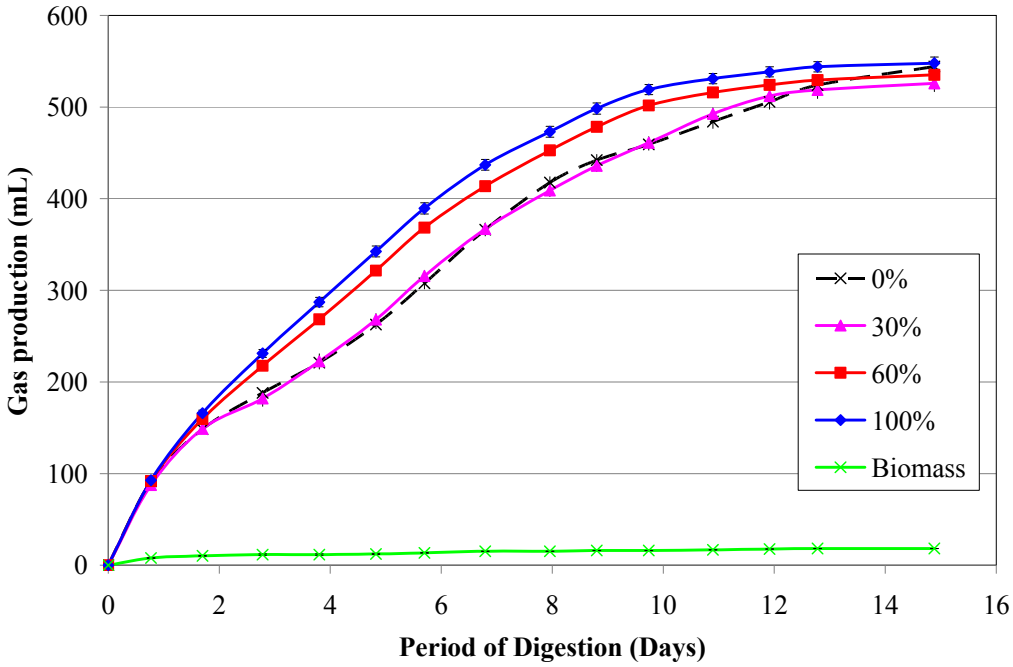

Figure 6.1: CBP for cycle 1

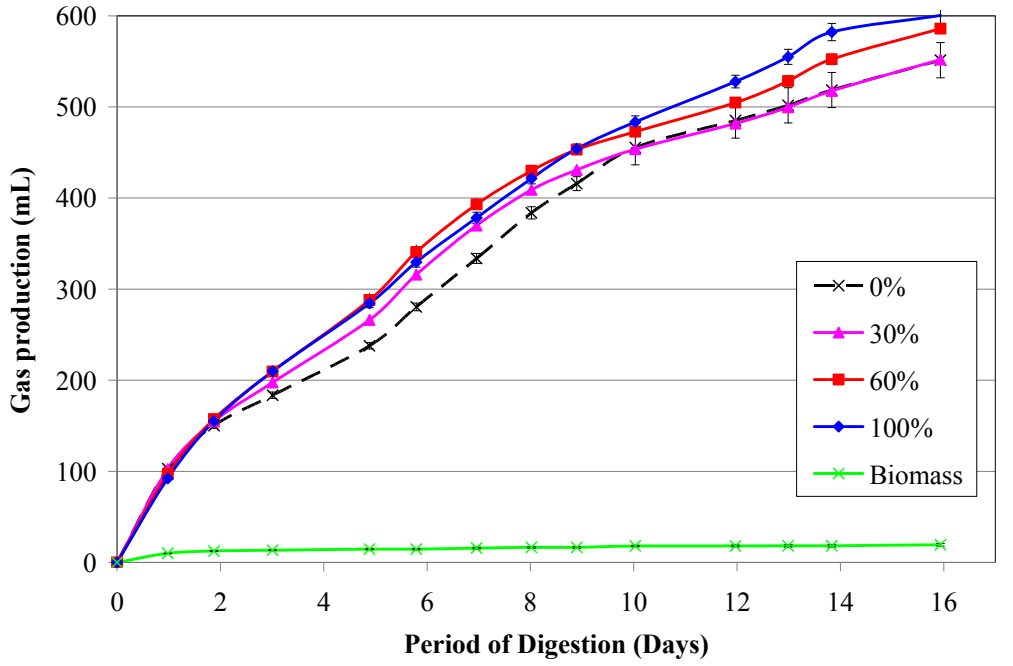

Figure 6.2: CBP for cycle 2

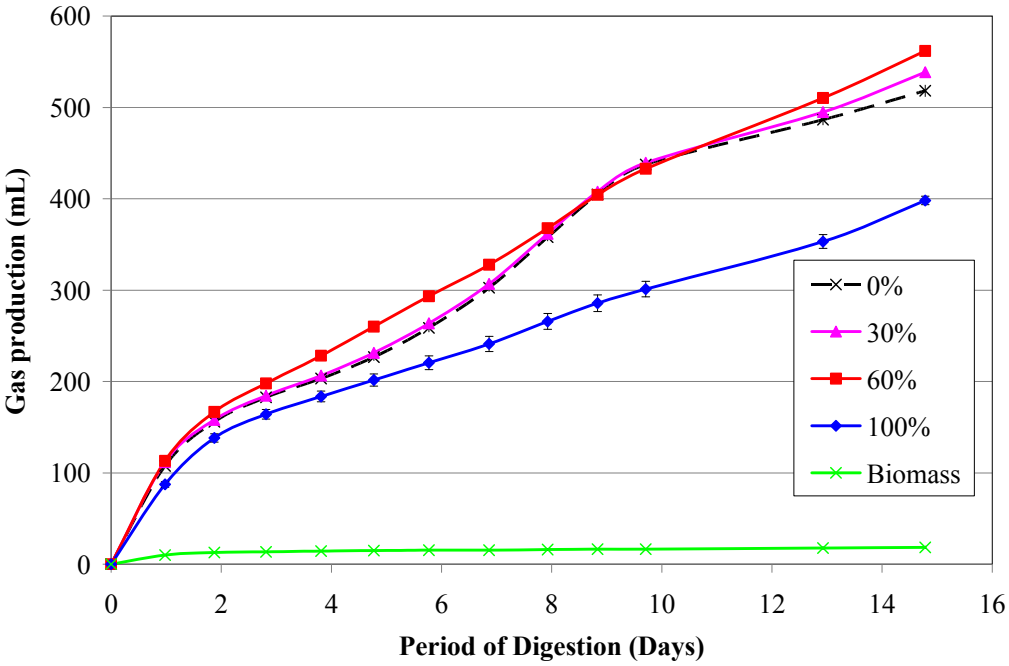

Figure 6.3: CBP for cycle 3

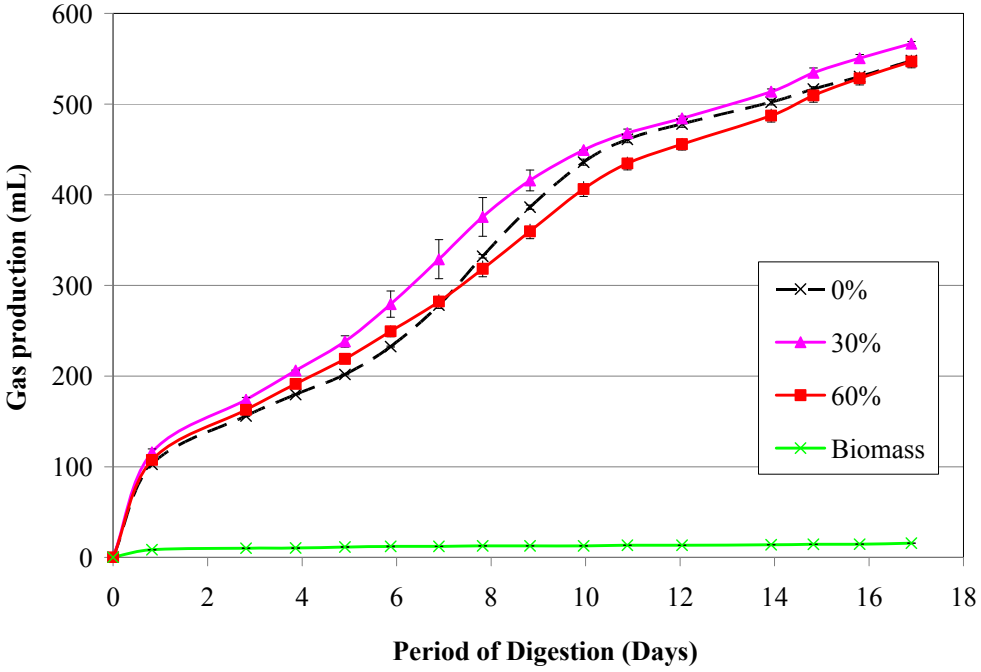

Figure 6.4: CBP for cycle 4

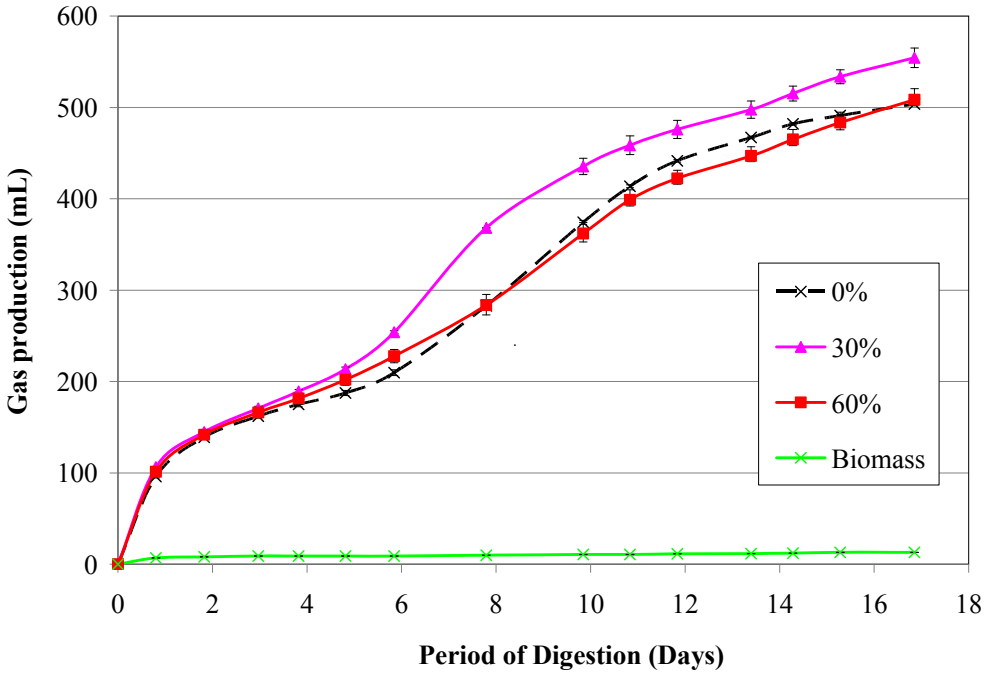

Figure 6.5: CBP for cycle 5

The percentage of TCOD and SCOD removal was not significantly different at the conclusion of the first run (Table 6.2), but concentrations of SCOD and VS assay with a greater proportion of leachate were higher than the control (R_0) (Table 6.1). The ammonia concentration in R_{100} was 746 mg/L which was not in the inhibitory range but was 77% higher than R_0.

In the second cycle (C_2), R_{60} and R_{100} produced the highest CBPs which respectively were 21 and 20% higher than R_0 after 