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Effect of Mild Microwave Pretreatment on Characteristics and Mesophilic Digestion of Primary Sludge

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EFFECT OF MILD MICROWAVE PRETREATMENT ON CHARACTERISTICS AND MESOPHILIC DIGESTION OF PRIMARY SLUDGE

by
Jian Zheng

A thesis submitted under the supervision of
Dr. Kevin Kennedy

In partial fulfillment of the requirements
for the degree of Master of Applied Science in Environmental Engineering

Ottawa Carleton Institute of Environmental Engineering
Department of Civil Engineering
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ABSTRACT

Wastewater treatment produces a large amount of contaminant-containing sewage sludge, disposal of which is of great concern and is tightly regulated. Anaerobic digestion of sewage sludge is used in most large-scale wastewater treatment plants prior to sludge end use or ultimate disposal mainly due to its advantages of low energy consumption and potential energy recovery. Thermal pretreatment has been studied and successfully applied to improve the quality of the digestion product. Microwave (MW) irradiation has become of interest with some advantages over conventional thermal pretreatment. The objective of this research is to investigate whether MW pretreatment can enhance the anaerobic digestion of primary sludge (PS).

The influence of MW irradiation on the characteristics of pretreated primary sludge was studied in terms of MW intensity, sludge solid concentration, and temperature achieved. The experimental range of sludge of sludge characteristics was sludge solid concentration of 1-4% (w/v) total solids (TS), temperature 35-90°C, and MW intensity of 40 and 80%. MW irradiation was found to increase the concentration of soluble COD (SCOD) in the sludge. The ratio of SCOD/TCOD increased from 2.5% to around 6-7% for 4% TS sludge and MW pretreatment temperature of 90°C. Both sludge solid concentration and MW irradiation temperature were shown to be the most important MW pretreatment parameters in solubulizing primary sludge. MW intensity in the range of temperatures studied had no impact on primary sludge solubilization.

Mesophilic biochemical methane potential (BMP) assays were applied to primary sludge pretreated at MW scenarios of 1-4% TS, temperatures 35-90°C, and MW intensity of 40 and 80%. Again, the BMP assay indicated no obvious difference in samples with the same TS concentration and pretreated to similar temperatures but at different MW intensities. Both higher MW pretreatment temperatures and higher TS concentrations significantly improved biogas production rate and reduced required digestion time to achieve 85% of ultimate digestion. For 4% TS primary sludge samples pretreated to 90°C, biogas production rate increased 37% or resulted in a 28% reduction in digestion

time to achieve 85% of the ultimate biogas production. There was some indication that MW pretreatment may have caused some very mild inhibition of the whole (soluble and suspended) sludge sample based on the existence of a 2-3 day lag phase for pretreated sludge samples. While MW pretreatment increased the rate of digestion of primary sludge it resulted in no significant increase in the ultimate biogas production and biodegradation of organic matter in terms of VS and TCOD removal. Analysis of biogas production results from the BMP assays indicated that they could be described by a first order reaction. The reaction rate constant increased with increase of TS concentration and MW pretreatment temperature, but was not affected by MW intensity.

BMP assay of the soluble fraction of pretreated primary sludge was carried out on 4% TS primary sludge pretreated at MW intensity of 80% and temperatures of 65°C and 90°C. The soluble fraction was shown to exhibit no methanogenic inhibitory effects.

In general MW pretreatment at the conditions tested did not result in any significant microbial inhibition and resulted in increased rate of primary sludge digestion without increase of the ultimate degradability of the sludge.

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NOMENCLATURE AND ABBREVIATIONS

a	Maximum Yield Coefficient
ALK	Alkalinity
ATP	Adenosine Triphosphate
b	Substrates Utilization Coefficient
BMP	Biochemical Methane Potential
BNR	Biological Nutrient Removal
BOD	Biological Oxygen Demand
C	Solid Concentration of Primary Sludge
CF	Centrifugal Force
COD	Chemical Oxygen Demands
COD_U	Soluble COD in Untreated Sample
COD_m	Soluble COD in Treated Sample
COD_a	Maximum Total Soluble COD in Alkalic Total Fusion Process (Alkaline 0.5mol/L for 22 Hours at Temperature 20 °C)
CST	Capillary Suction Time
DD_P	Solubilization of Protein
DD_{COD}	Solubilization of COD
DDcar	Solubilization of Carbon
DD_{BOD}	Solubilization of BOD
DR_0	Degree of Disintegration
DR_{COD}	Degree of Disintegration by COD
DS	Dry Solid Concentration
F	Solubilizaion Factor (SCOD/ Total COD)
F:M	Food to Microorganism
G-1000	Bacterial Lipase
GC	Gas Chromatograph
ISTD	Internal Standard Solution
HPH	High Pressure Homogenizer
HPP	High Pulse Power

HRT	Hydraulic Retention Time
k	Substrate Reduction Rate Coefficient
k'	Biogas Production Rate Coefficient
LC	Lysat Centrifuge
LCFA	Long Chain Fatty Acid
MAD	Mesophilic Anaerobic Digestion
MGD	Millions of American Gallons Per Day
MPN	Most Probable Number
MW	Microwave
NTU	Nephelometric Turbidity Unit
OLR	Organic Loading Rate
ORP	Oxidation Reduction Potential
O&M	Operation and Maintenance
PL-250	Poke Pancreatic Lipase
PS	Primary Sludge
Psup	Protein in Supernatant after Pretreatment
$Psup_0$	Protein in Supernatant before Pretreatment
Ptotal	Total Protein in Sample
R^2	Coefficient of Determination
r_g	Rate of Bacterial Growth
RCF	Relative Centrifugal Force
ROPEC	Robert O. Pickard Environmental Center (ROPEC) in Ottawa
S	Concentration of Substrate
S_μ	Ultimate Concentration of Substrate
SABR	Anaerobic Sequencing Batch Reactor
SBM	Stirred Ball Mill
SCOD	Soluble Chemical Oxygen Demands
SH	Shear-Gap Homogenizer
SRT	Solids Retention Time
SS	Suspended Solid
STOC	Soluble Total Organic Carbon

t	Digestion Time
T	Temperature
TCOD	Total Chemical Oxygen Demand
TOC	Total Organic Carbon
TS	Total Solid
TSS	Total Suspended Solid
TVFA	Total Volatile Fatty Acid
TWAS	Thickened Wasted Aerobic Sludge
UASB	Upflow Anaerobic Sludge Blanket Reactor
UD	Ultrasonic Disintegrator
UH	Ultrasonic Homogenizer
USEPA	United States Environmental Protection Agency
VFA	Volatile Fatty Acid
VFAs	Volatile Fatty Acids
VS	Volatile Solid
VSS	Total Volatile Suspended Solid
W	The Weight of The Prepared Crucible
W_0	Weight of Sludge Sample
W_1	Sludge Sample Weight after 103-105°C Treatment
W_2	Sludge Sample Weight after 550°C Oven Treatment
WAS	Wasted Activated Sludge
WW	Wastewater
WWTP	Wastewater Treatment Plant
X	Concentration of Microorganism
Y	Cumulative Biogas Production
Y_μ	Ultimate Cumulative Biogas Production
γ_{su}	Substrate Utilization Rate
μ	Specific Growth Rate of Bacterial Cells
Δp	Pressure Difference
α	Microwave Absorption Coefficient

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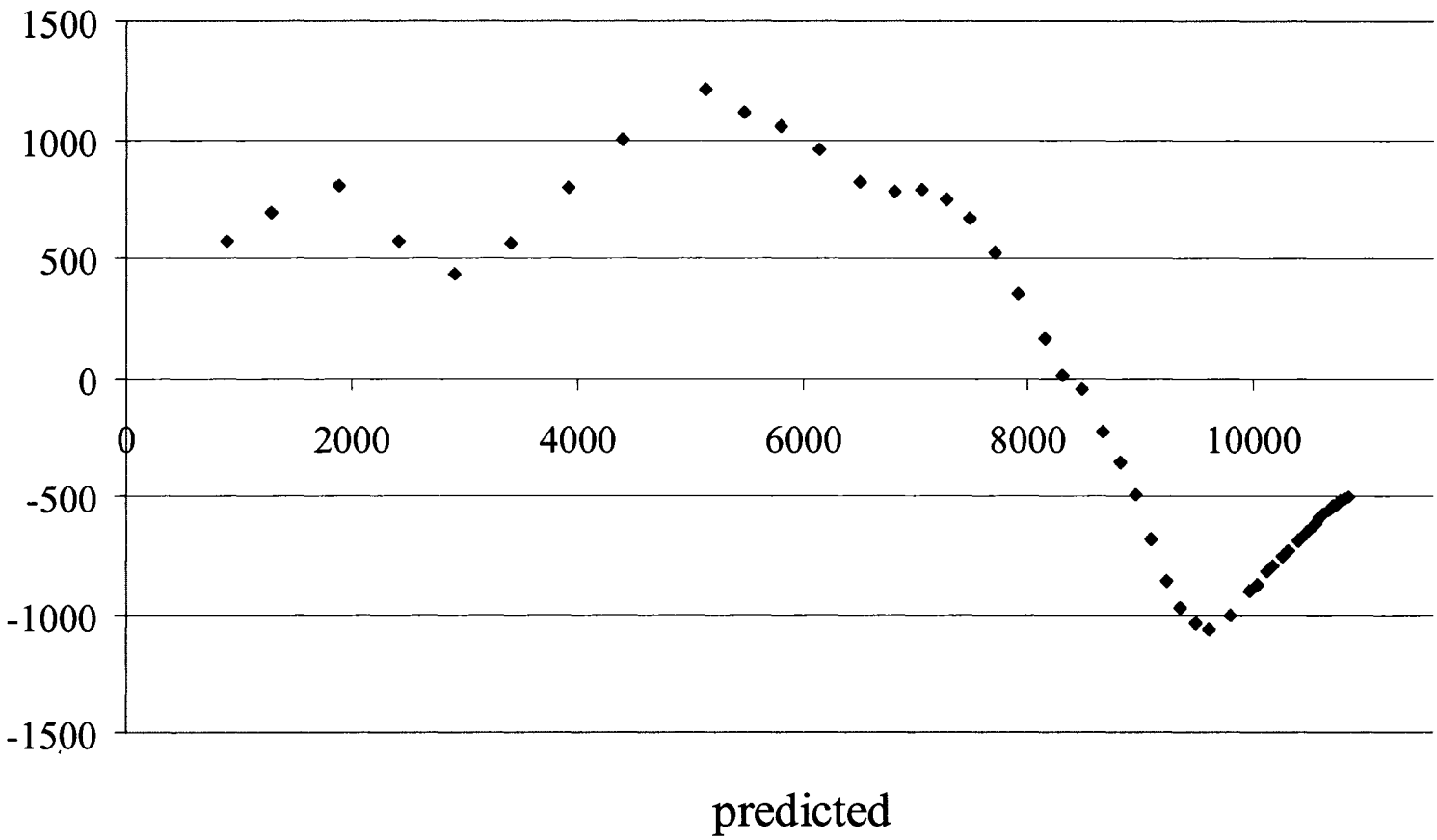
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CHAPTER 1
INTRODUCTION

1.1 Background

Municipal wastewater treatment has been developed to protect public health from infectious diseases and the environment from organic and inorganic contamination. Typical conventional wastewater treatment uses a series of processes, which include primary, secondary, and, in some cases, tertiary treatment. Physical, biological, and chemical technologies are employed in these processes to separate pollutant-containing solids from wastewater. Unfortunately, these separation processes also create large amounts of solid waste, so called sludge or sewage sludge.

Today, several options are available for municipal sludge treatment: stabilization (alkaline stabilization, anaerobic stabilization, aerobic stabilization, and composting) and heating drying. In spite of these methods of treatment, options for end use and ultimate disposal of treated sludge (biosolid) are very limited. In Canada, about 388,700 dry tons of annual biosolid are produced, about 43% are applied to land, 47% are incinerated, 4% are disposed in landfill, and 6% used for land reclamation and other uses (Apedaile, 2001). With the increasing public awareness of the pollution from incineration and landfill disposal, land application has been increasing recently. Land application also has the merit of lowest operation of cost, least land occupation, and resource reuse. However, the use of biosolids as a fertilizer can only be approved for biosolids that meet the most stringent standards. Obviously, new modifications of stabilization technology have become urgent due to the increasing environmental concerns and more restrictive regulations.

Typical large-scale wastewater treatment produces three main kinds of sludge: primary, secondary, in some cases, tertiary sludge. Presently, anaerobic digestion of mixed primary and secondary sludge is the most accepted sludge stabilization process. The advantages of this process include potential energy recovery from methane produced, low energy consumption, high organic loading rates, and low residue remaining for final disposal or use. As one of the sludge stabilization processing modifications, sludge

pretreatment technologies prior to anaerobic digestion process have been studied to improve either the extent of or rate of sludge stabilization. Some of these technology options are commercialized and successfully applied on existing facilities. (Müller, 2001)

Primary sludge (PS) consists of organic and inorganic particles from raw wastewater. Compared to secondary sludge, PS is more readily anaerobically degradable. The main obstacles existing in the degradation of PS are the big particle sizes and the highly degradation-resisting chemical structures. The difficulty in digestion of the secondary sludge lies in the microbial cell wall and membrane structure that acts as a barrier surrounding the interior organics and is strongly resistant to hydrolytic enzymes. The study of pretreatment technology aims to improve the solubility of sewage sludge by either disrupting the bacterial cell wall or deamalgamating organic particles. Among these methods, thermal pretreatment and alkaline pretreatment provide the digested sludge with the potential to meet the stringent requirement for land application by significantly destroying pathogens remaining in the sludge and substantially reducing biosolids volume for transportation and disposal. In comparison to conventional heating, the thermal effects from microwave irradiation have the advantages of higher energy efficiency, shorter processing time, more uniform heating, and easy control. The alleged athermal effect from microwave irradiation is another possible advantage researchers are looking for. All these positive characteristics make microwave irradiation a promising innovative pretreatment option.

1.2 Research Objectives

The overall purpose of this study is to assess the influence of microwave irradiation pretreatment on the anaerobic stabilization of primary sludge from the municipal wastewater treatment plant (ROPEC) in Ottawa. This objective will be met through the following specific objectives:

- Investigate the effect of microwave pretreatment on the characteristics of primary sludge. The investigated factors include microwave intensity, sludge solid concentration, and temperature achieved.