5 days of digestion, decreasing to 6 and 9% at the end of BMP assay (Figure 6.2). It is important to note that at both times and more importantly at the end of the assay the higher CBP was statistically significant compared to the control R_0. It is likely that a higher proportion of biodegradable COD as well as anaerobic biomass was carried over with R_{60} and R_{100} that resulted in the greater biogas production. Similar to C_1 assay bottles that used a greater proportion of leachate for dilution, they had higher residual alkalinity and pH. The elevated COD and VS concentration at the end of the assay suggests that there was also an accumulation of recalcitrant and/or less biodegradable material. At the conclusion of C_2 there were no significant negative effects associated with reuse of leachate.

Table 6.1: VS, SCOD, Alkalinity and pH at the end of each run

Cycle	1	2	3	4	5
Reactor			Effluent VS Concentration (g/L)		
R0	0.92±0.31	1.01±0.11	1.04±0.26	1.09±0.17	0.92±0.18
R30	1.35±0.25	1.49±0.16	1.71±0.05	1.63±0.09	1.36±0.04
R60	1.66±0.11	2.12±0.12	1.87±0.27	2.02±0.45	3.70±0.09
R100	2.33±0.14	2.05±0.19	3.19±0.16		
			Effluent SCOD Concentration (g/L)		
R0	0.18±0.01	0.17±0.03	0.66±0.01	0.49±0.08	0.53±0.03
R30	0.26±0.03	0.29±0.09	0.71±0.06	0.58±0.18	0.56±0.12
R60	0.29±0.04	0.30±0.00	0.71±0.04	0.67±0.03	0.81±0.19
R100	0.30±0.01	0.61±0.05	2.96±0.12		
			Alkalinity (mg $CaCO_3$ /L)		
R0	4972±72	5000±178	4950±141	5088±53	5025±35
R30	5931±95	6163±144	6250±71	6475±177	6600±141
R60	7097±95	8138±144	9500±71	9575±35	9400±0
R100	8025±177	11050±71	13275±35		
			pH		
R0	8.05	8.07	8.23	8.29	8.08
R30	8.06	8.11	8.22	8.30	8.06
R60	8.26	8.17	8.29	8.37	8.11
R100	8.34	8.37	8.44		