- Employ biochemical methane potential (BMP) assays to compare the biodegradability of pretreated primary sludge and untreated primary sludge. Investigated factors also include microwave intensity, sludge solid concentration, and temperature achieved.
- Conduct BMP assays on the soluble fraction of pretreated primary sludge to assess possible inhibition of microbial activity by soluble toxic compounds produced from microwave irradiation.
- Examine the suitability of a method for determining maximum disintegration of primary sludge in an attempt to assess the level of sludge disintegration from MW pretreatment.

1.3 Outline of Thesis

This thesis consists of five chapters and three appendices. Chapter 2 presents the literature review of relevant background knowledge, summarizes research achievements of various pretreatment methods, and briefly describes the mechanism of microwave irradiation. Chapter 3 describes the material and analytical methods used to conduct all the experiments performed in this study. Chapter 4 presents the data analysis and discussion. Lastly, based on the experimental results, conclusions and recommendations for future study are made in chapter 5. Appendixes include the characteristics of sludge used in the experiment and some supplementary information not included in chapter 4.

CHAPTER 2
BACKGROUND AND LITERATURE REVIEW

2.1 Biosolids Background

The term *sludge* is often applied to both inorganic and organic biosolids before treatment to meet beneficial use criteria. Thus *sewage sludge* should be the more accurate term for the sludge from municipal wastewater treatment plants. According to the United States Environmental Protection Agency (USEPA), after treatment to meet regulation 40 CFR503 (USEPA, 1994), sewage sludge can be categorized as *biosolids* and ready for beneficial reuse. Biosolids contain inorganic material (including trace elements), organic compound, and pathogens (Epstein, 2003; Metcalf & Eddy, 2003). Regulation 40 CFR503 also classifies biosolid products into two categories, class A and class B.

2.1.1 Characteristics of Municipal Sludge

In most municipal wastewater treatment plants, sludge is comprised of primary sludge from the primary clarifier before biological treatment and the secondary sludge from the secondary clarifier right after biological treatment. The primary sludge consists of the large organic and inorganic particles from the raw wastewater and is influenced by the wastewater source, weather conditions, and primary clarifier operation. The secondary sludge is composed of the excess microorganism cells and affected by the biological process employed and its mode of operation. The wasted secondary sludge from activated sludge system is referred to as waste activated sludge (WAS). Typical chemical and physical properties of primary and secondary sludge are presented in the Table 2.1. As can be seen in Table 2.1, comparing to secondary sludge, primary sludge has relatively higher dry solid concentration, higher grease and fat concentration, lower protein content, and higher cellulose content.

Table 2.1 Typical properties of municipal sludge.

Item	Primary sludge		Secondary sludge
	Range	Typical	Range
Specific gravity of sludge		1.02	1.005
Total dry solid (TS) %	5-9	6	0.8-1.2
Volatile solids (% of TS)	60-80	65	59-88
Grease and fats (% of TS)			
Ether soluble	6-30	—	—
Ether extract	7-35	—	5-12
Protein (% of TS)	20-30	25	32-41
Nitrogen (N, % of TS)	1.5-4	2.5	2.4-5.0
Phosphorous (P_2O_5, % of TS)	0.8-2.8	1.6	2.8-11
Potash (K_2O, % of TS)	0-1	0.4	0.5-0.7
Cellulose (% of TS)	8-15	10	—
Iron (not as sulfide)	2.0-4.0	2.5	—
Silicon (SiO_2, % of TS)	15-20	—	—
PH	5.0-8.0	6.0	6.5-8.0
Alkalinity (mg/L as $CaCO_3$)	500-1500	600	580-1100
Organic acid (mg/L asHAc)	200-2000	500	1100-1700
Energy content, kJ TS/g	23,000-29,000	25,000	19,000-23,000

Source: Adapted from Metcalf & Eddy (2003)

2.1.2 Municipal Sludge Treatment, Disposal and Reuse

There are several options for municipal sludge treatment, disposal, and reuse. A brief summary is shown in Fig. 2.1. Among those, land application has contributed the most in terms of a sludge disposal solution, and the anaerobic digestion process is the major treatment method prior to land application and disposal. As a matter of fact, the present focus on energy recovery and conservation and the potential beneficial reuse of anaerobic digested sludge will continue to contribute to the dominant position of anaerobic digestion.

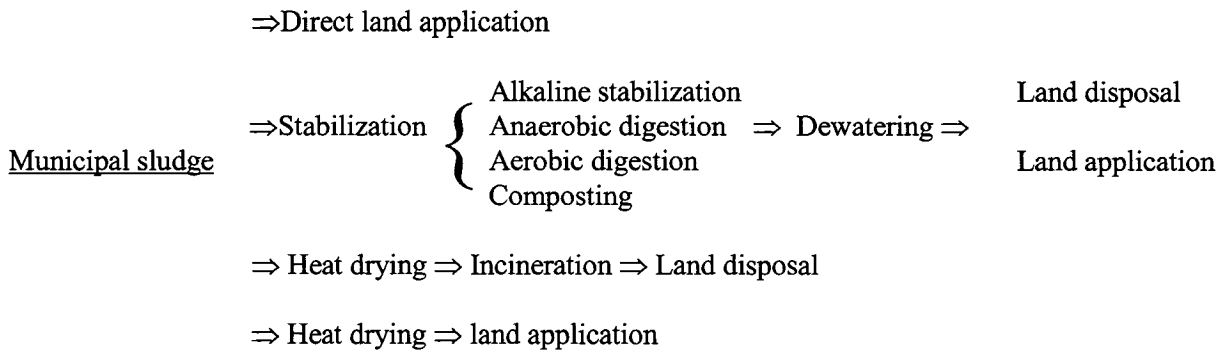


Fig. 2.1 Municipal sludge treatment, disposal, and reuse.

Source: Adapted from Epstein (2003) and Metcalf & Eddy (2003)

2.1.3 Land Application Considerations

Land application of treated sludge includes beneficial use in agriculture, horticulture, forestry, and land reclamation. The organic components in biosolid can improve soil physical properties, increase the soil microbial population, and furthermore, act as a fertilizer to provide better root growth and higher plant production (Epstein, 2003).

Because of the increasing pretreatment of industrial wastewater prior to discharge into the municipal sewage system, the concentration of heavy metals in biosolids has been decreasing in the last decade, and meet regulation 40 CFR Part 503 issued by USEPA. Biosolid's safety from heavy metal toxicity has also been confirmed by animal tests. Toxic organic compound concentrations in biosolids used in land disposal have been regulated in some European countries, but remain as a potential legal issue in North America. However, the incomplete reduction of organic compounds and remaining pathogenic microorganism in the stabilized residue present a potential risk to the environment and public health. Sludge treatment facilities also have great interest in decreasing the biosolid volume for transportation and final handling to reduce the capital and operating costs (Epstein, 2003).

USEPA issued "The Standards for The Use or Disposal of Sewage Sludge, Title 40 of The Code of Federal Regulations, Part 503", and its amendments. This standard sets

Pathogen requirements in sludge which are regulated by designating two classes of sludge: Class A and Class B. Class A sludge should meet one of the following requirement: a fecal coliform density of less than 1000MPN/g total dry solids (TS), a *salmonella* sp. density of less than 3 MPN/4g TS, treated at high temperature for a variable period of time depending on the temperature reached and sludge concentration, treated by alkaline, or tested for enteric viruses/viable helminth ova. Class B requirement is easier to meet in respect to pathogen concentration but its reuse and disposal are limited by site restrictions (Epstein, 2003).

2.2 Municipal Sludge Digestion Modification

During anaerobic digestion, energy is recovered through CH_4 production, most organic matter is removed, and solid volume is substantially decreased for reuse and disposal. It consumes less energy compared to aerobic digestion. But tightened regulatory policy and raised public concerns on environmental issues has resulted in increasing treatment requirements and further transformation of biosolids into a safer and more environmental benign and more useful commodity. Effort to further increase organic matter stabilization and pathogen removal reflects these requirements.

Several modifications of the anaerobic digestion process can be made to try to achieve better biosolids products. (Parker & Beland, 2003)

- Pretreatment technology prior to mesophilic digestion
- Digester operation (enhanced mixing, series operation, sludge recycling, thermophilic operation)
- Implementation of advance digestion technologies (temperature phased anaerobic digestion, 2-phase digestion)

2.3 Background Theory of Anaerobic Treatment of Municipal Sludge

2.3.1 Microbiology of Anaerobic Digestion

Digester type and operating conditions, in addition to the waste composition, define the functional anaerobic microorganisms in terms of species present, numbers, and their organization (Archer & Kirsop, 1991). However, in most cases, five different functional

groups of bacteria are involved in the anaerobic digestion of organic waste specifically (Parkin & Owen 1986). The interaction among the different bacterial species is known to include consumption, production, competition, and environmental mediation through their metabolism activity. Thus, a balance among bacterial species is the essence to achieve successful anaerobic stabilization.

Nevertheless, in terms of control, the anaerobic digestion process can be simplified into four steps: (1) hydrolysis → (2) acidogenesis → (3) acetogenesis → (4) methanogenesis (Figure 2.2). Moreover, hydrolysis and acidogenesis can be combined and referred simply to as hydrolysis (Archer & Kirsop, 1991).

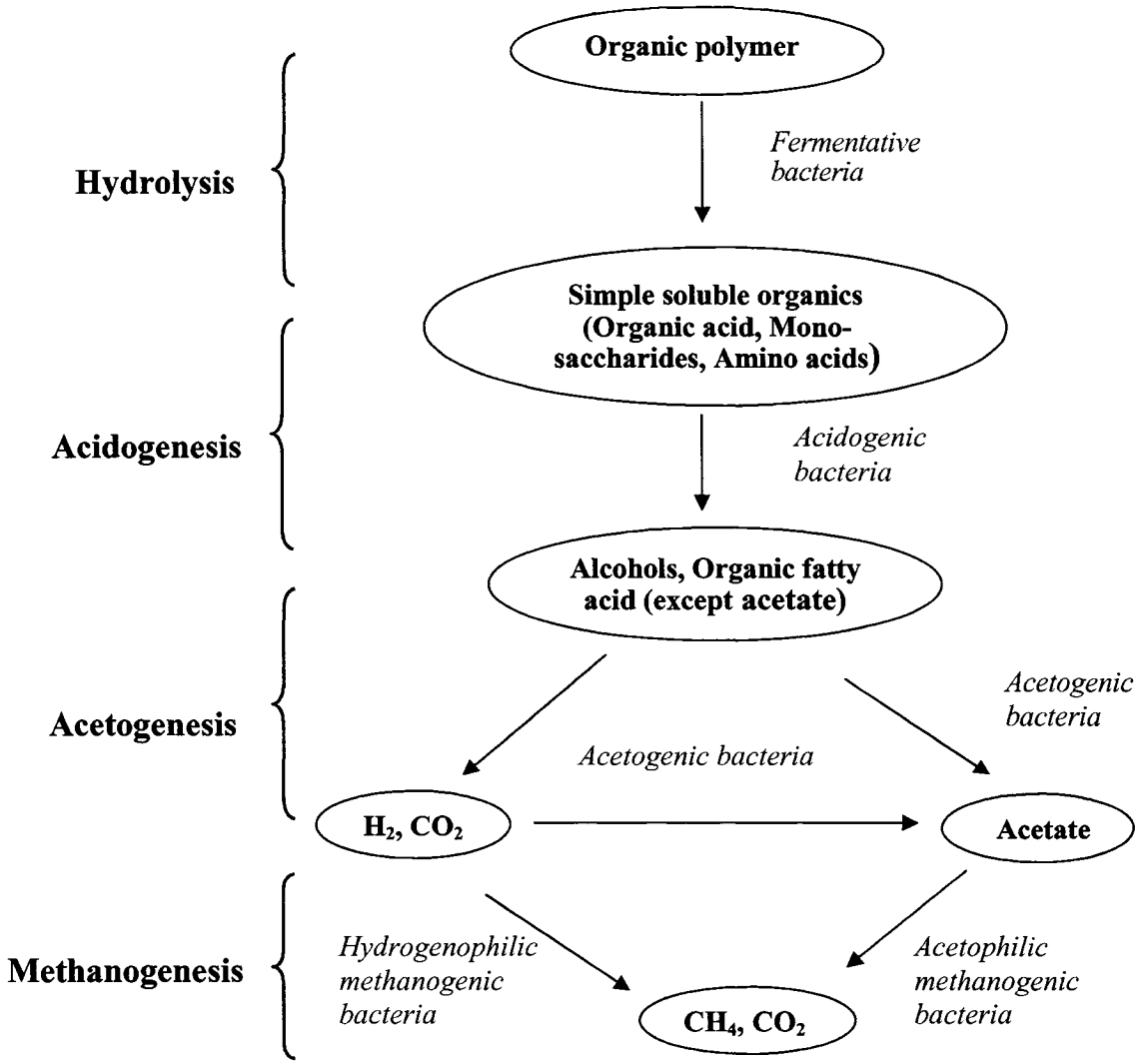


Fig. 2.2 Microbiology of anaerobic digestion metabolism.

Source: Adapted from Archer & Kirsop (1991), Kennedy (2004), and Metcalf & Eddy (2003)

Hydrolysis transforms large, complex soluble and insoluble molecules and particles into smaller soluble molecules suitable for transportation into the bacteria cell. Hydrolysis occurs as the result of the extercellular enzymes secreted by fermentative bacteria. The importance lies in the fact that, for complex substances, no further stabilization can be obtained without completing this step. In most cases, this is the rate-limiting step of sludge digestion (Archer & Kirsop, 1991; Metcalf & Eddy, 2003).

Acidogenesis converts hydrolysis products into long chain organic acids, sugars, and amino acids. It is performed by acidogenic bacteria (Archer & Kirsop, 1991; Metcalf & Eddy, 2003).

Acetogenesis eventually transfers organic compounds into H_2, CO_2, and short chain fatty acids, the most common of which is acetic acid. It is performed by the acetogenic bacteria (Archer & Kirsop, 1991; Metcalf & Eddy, 2003).

Methanogenesis converts the intermediate compounds of acetogenesis into end product, mainly CO_2 and CH_4. It is performed by complete-oxygen-inhibited methanogenetic bacteria, so called methanogens (Archer & Kirsop, 1991; Metcalf & Eddy, 2003). Methanogenesis is the final stabilization of organic substance. The escaping CH_4 gas recovered contains most of the energy from organic decomposition. CO_2 either escapes as gas or dissolves and then is converted into bicarbonate alkalinity (Kennedy 2004).

Among all the bacteria groups involved in the anaerobic digestion, methanogens are the most selective in terms of substrates utilized and the most sensitive to environmental condition. Only a limited range of substrates may supply their energy demand. Methanogens can be categorized into two functional groups. Most methanogens utilize $H_2 + CO_2$ to form CH_4 and therefore are known as H_2-utilizing methanogens. The second group, named acetate-utilizing methanogens, forms methane from acetic acid. A few acetate-utilizing species are more versatile in substrate and can also use $H_2 + CO_2$, methanol and methylamines, in addition to acetic acid (Archer & Kirsop, 1991).

The stoichiometric equations and free energy release for standard conditions for these two reactions are:

$H_2 + CO_2$

$$4H_2+H^++HCO_3^- \rightarrow CH_4+3H_2O \quad -136KJ/mol \tag{2.1}$$

Acetate

$$CH_3COO^-+H_2O \rightarrow CH_4+HCO_3^- \quad -30KJ/mol \tag{2.2}$$

H_2 and acetic acid serve as both final products of acetogenetic reduction and CH_4 forming substances. Additionally, instead of producing reduced organic acid, some of the acid-producing bacteria can also produce hydrogen by passing the electron to the hydrogen ion. Once the H_2 partial pressure is greater than approximately 10^{-5} atmosphere, the increased H_2 level may inhibit the degradation of propionic acid and butyric acid, as well as the metabolism activity of acetic acid-utilizing methanogenesis and some hydrogen-utilizing methanogenesis. Meanwhile, accumulation of organic acid causes pH decrease and an unsuitable environment for sensitive methanogenic bacteria. So there is a need not only to focus on methanogenic bacterial activity but the balance between non- methanogenesis (especially acetogenesis) and methanogenesis required in order to maintain a healthy digestion (Archer & Kirsop, 1991).

2.3.2 Anaerobic Digestion of Municipal Sludge

The most significant characteristics of municipal sludge is its insoluble nature, which results in hydrolysis being the rate-limiting step, while methanogens and other non-hydrolytic bacteria affect the hydrolysis process by removal of the decomposition products (Noone, 1991).

Organic polymers present in primary sludge are carbohydrates, proteins, and lipids, but mainly carbohydrates. Carbohydrates particles are hydrolyzed to smaller sugar molecules and then further degraded into volatile fatty acids (VFAs). Proteins are eventfully fermented into ammonia, VFAs, CO_2, hydrogen gas, and reduced sulphur. Lipids, mainly neutral fats and long chain fatty acids (LCFA), are degraded by the H_2-producing acetogenic bacteria into organic acid (Mohmoud, *et al,*. 2004). Generally, it is believed

that the degree of primary sludge stabilization is dependent on lipid hydrolysis by the fact that the first-order hydrolysis constant of lipid is only 2-50% of that of protein and carbohydrate (Masse, 2002). Additional factors affecting degradation are the particle size and particle structure. (Kennedy, 2004) The difficulty in hydrolysis of secondary sludge is due to its cellulose structure, which acts as a barrier surrounding the interior organics and is strongly resistant to hydrolytic enzymes (Noone, 1991).

In fact, not all organic compound present in municipal sludge can be hydrolyzed and not all hydrolysis products can be completely biologically stabilized. The sum of non-biodegradable components (so-called refractory compounds) compose the ultimate remaining organic fraction of the digestion residue.

2.3.3 Monitoring and Analysis of Anaerobic Digestion

Anaerobic digestion systems are usually very stable even at hydraulic retention times (HRT) of 10-15 days. The exceptional situation could be from some extreme conditions such as wide loading variation, beyond-limit environmental change, and unreliable process equipment. Considering the availability of many reliable monitoring sensors, it is suggested that only three parameters should be continuously monitored in practice: temperature, gas production and analysis, and sludge quantity (Noone, 1991). Gas production is sensitive to normal operating variation such as periodic feeding (Noone, 1991). Temperature has a significant effect on the biological solid dewatering) (Metcalf & Eddy, 2003). Regularly analyzed parameters include reduction of organic matter, pH, alkalinity (ALK), VFA concentration, ammonia concentration, and specific inhibitors (Noone, 1991). Combined comparison of pH, ALK, and VFA concentration gives indications of digester stability such as: acidity, pH buffering capacity, and the balance between acetogenesis and methanogenesis. Typical operational values are shown in Tables 2-2, 2-3, 2-4, and 2-5.

Table 2.2 Typical anaerobic digestion values for municipal sludge.

Items	Typical value
VS reduction (%)	
Primary sludge	40-70
WAS	30-50
COD removal (%)	
Primary sludge	40-60
WAS	30-45
Biogas yield (L/g VS destroyed)	
Primary sludge	1.00
WAS	0.75
Biogas composition (% volume)	
Methane	65-70
Carbon dioxide	30-35

Source: Adapted from Parkin & Owen (1986) and Malina & Pohland (1992)

Table 2.3 Environmental factors in anaerobic digestion operation.

Items	Optimal operational condition	Extreme operational condition
Temperature (°C)	32-37	20-42
pH	6.6-7.4	6.3-7.9
Volatile acids (mg/L as acetate)	50-500	2000
Alkalinity (mg/L as $CaCO_3$)	2000-3000	1000-5000
OLR as volatile solids ($kg/m^3/d$)	0.8-2.0	0.4-6.4
HRT (days)	12-18	7-30

Source: Adapted from Metcalf & Eddy (2003) and Kennedy (2004)
OLR: organic loading rate
HRT: hydraulic retention time, equal to the value of SRT in the completely mixed digester
SRT: solid retention time

Table 2.4 Inhibitor limits.

Items	Inhibition by single dose (mg/L)	Inhibition by continued supply (mg/L)
Free Ammonia	100	200
NH_4^+	3,000 (unclear situation)	
H_2S	250	1000
CN^-	5	100
Trichloromethane	1	50
Formaldehyde	100	400
Nickel	200	50

Source : Adapted from Henze *et al.* (2002)

Table 2.5 Inhibitor Limits (continued).

Items	Stimulatory concentration (mg/L)	Moderately inhibitory concentration (mg/L)	Strongly inhibitory concentration (mg/L)
Ca^+	100-200	2500-4500	8000
Mg^+	75-150	1000-1500	3000
K^+	200-400	2500-4500	12,000
Na^+	100-200	3500-5500	8000

Source: Adapted from Speece (1996)

2.3.4 Dewatering

For digested sludge dewatering may be the only required process before reuse. A dewatered non-fluid material is also non-offensive (odour), easier to handle, and much less expensive to transport. Four major phases of water exist in the sludge particles:

- Free water
- Capillary water
- Colloidal water

- Intracellular water

Free water is easily to be separated by gravity. Capillary water and colloidal water is bound inside the particle flocs and can only be removed by pressurized mechanical dewatering methods. Intracellular water has to be separated by heat drying in the pelletization process. In anaerobic stabilization practice, most of the biosolid is treated by pressurized mechanical facilities (Outwater, 1994).

After pressurized mechanical dewatering, digested primary sludge usually can achieve cake concentrations of 24-35%. Digested WAS, due to the fact that large quantity of intracellular water are not available for mechanical removal, can only reach solid concentration of 12-20%. Mixtures of digested WAS and primary sludge, unsurprisingly, reach the middle value of 15-20%. Chemical conditioning prior to mechanical dewatering can increase the dry solid concentration by 20-30% (Metcalf & Eddy, 2003).

2.4 Pretreatment Methods

2.4.1 Overview of Pretreatment Technologies Application

Several pretreatment technologies have so far been developed and applied to improve sludge handling. According to Müller (2001), the purpose of application of sludge pretreatment technology is to "enhance the sludge stabilization and disposal, bulking and foaming, dewatering, nitrogen and phosphorus removal, and pathogen reduction". However this review only focuses on the effect of pretreatment methods on sludge stabilization, pathogen reduction, as well as conditioning and dewatering.

Based on the mechanism of sludge disintegration, the applied pretreatment technologies mainly involve physical mechanisms, such as

- Mechanical pretreatment
- Ultrasonic pretreatment
- Thermal pretreatment

or chemical mechanisms, such as

- Chemical pretreatment

- Ozonation

or biological mechanism, such as

- Enzymatic pretreatment

or the combination of several mechanisms, such as

- Thermochemical pretreatment
- MicroSludge (chemical and mechanical pretreatment)

Most pretreatment technologies target at improving solubility of waste by hydrolysis, while some improve solubility and remove inhibitory compounds by oxidation (ozonation and enzymatic pretreatment).

Müller (2001) summarized the various pretreatment technologies in terms of operational behavior, subsequent sludge treatment processes, as well as operational and maintenance (O&M) cost. Detailed information is shown in the table 2.6, table 2.7, and table 2.8.

Table 2.6 Operational behavior of different pretreatment technologies.

	Mechanical pretreatment					**Thermal pre-treatment**	**Chemical pretreatment**		**Biological pre-treatment**	**Freeze/thaw pre-treatment**
	LC	**HPP**	**HPH**	**SBM**	**UD**		**Ozone**	**Acid/ Alkaline**		
Low energy consumption	+	+	0	0	-	- [TH]	0	++	++	--(++)[1]
Resistance to wear	+	-	--	+	+	-	0	0	++	+
Reliability of operation	+	+	-	+	+	0	0	+	+	+
Extent of research experiences	0	-	0	+	+	+	+	0	0	+
Stage of development for WWTP-application	+	-	-	+	+	+	+	+	+	0

Adapted form Müller (2001)

++ very good, + good, 0 middle, -poor, -- very poor

[TH] thermal energy, [1] natural freezing

LC: Lysat centrifuge, HPP: high pulse power, HPH: high pressure homogenizer, SBM: stirred ball mill, UD: ultrasonic disintegrator

Table 2.7 Different pretreatment technologies on subsequent sludge treatment process.

	Mechanical pre-treatment	Thermal pre-treatment	Chemical pretreatment		Biological pre-treatment	Freeze/thaw pre-treatment
			Ozone	Acid/Alkaline		
Rate of sludge degradation	++	+	+	++	+	0
Degree of sludge degradation	+	0	++	0	0	0
Bacteria disinfection	+	++	+	+	0	+
Amount of flocculants needed	-	0	--	-	-	0
Influence on the dewatering results	0	+	0	+	0	++
Concentration of recalcitrant	0	-	-	-	0	0
Pollution of sludge liquor	-	-	-	-	-	-
Generation of odor	0	--	-	-	-	0

++ very good, + good, 0 middle, -poor, -- very poor

Adapted form Müller (2001)

Table 2.8 Capital and O&M costs of different pretreatment technologies.

	Mechanical pre-treatment	Thermal Pre-treatment	Chemical pretreatment		Biological pre-treatment	Freeze/thaw pretreatment
			Ozone	Acid/ Alkali		
Capital costs	Medium	High	Medium	Low	Low	Low or [1] medium
Operational and maintenance costs	Medium to high	High or low[2]	Medium to high	Medium	Low	Low or high [1]

1) The cost could be quite low if natural freezing were feasible

2) The O&M cost could become low if free waste steam is available

Adapted form Müller (2001)

2.4.2 Measurement of Extent and Effect of Pretreatment

Various techniques and methods of evaluation of the extent of pretreatment have been proposed. Equations 2.3-2.6 summarize the parameters meant to determine the degree of cell rupture, cell disintegration, and cell rupture respectively. These equations utilize COD solubilization as a method to measure sludge pretreatment.

Cell Rupture (%)

$$Cell\ rupture\ (\%) = \frac{Present\ soluble\ protein\ concentration}{Maximum\ soluble\ protein\ concentration} * 100\% \qquad (2.3)$$

In case of cell rupture, maximum soluble protein concentration can be determined by two methods. One is to rupture the cells by using cell rupture equipment, such as a French press (500 bars). The second one is to rupture the cells in a glass tube with 1% aluminum powder at 2000 rpm for 20 minutes using a frictional bar. (Hwang *et al.*, 1997)

Degree of Disintegration by COD

$$DR_{COD} = (COD_m - COD_U)/(COD_a - COD_U) \qquad (2.4)$$

COD_U ---- *Soluble COD in untreated sample*

COD_m ---- *Soluble COD in treated sample*

COD_a ---- *Maximum total soluble COD in alkaline total fusion process (alkaline 0.5mol/L for 22 hours at temperature 20 ℃)*

(Müller *et al.*, 1998)

COD Solubilization (Solubilization Factor F)

$$COD\ solubilization\ (\%) = \frac{Soluble\ COD\ after\ pretreatment}{Total\ COD\ after\ pretreatment} * 100\% \qquad (2.5)$$

(Baier & Schmidheiny, 1997; Kim *et al.*, 2003)

Solubilization of Protein

$$DD_P = \frac{Psup - Psup_0}{Ptotal} \qquad (2.6)$$

Psup – protein in supernatant after pretreatment

$Psup_0$ – protein in supernatant before pretreatment

Ptotal – total protein in sample

(Gonze *et al.*, 2003)

2.4.3 Mechanical Pretreatment

Mechanical pretreatment includes

- Jet and smash
- Ball milling
- Shear milling
- Grinding
- Ultrasonic disintegration (reviewed separately in Section 2.4.4)

2.4.3.1 Jet and Smash

In laboratory-scale jet and smash treatment, a high-pressure pump jets intact WAS out of a nozzle on to a collision-plate. The intact WAS is crushed into small pieces under the affect of high pressure, collision and the dramatic speed change (Hwang *et al.*, 1997).