Table 6.2: TCOD and SCOD removal efficiency at the end of each cycle

Cycle	1	2	3	4	5
Reactor			TCOD removal (%)		
R0	77.5±0.3	81.3±0.7	83.8±1.1	86.6±1.2	90.3±0.5
R30	76.3±0.5	80.7±0.2	75.3±0.9	81.7±0.6	90.8±0.2
R60	76.2±0.1	71.5±0.5	72.5±0.5	80.1±0.4	72.3±0.6
R100	74.4±0.3	62.1±0.6	48.3±0.9		
			SCOD removal (%)		
R0	94.2±0.5	94.6±0.9	79.1±1.4	86.1±0.8	81.6±0.2
R30	92.2±1.2	91.3±1.1	79.6±0.9	84.7±0.4	81.3±1.5
R60	91.4±1.0	91.1±0.2	79.5±0.6	82.2±1.3	74.8±0.6
R100	91.3±1.5	81.9±0.5	28.5±1.0		

In cycle 3 (Figure 6.3) R_{60} had the greatest CBP and at day five CBP was 15% higher than R_0 (control), decreasing to about 8% with 72% TCOD and 80% SCOD removal at the end of the assay (Table 6.2). However assay bottles R_{100} which used 100% leachate produced significantly less CBPs than the other assay bottles. Additionally in R_{100} TCOD and SCOD removal dropped to 48 and 28%, respectively and VS and SCOD of leachate increased to 3.19 and 2.96 g/L respectively all indicative of a decrease in performance after 3 cycles when diluting M-OFMSW with 100% carried over leachate. Ammonia concentration in leachate of R_{100} (C_3) also increased significantly to 1331 mg/L which was approximately 3.0 times the concentration found in R_0. At the conclusion of the assay the VFA

concentration in R_{100} was 1301mg/L and pH of 8.4. Decrease in performance based on biogas production is most likely attributed to the elevated accumulation of ammonia which was inhibiting the anaerobic microbial consortia. The hydrophobic ammonia molecule may diffuse passively in to the cell, causing proton unbalance, and/or potassium deficiency (Chen et al. 2008). This result is in agreement with Kayhanian (1994) who reported that AD is stable with ammonia concentration in the range of 300-1000mg/L but at concentrations of 1200 mg/L methanogens were inhibited and the VFAs doubled from 600 to 1200mg/L. The specific activity of methanogenic bacteria has been found to decrease with increasing ammonia concentration (Chen et al. 2008). It should be noted that these ammonia findings are compounded by the accumulation of other microbial waste products and recalcitrant organics that likely exacerbate the inhibitory effect of ammonia. However the results would suggest that an ammonia concentration greater than 1000mg/L is potentially inhibitory for the system and should be avoided if possible. The inhibitory concentration of ammonia varies depending on origin of biomass, substrate, pH and temperature (Cuetos et al. 2008; Bouallagui et al. 2009). The higher pH also likely exacerbated the negative effect resulting from the elevated ammonia concentration. Kayhanian (1999) and Sung and Liu (2003) found that ammonia inhibition at a given concentration increased when pH was increased to higher than 7.2. At an ammonia concentration of 400 mg/L, 50% inhibition of methanogenesis was reported at pH 7.5 when compared with pH of 7.2. Interestingly Kayhanian (1994) mentioned that ammonia inhibition can be solved by diluting the digester contents with fresh water to reduce the ammonia concentration in the liquid phase which is what likely occurred in our systems as there was no observed inhibition in R_{30} and R_{60} which had a greater fresh water component than R_{100} and ammonia concentrations were lower than 1000 mg/L.

In cycle 4, R_{100} failed so it is not shown in Figure 6.4. At the conclusion of C_4 there was no significant difference in the final CBPs of the three remaining dilutions R_0, R_{30} and R_{60}. Keying on ammonia concentrations based on the results of C_3 and R_{100} it was found that R_{60} had the highest ammonia concentration of 875 mg/L which was 1.9 times the concentration in R_0. However this ammonia concentration was less than the 1300 mg/L threshold seen for R_{100} in C_3. Interestingly the VFA in R_{60} remained low at 193 mg/L and TCOD and SCOD removal of R_0 and R_{30} remained fairly high and steady but there seemed to be an increase in

TCOD, VS and SCOD in R_{60} at the end of C_4 that might suggest impending problems in the final cycle assay.