Hwang *et al.* (1997) conducted jet and smash treatment on thickened WAS (mean TS 1.7%) at jet speeds of 30-100m/s and pressures of 5-50 bar. Nah *et al.* (2000) also tested jet and smash treatment on thickened WAS (mean TS 1.4-1.8%, VS1-1.2%) at jet speeds of 30-100m/s and pressures of 10-40 bar. In experiments performed by Choi *et al.* (1997) on WAS, pretreatment pressures were 5-50 bar and jetting frequency was 1-12 times/s. Their experiments revealed a similar effect for pretreatment. During jet and smash disruption, the most significant changes were for particle size, SCOD, STOC, and soluble protein concentration. The reduction of particle size and increase in SCOD and soluble protein concentration from each study were in good agreement with one another. In Nah

et al.'s (2000) study, after pretreatment at 40 bar, SCOD increased about 3.3 fold from 240 to 800mg/L, soluble protein increased 2.7 fold from 450 to 1200mg/L, and SS decreased from 2.07% to 1.92%. In Hwang *et al.*'s (1997) experiment, mean particle size dropped from 69.1μm in raw WAS to 21.6μm for WAS pretreated at pressure of 30 bar and to 18.7 μm at 50 bar.

In subsequent batch mesophilic anaerobic digestion (MAD) experiments conducted by Huang *et al.* (1997), the efficiency of VS removal improved proportionally with the increase of pretreatment pressure up to 30 bar. Results of the batch test showed that, in terms of energy efficiency, the most promising operational pressure was 30 bar (VS removal 50%) since experimental pressures of 40 and 50 bar caused little further improvement in VS removal. In Nah *et al.*'s (2000) research, 1.2L continuous MAD reactors fed with untreated and sludge pretreated at 30 bar were compared. By shortening the SRT of pretreated digester from 13 to 6 days, no obvious decreases in VS reduction (30%), biogas yield (790-850 L/kgVS removal), and gas composition were observed. The reactor treating raw WAS was unstable and could not be operated at the lower SRT. Untreated sludge achieved a biogas yield of 610 L/kgVS removed and VS reduction of 24% under SRTs of 20-30 days.

2.4.3.2 Ball Milling

Baier and Schmidheing (1997) pretreated various kinds of WAS based on sludge age by ball milling at revolution speed of 2000, 3200, and 4200 rpm, using ball diameters of 0.2-1.5mm. They reported that, the effect of ball milling depends on the age of the sludge. Extended aeration sludge (TS 3.3%, SCOD 45mg/L) achieved solubilization increases up to 1080 mgCOD/L during pretreatment. In the subsequent BMP tests, pretreated extended aeration sludge generated an overall biogas production increase of 162%, VS removal increase of 200% from control values of 8.4%. COD reduction improved from 10.6% to 14.9%. However, anaerobic degradation of conventional WAS (SRT 5-7 days) did not change significantly after milling even though milling did raise the COD solubilization factor by 50-100%. This would suggest that if the WAS is easily degraded pretreatment has less impact on the extent of degradation.

Baier and Schmidheing (1997) also reported that anaerobically stabilized and aerobically stabilized sludge (primary-secondary sludge ratio not reported) behaved differently in milling treatment. After ball milling, aerobically stabilized sludge sample increased SCOD/TCOD ratio 3.75 fold from the original SCOD concentration of 95mg/L, a gas production increased 24%, and a VS removal increased from 38% to 50%. In comparison, ball milling resulted in no substantial increases in solubilization and the extent of subsequent MAD degradation for the anaerobically stabilized sludge.

In terms of COD solubilizaion (SCOD/ total COD), higher revolution speeds (4200rpm) significantly enhanced sludge disintegration.

2.4.3.3 Shear Mill

Müller *et al.* (2003) successfully applied high intensity shear technology to actively digesting solids from different wastewater treatment plants using a MAD digester equipped with and inline shear mill system. They reported that, in batch MAD tests, maximum gas production increased an average of 15% to 1.17 L biogas/Lsample, overall VS reduction increased an average of 30% from 14 to 20% VS destruction. Additionally in the first-56-hours of digestion a 33% sheared to 67% raw sludge mixture (VS 1.98%) the biogas production rate increased 46% to 10.6 mL biogas/L sample, which suggested that a significant amount of the solubilized and disrupted biomass was readily biodegradable. During full-scale operation on a 4.5 MGD domestic wastewater treatment plant with primary MAD and secondary unheated digester (SRT 30 days), the average TS reduction increased 21% in the primary digester and 17.2% in the secondary unheated digester or settler. Corresponding, VS reduction increased 21% in the primary digester and 11.1% secondary tank compared to previous no pretreatment conditions. No inhibition was observed from bio-floc disruption and methanogen-acidogen consortia by intensive shearing. Gas compositions and VFA concentrations remained stable, as well as most probable number (MPN) for total and fecal coliforms in effluent sludge, indicating that the digesters were more efficient and healthy after use of the internal shearing system.

One important note was that the colloid load in the primary MAD digester was increased by a factor of 3 by introducing shearing pretreatment. Correspondingly, average colloid (particle size 1.5-0.2μm) removal improved from 10.9 to 28.3 mg COD/gVS added and sub-colloid (particle size 0.2-002μm) COD levels increased from 4.8 to 7.2 mgCOD/gVS added.

The polymer demand, defined as "the polymer dose that gives the lowest capillary suction time for both the primary and secondary digesters during the course of study" increased 84.4% to 10.8g-polymer/kg-TS in primary digester effluent and decreased 12.4% for the secondary unheated settler to 5.3 g-polymer/kg-TS compared to the control non-shear situation. Overall, it was suggested that shear pretreatment reduced the dewaterability indicating greater use of polymer was required.

2.4.3.4 Comparison Between Stirring Ball Mill (SBM), High-Pressure Homogenizer (HPH), Ultrasonic Homogenizer (UH), Shear-Gap Homogenizer (SH)

Müller *et al.* (1998) compared the performance of various mechanical disintegration methods on WAS based on the specific energy input, which was defined as the amount of mechanical energy that was applied to a certain quantity of sludge. As a comprehensive measurement, specific energy input was used to evaluate WAS disintegration (DR_o) instead of various downstream MAD operational performance.

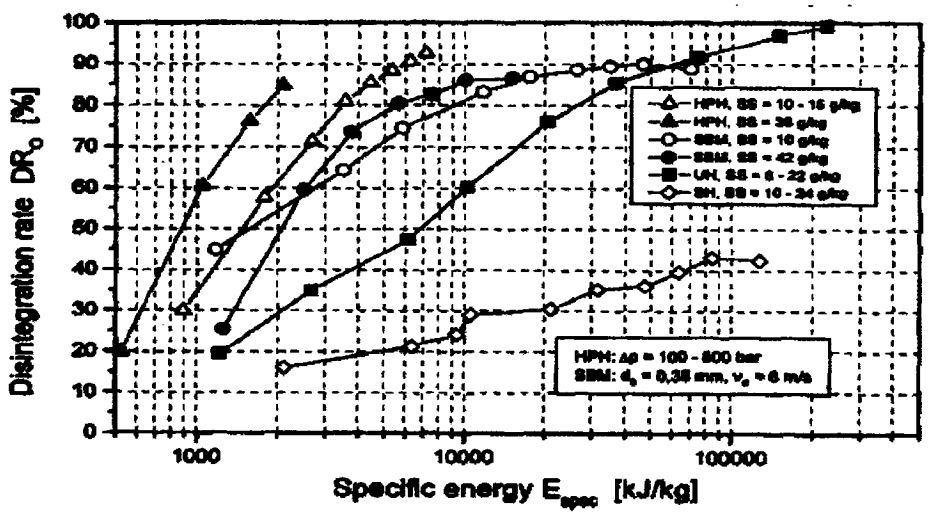


Figure 2.3 Degree of disintegration (DR_0) as a function of specific energy for different disintegration methods

HPH: high-pressure homogenizer SBM: stirred ball mill
UH: ultrasonic homogenizer SH: shear-gap homogenizer
Source: adapted from Müller *et al.* (1998)

Figure 2.3 clearly shows that most methods tested, except for the shear-gap homogenizer, produced high levels of cell disruption. Among them, the high-pressure homogenizer and stirring ball mill were the most economic disintegration methods in terms of specific energy consumption. Higher SS content also improved the extent of cell disruption at a fixed specific energy input level. In the case of HPH, for example, sludge with a SS concentration 3.8% reached a DR_{COD} level 60% higher than 1.0-1.5% SS sludge at energy input of approximately 1000 kJ/kg.

2.4.4 Ultrasound Pretreatment

Ultrasound is a magnetic-electrical wave at a frequency between 20 kHz and 10 MHz, which is beyond the audible range. Ultrasound at high power (hundreds or thousands KJ/L) and low frequency (around 20 kHz) is commonly applied to disintegrate microbial cells to extract intracellular material and break down macromolecules in both WAS and biosolids.

During ultrasonication, periodical compression and reflection of sound waves causes cavitation (gas bubbles) collapse in the liquid when the power intensity rises above a

certain threshold level. The gas bubbles grow and break within a few microseconds. One of two primary ultrasonic mechanisms related to WAS pretreatment is the hydro-mechanical shear force in the surrounding liquid resulting from violent cavitation collapse. It is most effective at frequencies below 100 kHz. The other primary ultrasonic mechanism is the sono-chemical reaction from localized extremely high temperatures and pressure (5000K and several hundred atmosphere) in these bubbles producing hydroxyl radicals. This extreme condition can cause thermal and chemical (oxidation caused by the hydroxyl radicals one of the strongest oxidizing agents) destruction of macromolecules and disruption of cell walls in and near cavitation bubbles. The most effective sono-chemical effect happens at frequencies of more than 100kHz. (Tiehm *et al.* 2001).

2.4.4.1 Effect of Ultrasonic Operation Factors on WAS

Effect of Ultrasound Frequency Tiehm *et al.* (2001) demonstrated that disruption of microbial cells and release of intracellular material from WAS were more effective at lower frequencies after evaluating ultrasound in the 41-3217 kHz frequency range at constant intensity 1.8 W/cm^2, temperature 25±3°C, WAS solids retention time (SRT) 16 days, and exposure 4 hours. As the frequency increased, median particle size of pretreated WAS rose consistently from 20μm to 100μm, DR_{COD} decreased from 80% to less than 10%, and turbidity dropped from 120 NTU to 10 NTU. They suggested that the lower frequency of 20 kHz might lead to the best results for subsequent MAD improvement. Other researchers saw similar results but suggested a frequency range of 20-40 kHz might be best. In fact, the majority of ultrasound pretreatment research and full-scale applications of ultrasound on WAS and stabilized biosolids is now conducted at frequencies between 20 kHz to 41 kHz. (Tiehm *et al.,* 2001; Gonze *et al., 2003;* Chu *et al.*, 2001; Tiehm *et al.*, 1997).

Effect of the Initial Sludge Solid Concentration Gonze *et al.* (2003) varied initial volumetric fraction (fv) of pretreated domestic WAS from 5% to 25% using energy levels between 0-70 KJ/L (fv is defined as the ratio between "total volume of particles" and "volume of suspension"). Biogas results showed that the volumetric reduction factor, which is equal to fv of pretreated sludge divided by fv_0 of untreated sludge, was

dependent on the total energy input rather than the initial solid concentration. Also, concentrations of both soluble protein and SCOD increased more in sludge with higher initial volumetric fractions at the same energy input. In other words, pretreatment of concentrated sludge was more economic from a commercial-scale application standpoint.

Effect of Power, Intensity, and Duration. Almost all the research and applications showed that disintegration and solubilization of WAS improved with either increased power level or increased pretreatment exposure time. However, Chu *et al.* (2001) found that ultrasonication had little additional effect when pretreatment lasted more than 4 hours. They also investigated the combined influence of power level (0.11-0.33 kW/L) and duration (0-2 hours) on WAS with a TS of 0.8% at ultrasound frequency of 20 kHz. Power level of 0.33 kW/L caused more than a 100% improvement in rate of floc size disintegration, bacterial die off, SCOD and biological oxygen demand (BOD) release, and capillary suction time (CST) value increase compared to 0.11 kW/L. Level of solubilization was also significantly improved with increasing duration, but was limited by the power level. Highest power level and longest exposure gave the best results.

Chu *et al.* (2001) also studied the effect of ultrasound intensity (0.1-1.5 W/cm^2) on domestic WAS and proved that energy intensity didn't obviously affect the disintegration efficiency based on the energy applied. His conclusion was based on the fact that the DR_{COD} data from different energy intensities was distributed in a narrow linear zone.

Effect of Temperature Rise Chu *et al.* (2001) compared improvements of SCOD/TCOD ratio from ultrasonication, with or without temperature control, with those from simple-thermal treatment. The results revealed that the degree of disintegration and solubilization seemed to be a summation of bulk thermal effects and the fixed-temperature ultrasonic effect.

2.4.4.2 Ultrasound on WAS

Particle dispersion is affected by the following parameters: bacteria makeup of sludge, dissolved oxygen concentration, organic load, sludge age, and ultrasonic operation

factors. Chu *et al.* (2001) found that, at a frequency of 20 kHz and a power level of 0.44 kW/L, ultrasound decreased floc size to 3μm (only 3% of the original floc size) in 20min, while a power level of 0.11 kW/L exhibited little effect. Tiehm *et al.* (1997) studied the performance of combined municipal sludge (53% primary sludge and 47% WAS in respect to dry solids weight) under ultrasound at a frequency of 31 kHz, power level of 6 kW/L, and non-fixed temperature. They achieved a floc size of 85μm after 96-second treatment, and 135 μm after 29.5-second treatment comparing to the original floc size of 165μm.

In a certain range, a linear relationship between improvements in WAS disintegration (DD_{COD}, DDp, DDcar, DD_{BOD}) and the increase of energy input has been reported by researchers. Wang *et al.* (1999) found that the concentration of protein, carbohydrate, and COD in WAS (TS 3.3-4.0%) supernatant appeared to increase linearly with ultrasonication time (10-40minutes) at a frequency of 9 kHz. After 40 minutes of ultrasonication, soluble protein, soluble carbohydrate, and SCOD concentrations reached 6000mg/L, 2000mg/L, and 5500mg/L respectively from initial concentrations of all species less than 100 mg/L.