In cycle 5 (Figure 6.5), there was some minor differences in CBP with R_{60} being 9% and 30% more than R_0 and R_{30} on day 6 respectively but at the end of the assay R_{30} had the greatest CBP which was statistically significant compared to R_0 and R_{60}. Ammonia concentrations were also below 700 mg/L for R_0 and 900 mg/L for R_{30} and R_{60} which were less than the threshold concentration at which R_{100} failed. Fractional TCOD and SCOD removal was 0.91 and 0.82 for R_{30} and 0.72 and 0.75 for R_{60}. Final VFA were also low in all assays with the highest concentration in R_{60} at 305 mg/L.

In general our results tend to parallel Nordberg et al. (1992) for digestion of alfalfa silage, who also reported inhibition when 100% recycled leachate was used, attributing it to accumulation of inhibitory ammonia levels. Similarly, Nordberg et al. (2007) observed the accumulation of organic and inorganic substances with 100% leachate that may have contributed to decreased performance in their system when digesting alfalfa silage. It should be noted that if a dual stage reactor configuration is employed for digestion of M-OFMSW there is an initial decrease in pH in the first stage when rapidly degradable substrate is acidified and also in the second stage when acidified effluent from the first stage is sent to the second stage (Shahriari et al. 2011b). Recycled leachte with high alkalinity can be used for M-OFMSW dilution, it would assist in dampening pH fluctuations and maintain it in favourable range which was suggested by Jarvis et al. (1995).

6.5. Conclusion

This study does not provide a definitive answer regarding the extent of leachate reuse that can be applied for the digestion of M-OFMSW. Based on the leachate/fresh water reuse strategy employed there are limitations regarding the number of times that it can be recycled. Based on the results of this research, the use of 100 % leachte for reuse is not recommended in the long term but may be used if necessary for short term acute dilution applications. Dilution with 40% water and 60% leachate (R60) did not result in observable inhibition after 5 cycles of reuse. However the gradual accumulation of ammonia suggests that long term application of R60 mixtures is likely not sustainable or advisable.

Speculating on the results it may be argued that the maximum water/leachate recycle scenario is no more than 50% (R50). More studies involving continuous reactor operation are necessary to refine the optimum leachate reuse conditions for the digestion of M-OFMSW.

CHAPTER 7

Overall Conclusions and Recommendations

7.1. Conclusions

This research was conducted to understand the effect of high temperature (>100 ºC) microwave (MW) pretreatment on organic fraction of municipal solid waste (OFMSW) characteristics as well as mesophilic anaerobic digestion (MAD) efficiency. The experiments were performed in three major phases to achieve these objectives, and can be described as solubilization, biochemical methane potential (BMP) assays and semi continuous tests. At the end, effects of using effluent for supplemental water addition (SWA) and liquid recirculation on AD of OFMSW was evaluated by using BMP assays. The main conclusions can be summarized as the following:

1. OFMSW solubilization improves as MW pretreatment temperature (T) and SWA increase. The greatest increase in waste solublization based on SCOD was achieved at 175 ºC and resulted in 1.61, 1.62 and 1.58 times higher SCOD concentrations for SWA30 versus control for high, medium and low MW intensity levels, respectively. Additionally for the same conditions, release of bound water of samples into the free liquid fraction was 1.39, 1.34 and 1.37 times greater than control.
2. Three factor fixed effect ANOVA showed that independently all three variables tested including; T, SWA and MW temperature ramp or intensity (R) have significant effects on COD solubilisation with a 95% confidence interval. Evaluation of T, R and SWA interactions showed that only T and SWA interactions were significant with a 95% confidence interval.