Some experimental results on conditioning and dewatering are somewhat controversial. For example, Gonze *et al.* (2003) reported higher settling speed, higher precipitate density, and higher supernatant concentration due to ultrasonication of WAS. As ultrasound energy input increased from 0 to 156 KJ/L, the initial rate of thickening increased from 0.5 to 2.40m/h, and the sludge volume index decreased from 218 to 125mg/L. The suggested explanation was that ultrasound improved the particles cohesion and density owing to release of water. By disrupting the floc and reducing the particle size, ultrasound also increased the solid concentration in supernatant and decreased the solid volume. But CST results obtained on WAS of TS 0.8% by Chu *et al.* (2001) showed that CST values increased from 188 seconds after pretreatment at 0.11 kW/L for 20minutes to 304 seconds after pretreatment at 0.33W/mL for 20minutes, then further increased to 489 seconds after pretreatment at 0.33W/mL for 60minutes. These results suggest that dewaterability became substantially worse with the rise of ultrasound power

level and irradiation time. However, it should be noted that since this test was done without polymer addition it cannot be stated with complete confidence that dewaterability was negatively affected. It is possible that better dewaterability might be achieved with lower polymer dose. This should be studied further.

Ultrasonicated WAS constantly performed better than untreated WAS in both batch and continuous MAD. Pretreated WAS required shorter digestion time in batch tests to achieve the same level of treatment. Shorter HRT, more stable digester conditions, and higher digestion efficiency were observed in continuous digesters. Wang *et al.* (1999) reported that, at a frequency of 9 kHz and a power level of 2 kW/L, ultimate methane production of WAS (original TS 3.3-4.0%) improved 12%, 31%, 64%, and 69% from control value of 200mL methane/gVSadded, for pretreatment duration of 10, 20, 30, 40 minutes, respectively. Destruction efficiency of organic matter increased by 11%, 20%, 38%, and 46% from the control organic destruction efficiency of 28 % for the exposure durations of 10, 20, 30, 40 minutes, respectively. Tiehm *et al.* (1997) found that, at a frequency of 31 kHz and a power level 6 kW/L, ultrasound raised the temperature of WAS from 15°C to 45°C. Subsequent MAD indicated no decrease in VS reduction (47-50%) in continuous digesters even when HRT was shortened from 22 days to 12 days compared to the control reactor, which showed a marked decrease in VS reduction.

Brown *et al.* (2003) examined the effect of ultrasound at the Wastewater Treatment Plant in Orange County Sanitation District (frequency of 20 kHz, power level 0.65 kW/L, and specific power input of 1 KJ/L). Two full-scale mesophilic digesters operated in parallel were fed with a mixture of 60% pretreated WAS or 60 % untreated WAS and 40% untreated primary sludge, the test digester showed substantial improvement over the control digester by producing approximately a 50% increase in both biogas production and specific biogas production/ mass VS fed through a 5-month operational campaign while TS destruction improved 38%. The control digester produced 100,000 scft/day of biogas, 5.5 cuft/1b VSfed, and reduced TS by 38%. Another advantage of ultrasonication reported in this trial was that the solid concentration in the final biosolid cake from the test digester improved 1.2-2.6 percentage points over the control (18.5-21 %TS) when

using a bench-scale belt press and similar polymer dose. The same gas production enhancement was also observed in a trial conducted in the U.K (Barber, date unknown).

A survey conducted by Barber (date unknown) pertaining to the influence of ultrasonication on digestion process efficiency in seven wastewater treatment plants, it showed that pretreatment improved hydrolysis rates by 20-25%. Depending on various operating conditions, ultrasound pretreatment allowed increasing MAD volumetric organic loading by 20-50% while maintaining HRT constant. Alternatively by keeping the organic loading rate constant, MAD could reduce HRT by 25-30% without a loss in VS reduction. This survey indicated that application of ultrasonication has the potential to decrease the volume of new digesters or increase the capacity for existing digesters. Ultrasonication also made it possible to feed a digester with 100% WAS.

2.4.4.3 Ultrasound Pretreatment of Biosolids

Onyeche *et al.* (2002) applied ultrasound to anaerobically stabilized biosolids at a frequency of 20 kHz, a power level of 0.5 kW/L, and a fixed temperature. By doubling biosolid concentrations from 1.8 to 3.6% TS, MAD biogas production was improved as much as 200% after 30 minutes of disruption. However, it was also report that there was no possible economic benefit to biosolids pretreatment since the majority of the biodegradable organics had already been digested and subsequent biogas production was insufficient to rationalize pretreatment.

2.4.4.4 Low-Power Ultrasonication

Chu *et al.* (2002) reported that, at low ultrasound energy levels, instead of fully destroying the floc structure and releasing intercellular material (such as soluble COD, soluble proteins, and soluble carbohydrates) directly into the supernatant, ultrasound deagglomerates and weakens bacteria cells. Thus, bacterial cells become easily being attacked by hydrolysis enzymes in the following anaerobic digestion phase. At a frequency of 20 kHz, a power level of 0.33 kW/L and a power input of 198 KJ/L, SCOD/total COD ratio of WAS (TS 0.94%) rose slightly from 8% to 10% after pretreatment. The subsequent batch digestion attained an enhancement of 290 % in

ultimate methane yields from 143 to 292 CH_4/kg-TS. Their studies also revealed that there was a significant increase in ATP, and decreases in ORP value, and floc size in the first 10 days of MAD. SCOD substantially increased from 10 % to 32-38% as well. Chu *et al.* (2002) concluded that these results proved that complete disruption of bacteria flocs occurred at the beginning of MAD instead of direct ultrasound treatment. It was concluded that low power ultrasonication has a potential to become more energy efficient technology than high power ultrasonication for enhanced MAD of WAS.

2.4.5 Thermal Pretreatment

2.4.5.1 Thermal Hydrolysis of Primary Sludge

Research results on the thermal pretreatment effect on primary sludge are controversial. Gavala *et al.* (2004) and Haug (1978) reported insignificant positive or even negative effects from pretreating primary sludge (TS~4.0%) at 70°C for 30 minutes or 170°C for 30 minutes in terms of MAD performance (biogas, VS reduction). But Pinnekamp (1989) optimized thermal pretreatment of primary sludge in the temperature range of 120-220°C. After pretreatment at an optimal temperature of 170°C, the biogas yield from the continuous MAD (SRT=20 days) was 259 L/kg·VSinfluent which represented a 20.3% increase over the untreated sludge. However, this achievement was less satisfactory in comparison with data obtained from WAS (biogas yield improvement 42-123%) in similar situations. This is not that unexpected as primary sludge is known to be readily biodegradable without pretreatment. At the long SRT (20 d) little increase in the ultimate degradability of the primary sludge is expected. The impact of pretreatment of primary sludge is more likely to be on the rate of digestion rather than the extent of the VS reduction.

Barnard *et al.* (2002) and Abraham *et al.* (2003) reported the effect of commercial-scale technology Cambi^{TM} on sewage sludge. Concentrated sewage sludge (~ 17% DS) was heated up to 160-170°C at a pressure of 6-8 bars by steam in batches for 20-45 minutes, followed by mesophilic or thermophilic digestion. Recaptured energy from pretreated sludge was used to preheat the cold raw sludge. The WAS hydrolysis mechanism during

pretreatment is via high temperature disruption and mechanical shock applied to WAS bacteria due to sudden pressure drop.

The Ringsend wastewater treatment plant (WWTP), Dublin, Ireland initialized the application of the Cambi system for primary sludge with high fibrous content (fiber represented 45% of the total dry solid) and high industrial wastewater (WW) component (around 30% of the influent). During the initiation, methane from the digester was around 55% in biogas composition, dry solid in the digester built up to 4-5% w/w, and volatile solid destruction efficiency was 60-70%. In contrast, in conventional digester, typical VS destruction from fibrous primary sludge would be expected at approximately 40%.

2.4.5.2 Thermal Hydrolysis of WAS

Optimal Thermal Treatment Temperature and Duration

Li and Noike (1992) studied the effect of treatment temperature and duration on digestion performance of WAS in the temperature range of 62-175°C and durations of 15-120 minutes. Pretreated WAS has a pH value of around 7, VSS concentration varied from 4.76-9.58 g/L, and TCOD level ranged from 13-16 g/L. It was observed that solubilization levels increased with the increase of pretreatment temperature and duration. Nevertheless, in terms of accumulative biogas production in mesophilic BMP tests, increased pretreatment temperatures resulted in less improvement in biogas production once the thermal pretreatment temperature reached 150°C, and a duration of 30 minutes. Conclusions from TCOD and VS removal data were slightly different. Based on TCOD removal 170°C was the optimal thermal pretreatment temperature, based on the highest TCOD removal 65% and VS degradation 60%.

Pinnekamp (1989) ran a continuous MAD (volume unknown) at different SRTs (5, 10, and 20 days) to degrade WAS that was pretreated at a temperature ranging from 120 to 220°C. Using the 20-day SRT reactor as a measure of the ultimate degradability, this study showed that the optimal pretreatment temperature was around 170°C. When SRT decreased to 10 days, best performance temperature dropped to around 135°C. As the SRT was decreased to 5 days the specific biogas yield (m^3/Kg VS added) decreased but

was still higher than the control. Interestingly the specific biogas yield of 220°C pretreated WAS was less than the control indicating the possible formation of inhibitory compounds at high pretreatment temperatures.

Haug (1978) reported that the effect of thermal pretreatment on solubilization of WAS (original TCOD 43.6g/L) started to decrease once temperatures were higher than 175°C; and the effect of holding time appeared to have little further influence after 1-hour contact.

Thermal pretreatment scenarios of 170°C and a holding time of 0.5~1.0 hour are widely accepted and applied in research and commercial-scale technology. However, Tanaka *et al.* (1997) reported that WAS solubilization was close to its maximum level after 5-min holding (temperature 130°C and alkaline dose 0.3g NaOH/g VSS), while Vlyssides & Karlis (2004) found that 5 hours or even more than 10 hours at 50-90°C was needed. Unfortunately, not all papers report the source or conditions used to produce the WAS (SRT, food and microorganism (F:M) ratio, conventional, extended aeration, biological nutrient removal (BNR) or biofilm WWTP pretreated. It is expected that the differences in results may be related to differences in the furnace used for pretreatment.

Effect of Organic Loading Rate of WAS

Pinnekamp (1989) studied thermal pretreatment of WAS from activated sludge reactors with different organic loading rates. WAS from a low-loading rate (0.03 kg BOD/m^3.d), normal loading-rate (0.15 kg BOD/m^3.d), and high-loading rate (2.00 kg BOD/m^3.d) likely corresponding to long, normal and short SRTs were pretreated. After thermal treatment, continuous MAD results indicated that pretreated WAS from the lower loading rate as system resulted in an greater increase in the maximum biogas yield (m^3/kg VS added): biogas production from WAS with source OLR 0.03 kg BOD/m^3.d increased 123 %, OLR 0.15 kg BOD/m^3.d increased 73 %, and OLR 2.00 kg BOD/m^3.d increased 42 %.

Effect of Thermal Pretreatment on WAS

Haug (1978) performed a study using WAS with a TCOD concentration of 43.6 g/L. After pretreatment at 175°C for 1 hour, the COD solubilization reached 42.7% from the original value of 5.1%, and ammonia concentration increased to 770 mg/L from 470 mg/L. In the following continuous MAD, comparison of control and pretreated digesters, resulted in total biogas accumulation increased 57% to 822 mL/d, COD removal improved from 28.4% to 40%, and VS destruction was enhanced from 27.3% to 48%. Haug also reported a slight decrease of total COD value after heating to 200°C and 225°C, which was suggested to be the result of the loss of volatile organic molecules.

Inhibition for undetermined reasons was observed in the digester fed with WAS pretreated at 175°C for 1 hour. Comparing to the first set of digesters, pretreated sludge produced 80% more biogas than the control in the first 8 days. After the immediate and persistent response, gas production from the pretreated digester started to decrease, gradually approaching and eventually identical to the control at the 32nd day. Afterwards, likely as a result of acclimation, gas production values climbed to above 50% over the control and remained there for the next 20 days until the end of study. The second set of control and pretreated digesters behaved similarly to each other (with a initial sludge solid concentration half that of the first set of digesters). Both of them presented characteristics of ammonia toxicity. But for the two pretreated digesters the calculated values of undissociated ammonia were 70mg/L and 30mg/L, respectively, which were well below the inhibitory level of 100mg/L. Researchers suggested that the toxicity was due to the presence of other toxic compounds from heating instead of free ammonia. In comparison, only slight inhibition was observed in 135°C-pretreated digester, and no indication of inhibition was even noticed with 100°C-pretreated sludge.

Li & Noike (1992) found that most organic solubilization products from thermal pretreatment were anaerobically degradable. They pretreated WAS at a temperature rang of 62-175°C for 15-120 minutes. Pretreated WAS has a pH value around 7, VSS concentration varied from 4.76-9.58 g/L, and TCOD level ranged from 13-16 g/L. For a thermally pretreated 2-L MAD digester at SRT of 10 days, the effluent SCOD was only

slightly above the control. Microscopic examination also showed that the population levels of total methanogenic bacteria, specific formate-consuming methanogenic bacteria, methanol-consuming methanogenic bacteria, and acetate-consuming methanogenic bacteria didn't vary significantly as the SRT was shortened from 10 days to 1.5 days.

Haug (1978) found that thermal pretreatment potentially improved the dewaterability of both MAD primary sludge and MAD WAS at the end of treatment. Before digestion, the dewaterability of pretreated primary sludge and pretreated WAS was also seen to improve significantly with the increase of pretreatment temperature. MAD increased the dewaterability of primary sludge to a greater extent while it had less effect on WAS.

2.4.5.3 Thermal Treatment of Biosolids

Sawayama *et al.* (1996) investigated the effect of thermal pretreatment of anaerobically digested and dewatered biosolids (dry matter 15.7%). After treatment at 170°C for 40 minutes and then centrifuged at 1000rpm for 10 minutes, biosolids were separated into a supernatant part and a precipitate part. Three samples were evaluated, control biosolids, whole pretreated biosolids referred to as liquidized biosolids and the liquidized biosolids supernatant. The VS/TS ratio was 68.3% in the original biosolids and 65.8% in liquidized biosolids while the supernatant had a higher VS/TS ratio of 94.7% which resulted in a greater improvement in MAD performance. The 8-day anaerobic digestion ratio based on measured and ultimate biogas yield were 27%, 41%, and 61% for original sludge, liquidized sludge and supernatant, respectively. The corresponding 8-day biogas yields were 154, 254, and 339 mL/g-added VS for original sludge, liquidized sludge and supernatant, respectively.