3. The results of BMP assays showed that in general, the whole OFMSW pretreated at 115 and 145 ºC had 4 to 7% improvement in biogas production over untreated OFMSW (control). When pretreated at 175 ºC, biogas production decreased due to formation of refractory compounds, inhibiting the digestion.
4. For the liquid fraction of OFMSW, the effect of pretreatment on the cumulative biogas production (CBP) in BMP test was more pronounced for SWA20 at 145 ºC, with a 26% increase in biogas production after 8 days of digestion, compared to the control. When considering the increased substrate availability in the liquid fraction after MW pretreatment, a 78% improvement in biogas production vs. the control was achieved.
5. Combining MW and H_2O_2 modalities did not have a positive impact on OFMSW stabilization and enhanced biogas production. In general, all samples pretreated with H_2O_2 displayed a long lag phase and the CBP was usually lower than MW irradiated only samples.
6. Maximum acidification of M-OFMSW under anaerobic condition was determined to be 2 days based on a modified BMP assay which was selected for the HRT of the acidification stage of the dual digestion system.
7. MW pretreatment (145 ºC) did not enhance the AD of the whole waste.
8. Staging of the AD process had a great positive impact on waste stabilization and improved methane yield compared to single stage reactors or MW pretreatment. The dual system with untreated whole waste had the best performance at the shortest HRT of 9 days, with methane production 60% greater compared to the single reactor control or single reactor with pretreatment Conversely,
9. For free liquid after pretreatment in two stage reactors at 20 day HRT methane production was tripled. MW pretreatment increased the solubilization and volume of free liquid from M-OFMSW. However, pretreatment and digestion of the free liquid fraction only, is not a sustainable option.
10. Cyclic BMP assays indicated that using an appropriate fraction of recycled effluent and fresh make up water can stimulate methanogenic activity and enhance biogas production. Conversely increasing the percentage of recycled effluent in the make up water eventually causes methanogenic inhibition and

decrease in the rate of OFMSW stabilization. Inhibition is possibly attributed to accumulation and elevated concentrations of ammonia as well as other waste by products in the recycled effluent that inhibit methnogenesis. Speculating on the results it may be argued that the maximum water/effluent recycle scenario is no more than 50% (R50)

7.2. Recommendations

In order to improve the understanding of all the phenomena involved in MW pretreatment studies, the following recommendations are suggested;

1. It is recommended to examine the effect of MW pretreatment on the real waste that has lower percentage of biodegradable compounds and will be relatively less biodegradable.
2. Other pretreatment alternatives such as addition of chemical agents (NaOH) with MW pretreatment may enhance solubilization and biodegradability.
3. There is still need for better understanding of two stage reactors and also combination of staging and co-digestion with WAS.

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Appendix A

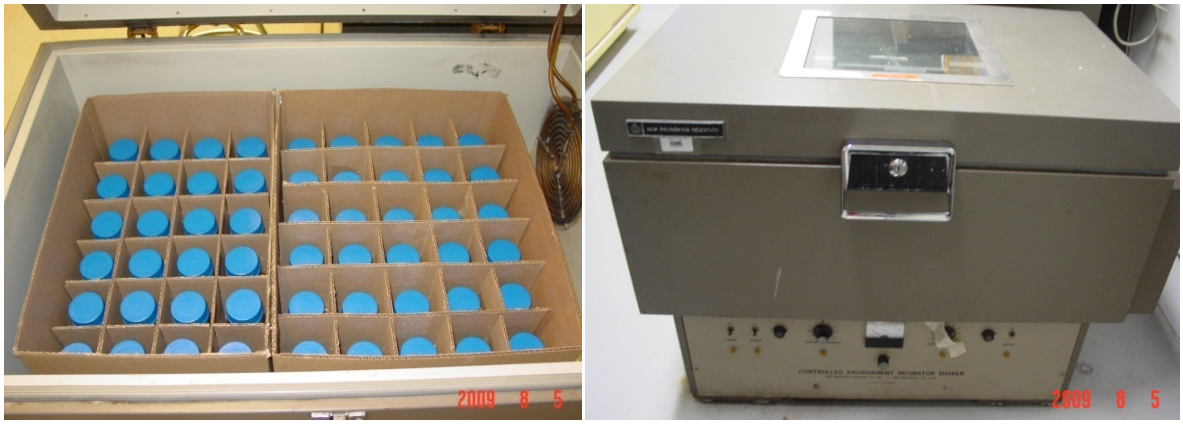
A.1 Microwave Oven

Throughout the research, microwave (MW) pretreatments were carried out with a MW accelerated reaction system, Mars 5 (Mars 5®, CEM Corporation). Mars 5® (Figure A.) has a frequency of 2450 MHz and can deliver 1200 W±155 of MW energy at full power with complete MW penetration of the 100 mL sample vessels. It is possible to monitor and control operating conditions up to 250 ºC and 34.5 bars, with its fiber optic temperature and electronic pressure sensor. Pressure vessels were filled with 50 mL of M-OFMSW and a temperature and pressure profile was programmed and monitored.