The precipitate contained less moisture (76.3%w/w) than the original biosolids (moisture level 84.3%w/w). The calculated low heating value increased from -1.6 MJ/kg for dewatered digested sludge to 0.4 MJ/kg for dewatered precipitate, which implies that the precipitate was more suitable for incineration because it consumed less supplementary fuel. Another advantage of using the precipitate for incineration was that its relatively lower nitrogen content decreased the NO_X emission from incineration.

2.4.5.4 Thermal Liquidization of Food Waste

Sawayana *et al.* (1997) and Tsukahara *et al.* (1999) studied the effect of thermal pretreatment on food waste. Its components were sliced cabbage (92.4 wt%), boiled rice (5.3 wt%), small dried fish (0.6 wt%), shells (1.1wt%), and butter (0.6wt%). Food waste was treated at 175°C for 1h and filtered at 20 μm. The filtrate, with 82.9 wt% of the original garbage, had similar VS/TS ratios and batch digestion performance as original garbage. In a continuous mesophilic upflow anaerobic sludge blanket reactor (UASB), the TOC, COD and BOD removal efficiencies reached 68%, 68.7%, and 80.3% respectively with an influent TOC concentration of 10.1-11.1 g/L and an organic volumetric loading of 4.8-5.3 gTOC/L·d. Methane production was around 0.35-0.61 L/g-TOC removal.

The solid fraction had less moisture content (69.9%) and a higher low heating value (3.9 MJ/kg solid fraction) than raw sludge, which had a moisture content of 88.7% and a low heating value of –1.8% MJ/kg solid fraction. Taking the energy consumption/generation of liquidization, filtration, biogas production, and incineration into account the final energy balance suggested around 10% less fuel consumption compared to direct incineration of the original food waste.

2.4.5.5 Thermal Liquidization of Pharmaceutical Waste.

Dohanyos *et al.* (1997) prepared lysate by heating actively digesting biosolids at 100°C for 30 minutes and examining the effect of adding lysate into WAS from pharmaceutical wastewater treatment (ESP)(TS 1.48%, VS 1.24%), biomass from threonine production (B)(TS16.8%, VS16.0%), and mycelium after penicillin extraction (M)(TS 30%, VS 27%), separately. With lysate (TCOD 32.4g/L) accounting for around 8% of the total COD of digestion substrate, batch methane production from ESP, B, and M was increased by 23.2%, 20.2%, and 36.6% respectively.

2.4.6 Freeze and Thaw Pretreatment

Dohanyos *et al.* (1997) studied the effect of repeated freezing on sewage sludge (TS 3.85%). They found that by adding repeatedly frozen lysate (TCOD 225.8g/L) into raw sewage sludge, the specific CH_4 production per mass of initial COD was increased by 96.4%. Wang *et al.* (1999) reported that freezing at -10°C once didn't affect digestion performance as indicated by the VFA profile in a batch test.

2.4.7 Chemical Pretreatment

Agents applied in chemical pretreatment could be one or a combination of several compounds, which are

- Bases: NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, NH_3H_2O
- Acids: HNO_3, H_2SO_4, HCl, acetic acid

There are three major concerns about alkaline pretreatment. One possible set-back is the toxic effect of sodium ions (Na^+) and potassium ions (K^+) on subsequent MAD. The biotoxicity is defined by the complexity of digestion substrate and digestion operation (batch or continuous) (Mouneimne *et al.,* 2003). Another concern is that, as Kim *et al.* (2003) found, monobasic agents (Na^+, K^+) performed better than dibasic ones (Mg^{2+}, Ca^{2+}) in terms of solubilization improvement. The suggested reason for the poor performance was the partial dissolution of dibasic agents. The third concern is that chemical disintegration caused non-neutral conditions which need to be rectified prior to MAD. But due to the economic consideration, buffering or blending with untreated sludge (such as raw primary sludge) is the most common method to adjust pH values prior to digestion except for extremely high pH pretreatments.

2.4.7.1 Alkaline Pretreatment

Chih *et al.* (1997) found that both ORP decrease and SCOD increase happened in the first 2 hours of alkaline pretreatment of WAS. After 2 hours, the SCOD curve leveled off and ORP curve started gradually increasing. It seemed that the optimum duration of NaOH pretreatment should be around 2 hours. It was also suggested that in alkaline pretreatment ORP measurement could be used as an on-line parameter for hydrolysis monitoring.

In an experiment on combined WAS (wasted aerobic sludge from biological treatment of domestic-industrial-combined wastewater) (TS 0.84%, TSS 0.45%) conducted by Tanaka *et al.* (1997), alkaline pretreated WAS showed a constant increase in SCOD/TCOD solubilization of 15 % as Na^+ concentrations reached 0.1 mol/L and no further increase was observed until Na^+ concentration reached 0.17 mol/L. Lin *et al.* (1997) reported that, for domestic WAS TS 1%, solubilization at 20 and 40 meq NaOH/L raised the SCOD/TCOD ratio from 2% to 25.5% and 37.5% respectively. Volumetric gas production rates in the following continuous MAD (1L digester) was also around 30% higher than the control, which was 83 $mL/m^3/d$ at 20-day HRT. For a 7.5-day HRT, in contrast to the decrease of biogas production from untreated sludge, biogas production from alkaline pretreated sludge was enhanced to 247 $mL/m^3/d$, which was an 86-94% improvement over the control.

Lin *et al.* (1999) analyzed the components in raw WAS (0.35% VS) and in the supernatant of alkaline-solubilzed sludge. They found that after alkaline solubilization, most of the biodegradable material, such as soluble matter or small particles, stayed in the supernatant. After pretreatment at 20 meq NaOH/L, supernatant showed 65% COD removal while raw WAS only reached 48% and particulate reached 31%.

2.4.7.2 Acid Soaking

Besides base and ammonia hydrolysis, acid soaking of cellulose has also been widely studied. The most extensively used agents are H_2SO_4 and HCl, concentrated or diluted. In high concentration acid soaking, economic feasibility becomes a problem for industrial application. One solution is utilizing medium acid concentrations (such as 41% HCl) and then recovering the used acid. Another reasonable process is using diluted acid (1% H_2SO_4) combined with thermal treatment (above 150°C), which leads to a 50-65% decomposition. (Xiao & Clarkson, 1997)

Xiao & Clarkson (1997) also tested the effect of various combinations of HCl, HNO_3, and acetic acid on newsprint digestion. They found that adding 35% acetic acid, 0.25-0.5% HNO_3, and 1.5-1.75% HCl (total acid concentration was constantly 37%) caused

around 36% lignin solubilization in the pretreatment. The improvement of methane production was around 250% from 100mL/gVS in the following mesophilic BMP test. The function of HNO_3 was suggested to be as a catalyst instead of as an acidifier based on the fact that even extremely low HNO_3 concentrations of 0.25% caused significant improvement of SS removal from 26.1% to 35.5% (total acid concentration remained 37%).

2.4.8 Thermochemical Pretreatment

By combining relatively lower chemical doses with lower temperatures, thermochemical pretreatment performs better than chemical or thermal solubilization alone. It is theorized that heating could increase the rate of reaction between organic material and chemicals, besides its own function. (Tanaka et al., 1997)

According to Tanaka et al. (1997), after thermochemical treatment at 130°C and 1.35 mol NaOH/L for 5 minutes, the profile of three organic components (protein, lipid, and carbohydrate) in the supernatant of domestic WAS showed that soluble protein, lipid, and carbohydrate ratios rose from 3%, 7%, and 20% to 65%, 60%, and 90%, respectively. Due to the complex and refractory nature of industrial wastewater, solubilizaiton of combined WAS (35%) only reached half of that of the domestic WAS (70%). Combined WAS behaved differently from domestic WAS in methane production as well. The digestion of domestic WAS finished in 10 days, while the digestion of combined WAS lasted 18 days. But combined and domestic WAS presented similar improvements in methane production (combined WAS from 20 to 35%, domestic WAS from 35 to 50%).

Kim *et al.* (2003) reported that, for domestic WAS (TS 3.8%), pretreatment at NaOH doses of 7 g/L at 121°C for 30 minutes raised COD solubilization from 45% to 86.4%. At lower pH values of 12 with various types of bases, in conjunction with the thermal treatments of 121°C for 30 minutes, consistently added 10 percentage points to COD solubilization. Vlyssides and Karlis (2004) studied concentrated WAS (10% TS) from a soft-drink WWTP at lower temperatures (<100°C) and more neutral pH values (pH 8-11)

and achieved reasonable improvements for COD solubilization. After pretreatment at pH 11 for 11 hours, soluble COD rose to 7,000 mg/L from less than 100 mg/L in the control.

2.4.9 MicroSludge (Combination of Chemical and Mechanical Pretreatment)

MicroSludge was a patented commercial-scale process and specially targeted at both degradation rates and efficiency of WAS at MAD. Its major mechanism was alkaline treatment to weaken cell membranes followed by cell disruption from dramatic pressure change. There were other assisting operations such as mechanical shear to reduce particle size and a screen to remove oversize debris before homogenization. Pretreated WAS was fed into the digester together with neutral primary sludge. (Stephenson *et al.*, 2003; Shaw *et al.*, 2004). Stephenson *et al.* (2003) and Shaw *et al.* (2004) investigated and reported the effect of MicroSludge on WAS and compared it with other commercialised WAS pretreatment technologies. Optimum MicroSludge operation conditions are shown in Table 2.9. The effect of MicroSludge processing on anaerobic digestion is shown in Table 2.10. As can be seen in Table 2.9, after pretreated at high pH and high pressure, WAS has to be mixed with PS to reach neutral condition to optimum the following anaerobic digestion. Table 2.10, reveals the MicroSludge increased the efficiency of anaerobic digestion in terms of VS removal and NH_3 production. It also improved the stability of digester in terms of the SCOD concentration, BOD concentration, TVFA concentration in effluent, as well as the fact that MicroSludge pretreated sludge can be stably digested at much lower HRT than unpretreated sludge.

Table 2.9 Optimal MicroSludge operation conditions

Processing step	Optimal setting
Chemical pretreatment	1. <300mg/L Na+ (added as NaOH) in anaerobic digester
	2. WAS pH>10 to promote cell lyses
	3. Holding time of 1 hour or more to promote cell lyses
Homogenizer pressure	12,000 to 14,000 psig (83,000 to 96,000kPag) for maximum cell lysis
Anaerobic digester pH	~ 7.0 to minimize ammonia toxicity by blending primary sludge with MicroSludge processed secondary sludge at ratio 40:60

Table 2.10 Effect of MicroSludge processing on anaerobic digestion.

Pretreatment		Anaerobic digester HRT (days)	Effluent					Total VS reduction (%)	Particulate VS remaining for disposal (%)
			SCOD (mg/L)	VS (mg/L)	Total VFAs (mg/L)	BOD (mg/L)	NH_3 (mg/L)		
	40:60 Primary:secondary sludge feed	---	9,490	22,640	2,723	4,230	527	---	---
MicroSludge	Digestion	5	920	4,940	195	415	1,160	78	14
		10	498	4,780	74	135	1,210	78	12
		15	305	6,460	159	230	1,180	71	14
Conventional	Feed	--	8,330	34,269	1,601	3,420	280	---	---
	Digestion	15	7,870	20,330	2,415	3,200	1,180	41	44

Nominally, each gram of volatile solid reduction lead to 1 litre of gas production.

The intensive chemical/physical conditioning during the MicroSludge process provided significant pathogen destruction. Combined with thermally pretreated primary sludge, stabilized biosolids resulting from a 40:60 mixture of primary/secondary sludge could meet the USEPA requirement for Class A Biosolids. Digested sludge dewaterability improvement were inconclusive as the level of improvement and polymer demands were very different.

2.4.10 Ozonation Pretreatment

As a strong oxidant, ozone can oxidize inhibitory and refractory compounds, such as aromatic compounds and humic acids into CO_2 to eliminate toxicity. This special function, along with the liquidization function of ozone, encourages the use of ozonation-digestion systems on toxic wastewater, such as vinasse and olive mill wastewater. Tests conducted by Benitez *et al.* (1997) on olive mill wastewater and tests conducted by Martin *et al.* (2002) on vinasse reported significant COD removal and solubilization during ozonation and kinetic improvement in the consequent digestion.

Weemaes *et al.* (2000) applied ozonation on sewage sludge (TS 5.92%, VS 4.74%) for around 3.5 hours and varied the dosage from 0.05 to 0.2 gO_3/gCOD. At a dosage of 0.2 O_3/gCOD, they found that total COD decreased from 7.9 to 4.9 g/L, SCOD increased from 0.06 to 2.3 g/L, SS decreased from 9.5 to 3.8 g/L, VSS decreased from 5.7 g/L to 1.8 g/L, and pH dropped from 7.8 to 4.9. In the following batch study, ozonization demonstrated a positive effect on anaerobic biodegradation. In the first week the average methane production rates were 6.8 mg CH_4/(gCOD·d) for sludge pretreated at 0.05 gO_3/gCOD and 9.1 mg CH_4/(gCOD·d) for sludge pretreated at 0.12 g O_3/gCOD, compared to 4.3 mg CH_4/(gCOD·d) for untreated sludge. After digestion for 30 days, the degradation efficiency (based on TCOD) reached 54%, 63%, and 47% for the sludge pretreated at dosages of 0.05, 0.1, 0.2 gO_3/gCOD and untreated sludge, respectively. Ozonation of sludge at 0.2 gO_3/gCOD also dramatically increased the CST value from 33-44 seconds for untreated sludge to 309-313 seconds for pretreated sludge suggesting a potent decrease in dewaterability.

Müller *et al.* (1998) compared ozonation (100 mg/L) to a high-pressure homogenizer (Δp=200,400bar) on WAS and reported no additional influence from ozonation. One possible reason postulated was that the inhibitory effect of ozonation on sewage sludge was so notable that oxidation did not enhance MAD.

2.4.11 Aerobic (Enzymatic) Pretreatment

Masse *et al.* (2001, 2002) conducted a series of tests to investigate the effect of enzymatic pretreatment on a mixture of pork (or beef) slaughterhouse wastewater and lipid particles with different particle sizes. More than 67% of particular COD and less than 1% of SCOD in a fatty mixture, mainly composed of triglycerides (neutral fats), were lipid based. In anaerobic digestion, lipids are first hydrolyzed into free long-chain fatty acids (LCFA) and glycerols, and then oxidized to shorter chain fatty acid. But high LCFAs concentration can have an irreversible inhibition on anaerobic digestion.

Enzyme selection tests were conducted with pork pancreatic lipase (PL-250), bacterial lipase (G-1000), and plant lipase (ecosystem plus). Plant lipase produced no reduction of particle size and no change in SCOD concentration. Bacterial lipase was not considered practical because of the high dose required (>1000mg/L). PL-250, which was designed to effectively degrade neutral fat and LCFAs, slightly increased SCOD and significantly reduced fat particle sizes. But in the following anaerobic sequencing batch reactor (ASBR) at 25°C, pretreated fatty mixtures, with smaller average particle size than untreated mixtures, showed lower first-order neutral fat hydrolysis rates (0.43-0.68 d^{-1}) than untreated mixtures (0.58-0.72d^{-1}). In the end, enzyme pretreatment showed no beneficial effect on the total hydrolysis of neutral fat. This might suggest that, without hydrolysis, decrease in particle size (characterized by the concentration increase of SCOD) during pretreatment was not intensive enough to significantly improve the following MAD.

This research also showed that enzyme inhibition, characterized by slowing down of both fat particle size decrease and increase of free LCFA in solution, was observed after

performing the pretreatment for 4-6 hours. It was suggested that enzymes were inhibited by LCFA accumulation around the particle surface and the subsequent surface concentration decrease of triglycerides. Particle size reduction increased with PL-250 dose, but enzymatic benefit decreased significantly as PL-250 concentration increased higher than 250 mg/L.

2.4.12 Microwave Pretreatment

Microwave (MW) is the electromagnetic light wave in the approximate frequency range of 1-300 GHz. Microwave pretreatment causes temperature increase and controversial (conflicting reports of effect) athermal effects on the irradiated object by induction heating and dielectric polarization. Microwave application frequency, microwave heating mechanism, MW penetrating depth and temperature gradient in microwave ovens, and advantages of microwave heating over conventional heating are described in section 2.5.

Park *et al.*(2004) investigated the effect of microwave irradiation on solubilization and subsequent continuous digestion of secondary sludge. All the tested sludges were adjusted to a VS concentration of 1.9% by gravity settling prior to the experiment. Carbohydrate, protein, and lipid concentration for the adjusted sludge were 0.51%, 0.98%, and 0.15%, respectively. The ratio of SCOD/TCOD constantly increased from 0.02 to 0.19 as sludge temperature increased from 10°C (untreated sludge) to 91°C after microwave irradiation for 7 minutes. But the SCOD/TCOD pretreatment efficiency did not increase significantly from exposure to 7 or to 15 minutes of irradiation when the temperature of pretreated sludge remained 100°C (boiling) in spite of the energy input. Researchers also determined the release of Ca^{2+} that functions as stabilizer of WAS floc structure. Test indicated the disintegration of sludge floc by the increase of Ca^{2+} concentration increased gradually from original 83.8 mg/L to 101.8 mg/L after microwave irradiation for 15 minutes.

Sludge pretreated at 91°C and untreated sludge were fed into 5-L digesters and their MAD performance were compared. The pretreated digester was run at 15, 12, 10, and 8 days SRT, while the control digester was run at 15 and 10 days SRT. For all SRTs, VS

removal for the pretreated digester remained 25.9-25.1%, which were slightly higher than the VS removal of 23.2%- 23% for the control digester. In comparison, TCOD removal for the pretreated digester decreased from 23.6% to 19.8% while the SRT decreased from 15 days to 10 days. TCOD removal for the control digester remained lower than that for the pretreated digester at 14.4-13.8% at 15-10 days SRT operation. The discrepancy between VS removal and TCOD removal was not addressed.

The characteristics of effluent supernatants indicated greater stability of the pretreated digester than the control digester. For both the pretreated and control digesters, the VFA concentration as acetate and SCOD concentration appeared to be less than 30 mg/L and less than 500 mg/L, respectively. As the SRT of control digester was shortened from 15 days to 10 days, the VFA concentrations as acetate dramatically increased to 291 mg/L and SCOD concentration increased to 1379 mg/L. These changes showed the initial signs of unstable operation. In contrast, shortening of the SRT for the pretreated digester to 10 days and 8 days only slightly increased the VFA concentration as acetate to 65mg/L and the SCOD concentration to 705 and 784 mg/L, respectively.

2.5 Mechanism of Microwave Effect

2.5.1 Application Frequency

In North America, under both national and international regulations, the frequency of 2,450 MHz is called an "exclusive frequency" and is used for home microwaves and industrial heating without requirements for special permission. The frequency of 915 MHz is used in large plants with very strict requirements. (Copson, 1962; Vollmer, 2004; "Microwave and radio frequency processing" by U.S. Food and Drug administration center for food safety and applied nutrition, 2000)

2.5.2 Microwave Heating Mechanism

The interactions of electromagnetic field with the charged particles in the material lead to temperature increase of the object irradiated. Two major effects can be used to describe the mechanism of microwave heating.

A. Induction Heating

Under a microwave field, the migration of free charged particles in opposite directions induces a current. The current causes the temperature of the object to rise due to electrical resistance. This heating effect is defined by the induced current and the electrical resistance of the object.

B. Dielectric Polarization

On the other hand, bound charged particles in the object will be caused to align with the radiation field by rotation in order to balance the electric forces. Generally, dielectric polarization is the primary mechanism responsible for microwave heating of water solutions. At a microwave frequency of 2,450 MHz, dielectric particles consistently rotate according to the alternating electromagnetic field without ever completing this dielectric reorientation due to the frequent changes of the field. Therefore, the phase difference between orientation of the field and that of the dielectric, termed as "dielectric loss", causes dielectric heating. In liquids, alignment takes a much longer time as it is inhibited by the surrounding molecules. The energy for the rotation of the dielectric particles is supplied by the electromagnetic field.

The rate of heat generation by volume under a microwave field is affected by the dielectric loss factor of irradiated material. In another words, the material, which has a higher loss factor, can be more quickly heated in a microwave field. (Copson, 1962; Metaxas & Meredith, 1983; Vollmer, 2004; "Microwave and radio frequency processing" by U.S. food and drug administration center for food safety and applied nutrition, 2000)

Under microwave irradiation, material can behave as absorbers (water, aqueous substance, tissue, and food), transparents (glass and ceramics), or reflectors (metal). (Copson, 1962)

2.5.3 Penetrating Depth and Temperature Gradient in Microwave Oven

The MW penetrating depth is defined as the depth at which the power density decreases to $1/\alpha$ (α: penetrating coefficient of microwave heating) of its initial value at the material surface. (Copson, 1962) Penetrating depth is a function of material composition,

concentration and temperature. At room temperature, the penetrating depth for paper is around 20-60 cm, meat 0.9-1.2 cm, and hollow glass about 35cm. For pure water, penetrating depth decreases from about 5.7cm at 95°C to about 1.4cm at 25°C, but increases to 1100cm at -12°C (solid ice). (Copson, 1978; internet resource http://www.pueschner.com/engl/basics/depths.html)

The MW penetrating depth is the major reason for non-uniform microwave heating in a random MW chamber. At the frequency of 2,450 MHz, studies showed that heating temperatures dramatically dropped from the material surface to the core of an irradiated material (Copson, 1962). The color image obtained from a thermal infrared camera showed that there was a horizontally non-homogeneous power distribution, which may lead to uneven heating. In a domestic microwave oven, a rotating turntable is equipped to mimimize this local uneven heating. (Vollmer, 2004)

2.5.4 Advantage of Microwave Heating Comparing to Conventional Heating

Microwave heating and conventional heating rely on different mechanisms. In conventional heating, temperature differences across the material act as a driving force to create thermal conductivity and convection currents to heat the material gradually. In microwave heating, due to the penetrating nature of microwave irradiation, substances inside the material (i.e. primary sludge or WAS) can absorb the microwave radiation immediately and can achieve much faster heat transfer. Because of the specific structure of microwave heating ovens and the unique mechanism of dielectric polarization, microwave heating presents several widely accepted advantages over conventional heating (Plazl *et al.*, 1995; Copson, 1962) :

- Selective heating on highly dielectric substances
- Higher energy efficiency
- Shorter processing time
- Instant control
- Decreased equipment size
- More uniform heating

The non-thermal microwave effect, also called "subthermal" or "athermal" microwave effects, remain a matter of controversy. Until now, most research on the non-thermal effects of microwaves specifically focused on pathogen reduction for food processing and medical treatment. The non-thermal effects of microwave on bacterial cells may be explained by four hypotheses: selective heating, electroporation, cell membrane rupture, and magnetic field coupling.

Some research on the behavior of protein and DNA in microwave fields showed that their hydrolysis proceeded much faster under microwave irradiation than conventional heating. According to the doctoral thesis by Seung-Mo Hong at University of Wisconsin-Madison in U.S.A. (2002), the primary factors affecting the chemical bonds were: "microwave frequency, radiation time, concentration, particle size, viscosity, and penetration depth."

But it seems that most research has concluded that there was little or no non-thermal effect of microwave irradiation. Given the limitation of lab research techniques and facilities, some positive research results pertaining to the athermal effect remain under question and require further proof. (Copson, 1962; Kroll *et al.*, 1998; "Microwave and radio frequency processing" by U.S. food and drug administration, 2000; Epstein, 2003)

2.6 Discussion

Among the various pretreatment methods conventional thermal pretreatment technology apparently produced relatively higher rates of sludge degradation, a possibly greateer dewaterability, and adequate pathogen reduction to meet Class A requirements for end reuse and ultimate disposal. The development of microwave pretreatment methods could improve thermal pretreatment technology through higher heating efficiencies and higher operational reliability. Additionally, microwaves electromagnetic nature presents potential non-thermal effects on WAS and primary sludge and their chemical components. Athermal effects have the potential to produce extra effects, positive or negative, on sludge digestion in addition to thermal hydrolysis.

CHAPTER 3
MATERIALS AND METHODS OF ANALYSIS

The experimental approach used in this research can be sub-divided into five major parts:

- Acclimation of anaerobic seed culture
- Collection and preparation of PS
- Microwave pretreatment of PS
- Biochemical methane potential (BMP) assays on PS
- Biochemical methane potential assays on the soluble fraction of PS

Additionally a method for estimating the maximum possible solubilization of PS suspended solids was also tested.

The cultivation of anaerobic seed was initiated 2 months prior to any of the BMP tests to ensure a well acclimated culture. Using this culture BMP assays on untreated and microwave pretreated PS were conducted in 2 sets of experiments using 2 different microwave intensities: 80% and 40%. In each set of experiments, raw PS at various solid concentrations was pretreated by microwave (MW) irradiation to different final temperatures. Both raw (untreated) and MW pretreated PS were characterized to evaluate the influence of microwave irradiation pretreatment. This characterization was used to help explain the results of BMP assays. The impact of MW pretreatment of PS on anaerobic sludge stabilization was assessed using the standard BMP test. Based on sludge BMP results two MW pretreatment scenarios were then selected to evaluate the effect of MW pretreatment of PS on the digestion of the soluble organic fraction using the BMP assay. Tests used to characterize the raw and pretreated primary sludge samples and evaluate the BMP assays are summarized in Table 3.1 and Table 3.2.

Table 3.1 Summary of sample characterization and BMP assays monitoring.

Parameter	Anaerobic seed acclimation	Undiluted raw sludge	Pretreatment and BMP assay of primary sludge			
			Untreated sludge	Pretreated sludge	BMP Assays monitor	Digested sludge after BMP test
Alkalinity	+	+	o	+		+
Ammonia	+	+	o	+		+
Biogas composition	+				weekly	
Biogas production	+				daily	
Capillary suction time (CST)						+
pH	+	+	o	+*	weekly	+
Temperature	+		+	+	daily	
TCOD		+	o	+		+
SCOD		+	o	+		+
TS and VS	+	+	+	+		+
TSS and VSS		+*	o*	+*		+*
VFA	+	+	o	+	weekly	+

+ Test
o no test, but can be calculated by related data
* only applied on the 1st set of experiment

Table 3.2 Summary of sample characterization and BMP assays monitoring (continued).

Parameter	Pretreatment and BMP assay of the soluble part of primary sludge				Determination method for maximum sludge disintegration
	Untreated sludge	Pretreated sludge	BMP assays monitor	Digested sludge after BMP test	
Biogas composition			once		
Biogas production			daily		
pH				+	+
Temperature			daily		
TCOD	+				
SCOD	+	+		+	+
TS and VS	+				+

+ test

3.1 Background of Primary Sludge Production

Sludge used in this study was obtained from the Robert O. Pickard Environmental Center (ROPEC) in Ottawa, ON. Based on the information in the City of Ottawa website accessed in December 2005 (http://www.ottawa.ca/city_services/wastewater/env_pro_en.shtml), the facility serves an area of 2,767 square kilometers with a population of 750,000 and treats domestic, commercial, and industrial wastewater, as well as some surface run-off before returning treated water to the Ottawa River. The statistical data showed that the average volume of wastewater treated in ROPEC was 420,000 m^3/day with maximum peaking factor of 2.01 (peak volume reached 842,000 m^3/day in 2000).

Wastewater treatment at the ROPEC plant involves preliminary treatment, primary treatment, secondary treatment, phosphorus removal, biosolids management. Chlorine disinfection is applied on the treated wastewater prior to discharge into the Ottawa River from May 16th to November 15th annually. Coarse screening, fine screening and grit removal are employed in preliminary treatment to remove large objects and heavy solid materials. The fine screening facility has a screen opening of 0.25mm. In primary treatment, settable solids and floatable material are removed in 15 evenly sized rectangular primary clarifiers. Primary sludge, discharged from the primary settler is transferred to the biosolid management facility and anaerobically digested (35°C) along with thickened wasted aerobic sludge (TWAS) from secondary biological treatment. Primary sludge used in this experiment was sampled from the transfer line monitoring station between the primary clarifier and the biosolid management system.