Figure A.1: Mars 5® Microwave oven

A.2 Batch Anaerobic Digestion

The biochemical methane potential (BMP) analysis was performed using 250 mL (155 mL working volume) Kimax glass bottles (Figure A.2) with butyl rubber stoppers (Wheaton, lyophilization stopper) with screw cap size of 43 mm (VWR, Montreal, QC, Canada) as reactors. For model organic fraction of municipal solid waste (M-OFMSW) digestion, the concentration



(a) (b)

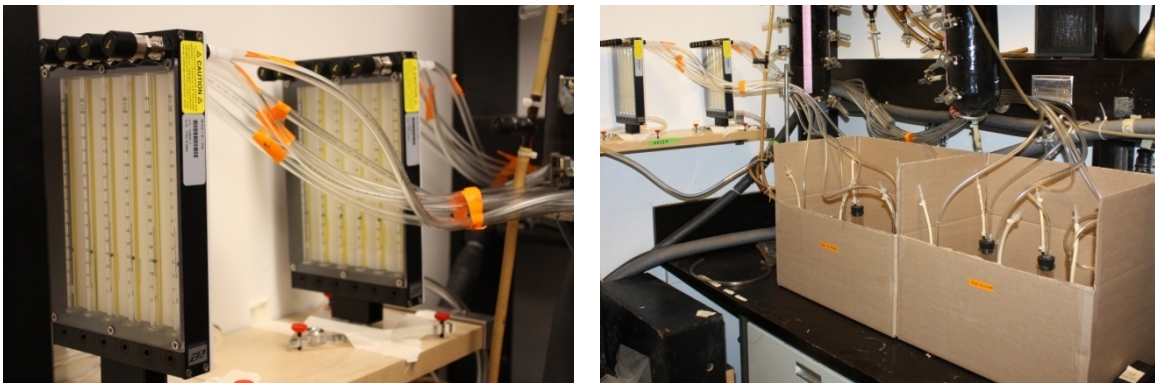
Figure A.2: BMP experimental set up (a) batch reactors and (b) incubator.

of COD used in the BMP assays was set approximately 7 g/L, which necessitated diluting the M-OFMSW with distilled water after pretreatment. A 120 mL volume of diluted, was added to 35 mL of acclimated inoculum in each reactor and mixed. Whole M-OFMSW was the sample as produced after or before pretreatment. The free liquid fraction was obtained by centrifuging the whole M-OFMSW sample at 9725 relative centrifugal force (RCF) for 40 minutes and decanting the liquid phase. Nitrogen was sparged through each bottle for 2 minutes prior to sealing the BMP bottles. BMP tests were performed at 33±1 ºC in an incubator shaker (PhycroTherm, New Brunswick Scientific Co. Inc, NB, Canada) rotating at 120 rpm. Biogas production was measured by using a manometer (Figure A.3).

Figure A.3: Manometer

A.3 Microaerophilic Condition

Microaerophilic (oxygen less than 1 mg/L) condition tests were done in 500 mL erlenmeyer flask (400 mL working volume).



(a) (b)

Figure A.4: Microaeration system, (a) flow meters and (b) reactors with microaeration

Flowmeters (WU-03215-76, Cole-Parmer System, Multi-Tube Frames, for Six 150 mm flowtubes, Common flow pattern; Aluminum wetted parts) kept the volume of injected air constant (3.11 mL/min), Pyrex course grained diffusing stones mounted on 8 mm diameter glass rod were used to introduce air to samples. The diffusing stone was 2 cm from the bottom of flask. The air was passed through a pressure regulator, then a disk shaped-Hepta filter then to an air flow meter with six parallel lines. Each line was connected to one reactor. Two flowmeters provided the air for total of 12 digesters (including duplicates) under microaeration. Another 12 reactors run without injecting air under completely anaerobic digestion (AD) condition. The duration of monitoring was 6 days which volatile fatty acids (VFAs) and pH were measured every day.

A.4 Semi-Continuous Anaerobic Digestion

The semi-continuous AD was performed using 1 L Kimax glass bottles (600 mL working volume) with 45 mm butyl rubber stoppers (Figure A.5 and Figure A.6). The acid phase digesters of dual stage systems were 500 mL bottles (200 mL working volume). Ports in the rubber stoppers were used to collect biogas and withdraw sludge and inject the feed. Tedlar bags (Chromatographic Specialties Inc., ON, Canada) were used to collect the gas and biogas production was measured by using a manometer. The reactors were kept in a New Brunswick incubator at a rotational speed of 95 rpm at 35±1 ºC. Reactors were fed semi-continuously (i.e. one feeding everyday). Volume of daily biogas collected was measured by a manometer.

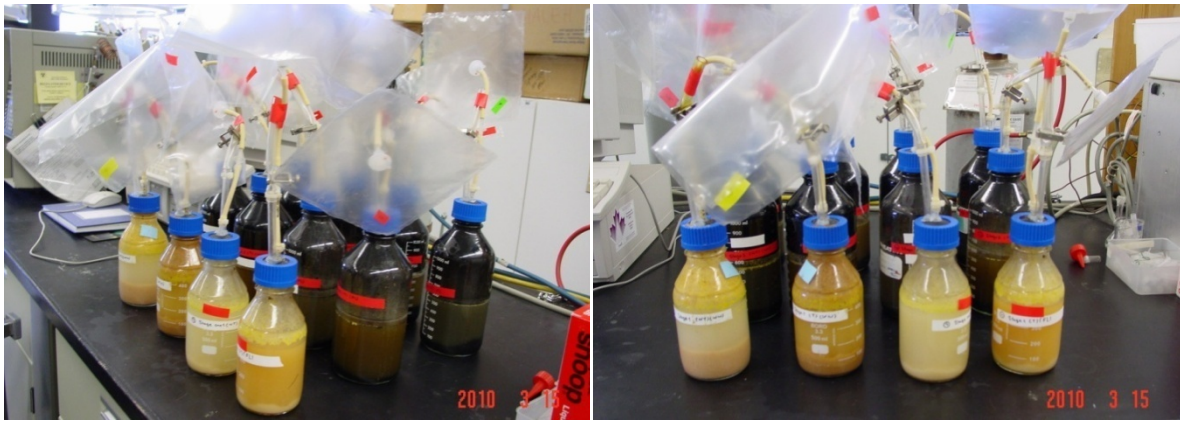


Figure A.5: Experimental set up for semi-continuous reactor

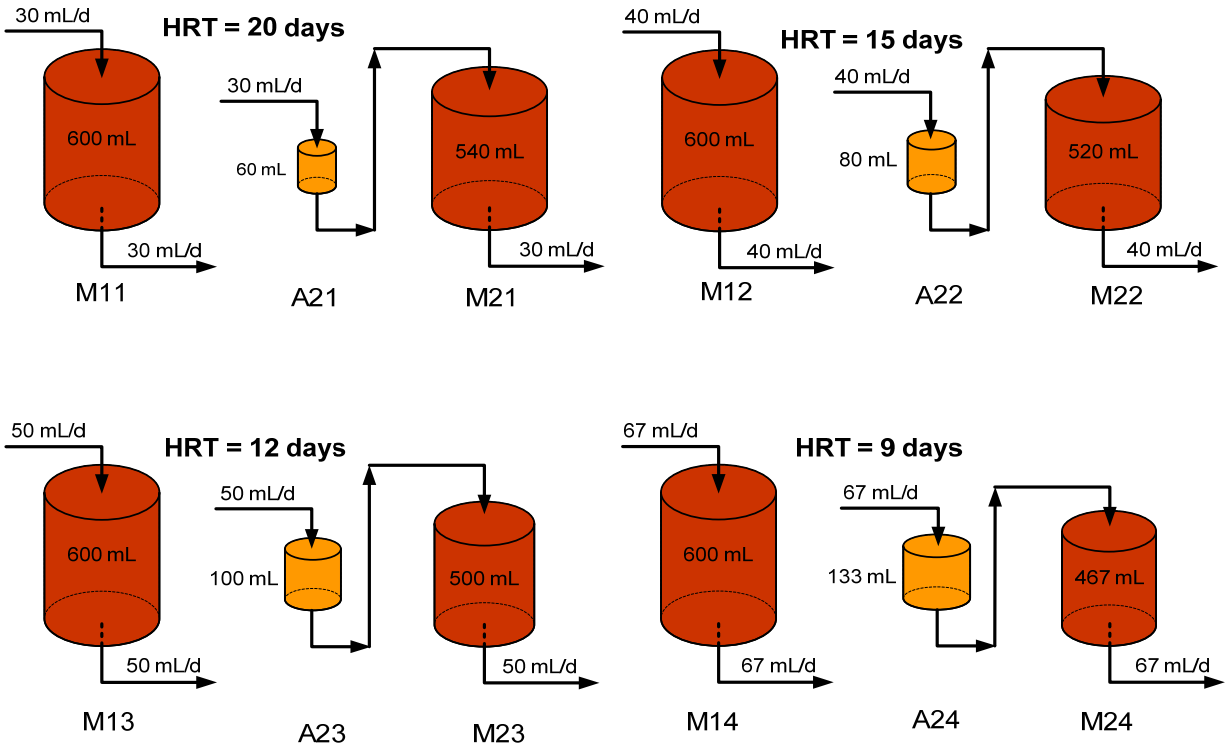


Figure A.6: Schematic of experimental set up for different hydraulic retention times