3.2 Experimental Protocols

3.2.1 Acclimation of Anaerobic Digestion Seed

The initial anaerobic digestion seed culture was collected from anaerobic digestion residue of microwave pretreated PS. About 7 L of digested sludge was transferred to a 20-L plastic bottle equipped with a biogas vent and feed/withdrawal port, placed on a shaker rotating at 100 rpm and located in a hot room maintained at 35°C. The solids retention time (SRT) of the acclimation reactor was kept in a range of 20 to 25 days corresponding to a volumetric loading of about 1.5 g VS/L·d by withdrawing a certain

amount of digested sludge and adding the same amount of MW pretreated primary sludge. Distilled water was periodically added to the acclimation reactor to compensate for evaporated water that escaped biogas. Feed was prepared by microwaving primary sludge from ROPEC (4% SS w/v) to a temperature of 85°C. To assess the level of acclimation, during the first 1-2 months of cultivation, digestion performance was monitored by measuring biogas production daily with a tag bag. TS, VS, pH, VFAs, and gas composition were measured weekly. It required approximately 3 weeks for performance parameters in the acclimation reactor to stabilize. From then until the end of the experiment, biogas production and pH were measured weekly. Monitoring and analysis of other parameters were only conducted two weeks before the utilization of anaerobic digestion seed. A photo of the acclimation setup is shown in Figure 3.1.

3.2.2 Collection and Preparation of Primary Sludge

PS samples were collected in 10-L and 20-L clean plastic gasoline-type tanks one day prior to each experiment and stored in a 4°C refrigerator. PS obtained from ROPEC had a solid concentration of 4.0-4.3% (w/v). To ensure homogeneous sample characteristics sludge from individual gasoline cans were vigorously blended together in a large tank before taking samples for analysis or use. In preparation for use, dilution to desired solid concentrations of 1, 2, 3, and 4% (w/v) was carried out by adding distilled water. Prior to use, the diluted sludge was allowed to warm up to room temperature until it reached 20°C. All samples pretreated in the microwave had an initial starting temperature of 20°C.

3.2.3 Microwave Pretreatment of Primary Sludge

Microwave irradiation of sludge was performed at a frequency of 2.45 GHz in a 1,460 W domestic Panasonic microwave oven equipped with rotating tray. The model number was NN-S693 and the oven cavity size was 469 mm × 470 mm × 278 mm.

850g of PS (at various concentrations) was placed in a shallow 2-L polypropylene container (254mm×152mm×75cm) and weighed on a balance. MW pretreatment of the sludge was carried out in the same container. During microwave irradiation, two sources of experimental error were the escape of volatile substances in the sludge and residual

heat remaining in the oven cavity from the previous microwave pretreatment operation. To minimize experimental errors and improve precision of the microwave operations temperature of the MW cavity was checked prior to irradiation and the container was sealed by covering with plastic wrap. Following microwave irradiation, the sludge was mixed by shaking the container vigorously with the container covered. Final sludge temperature was measured using a series of 5 thermocouple probes inserted in the middle of the sample. The recorded final temperature was the highest temperature shown on the connected monitor and used later in the "Results and Discussion" section as the MW temperature. The photo of the microwave irradiation setup is shown in Figure 3.2.

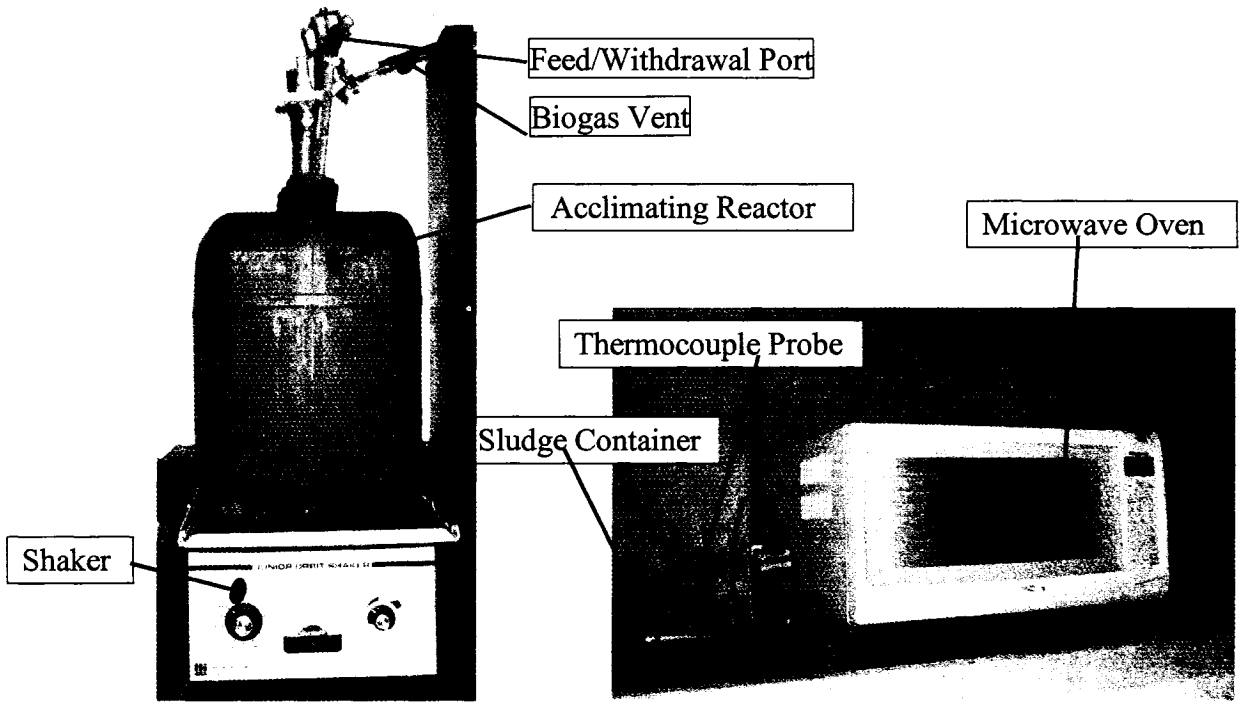


Figure 3.1 Acclimation reactor setup.

Figure 3.2 Microwave irradiation setup.

In this experiment, regardless of variation in sludge solid concentration, a fixed amount of microwave irradiation time was required to achieve a certain temperature. The required pretreatment time was estimated based on experimental results provided by Gabriel Thibault and checked using tap water. The relationships between MW pretreatment duration and final temperature achieved are presented in Appendix A-1, the relationships between MW energy input and final temperature achieved are presented in Appendix A-2.

Microwave pretreatment in all microwave scenarios was carried out in duplicate. Cooled duplicate samples were well mixed in a 2-L bottle and then distributed into 2 parts for BMP assays and characterization of pretreated sludge. All sludge samples were stored in a 4°C refrigerator. The same amount of untreated sludge at 1, 2, 3, and 4% TS was also sampled, distributed and preserved as controls.

In the first experiment, microwave intensity was fixed at 80%, and diluted sludge (TS 1, 2, 3%) was pretreated from 20°C to 35, 65, and 90°C. Sample temperature hold time was set at 0 minutes. The second set of experiments consisted of two parts. In the first part, at fixed microwave intensity of 40%, diluted sludge (solid concentration 2, 3, 4%) was pretreated from 20°C to 35, 65, and 90°C. In the second part, at fixed microwave intensity of 80%, diluted sludge of solid concentration 4% was pretreated from 20°C to 35, 65, and 90°C. Again, sample temperature hold time was set at 0 minutes.

3.2.4 Effect of Microwave Pretreatment on Characteristics of Primary Sludge

This study investigated the influence of temperature, microwave intensity and sludge solid concentration on the characteristics of PS. Microwave irradiation was conducted as described in section 3.2.3. The preservation and analysis methods will be fully described in section 3.3 and 3.4. Untreated sludge at each solid concentration was used as the corresponding control.

3.2.5 Biochemical Methane Potential (BMP) Assay on Primary Sludge

After the microwave irradiation described in section 3.2.3, digestibility of pretreated sludge and control samples were evaluated using BMP assays. BMP assays were conducted in 1-L Wheaton borosilicate glass graduated media bottles. The bottles were closed with black butyl stoppers and secured with plastic screw caps. The screw cap had a circular opening in the center that allowed for the sampling of biogas and supernatant during the BMP test. A picture of BMP reactors inside a orbital shaker is shown in Figure 3-3,

The BMP test was conducted by addition of 500g of well-mixed sludge sample (pretreated or control) into a reactor bottle. The sludge was weighted on a balance. 100-

mL acclimated digestion seed and alkalinity mixture were added into the bottle after the sludge sample. The alkalinity mixture of 4.1g $KHCO_3$ and 4.1g $NaHCO_3$ for each sample was designed to obtain a total alkalinity concentration of around 9000 mg/L (as $CaCO_3$) and ensure adequate buffering capacity for the sludge with 4% solid concentration. To minimize aerobic biodegradation, nitrogen gas was sparged into the digestion mixture in the reactor bottles for 10 minutes. BMP reactor bottles were then sealed and put into a temperature-controlled New Brunswick incubator to perform the BMP test. The incubator maintained a rotating speed of 50 rpm and a temperature 35±1°C. BMP reactors were placed in a 20°C environment for less than 20 minutes per day for biogas measurement or pH sampling during the BMP test. Reactors were kept sealed during the digestion process. Once biogas production ceased indicating that digestion was complete reactor bottles were uncapped to terminate the BMP assay. The digested sludge was stored in a 4°C refrigerator until final sludge characterization was completed. The BMP assay setup is shown in Figure 3.3.

The same sludge samples were used for both the BMP assays and MW pretreatment characterization as described in section 3.2.3 and 3.2.4. Allowing for comparison of pretreatment and BMP results. Biogas measurement was performed daily by inserting a manometer-connected needle through the rubber cap (Fig 3.4). Supernatant was sampled weekly with a 27-gauge needle syringe to examine in-bottle pH and VFAs concentrations. Characterization of the digested sludge was performed after BMP assays were terminated. Measured parameters and measuring frequency were described in Table 3-1.

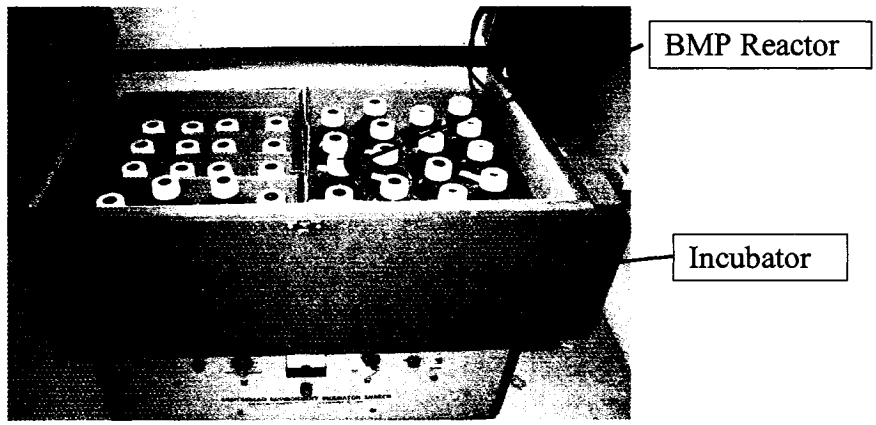


Figure 3.3 Biochemical methane potential setup.

3.2.6 Biochemical Methane Potential Assay on Soluble Portion of Primary Sludge

Based on BMP assay performance of MW pretreated primary sludge, two promising microwave irradiation scenarios were chosen to conduct a BMP assay on the soluble portion of the PS. The experimental approach of the BMP test on the soluble portion of the PS was similar to that used for the PS as described in sections 3.2.2, 3.2.3, 3.2.4, and section 3.2.5. The following description only involves special aspects of the experimental approach used for the soluble substrate.

PS collected from ROPEC was characterized and diluted to a sludge solid concentration 4%. 500g of 4% sludge was microwaved to a temperatures of 65 and 90°C at a microwave intensity of 80%. Again, sample temperature hold time was set at 0 minutes. 500g of untreated 4% sludge was sampled as a control. Sludge samples were then centrifuged at relative centrifugal force (RCF) 7000 for 20 minutes and filtered through 0.45μm microglass filter paper to obtain the soluble part of the sludge. More details about the centrifuge and filtration are presented in section 3.3.9: Soluble Chemical Oxygen Demand (SCOD) analysis.

To evaluate the potential production of inhibitory substances during microwave pretreatment, BMP assay were conducted on pretreated and untreated samples. The SCOD value was determined for pretreated and control samples; then a portion of both pretreated samples was used to in the BMP assay to evaluate as produced and the same SCOD concentration as the control sample.

These BMP assays were conducted in 125-mL clear borosilicate glass serum bottles sealed with gray butyl rubber stoppers and standard aluminum caps. The SCOD BMP test reactor is shown in Figure 3-5. The digestion mixture consisted of 90 g of the soluble portion of primary sludge, 0.6 g $KHCO_3$ and 0.6 g $NaHCO_3$, and 16 mL acclimated digestion seed. Due to the nature of the sample in this experiment, sample determination prior to and after digestion only involved SCOD and pH. During the BMP test, biogas production was measured daily and biogas composition was analyzed once right before digestion termination. All BMP tests were conducted in duplicate.

Figure 3.5 Setup of biochemical production measurement on soluble portion of primary sludge

3.2.7 Method for Maximum Disintegration of Primary Sludge

15N NaOH solution was prepared one day before use. Sixteen 125-mL clear borosilicate glass serum bottles were organized into two groups of 8 serums. 90mL of fresh raw PS (4% TS) was transferred into each serum bottle. In each test group, 0, 3.1, 6.1, 12 mL respectively of 15N NaOH solution were added into duplicate bottles. Oxygen was removed by sparging nitrogen gas into the mixture for 3 minutes then the bottles were closed with gray butyl rubber stoppers then secured with standard aluminum seals. Samples were shaken vigorously then put on a orbital shaker rotating at 100 rpm at room temperature for 24 or 48 hours. All experiments were performed in duplicate.

After 24 or 48 hrs bottles were opened and neutralized with concentrated sulfuric acid to pH 7. SCOD analysis was performed on the neutralized sludge as described in section 4.4. The change in SCOD with treatment conditions and time were recorded as a measure of the solubilization of PS.

3.3 Analytical Methods (Parameters Evaluated At Each Stage)

3.3.1 Alkalinity

Bicarbonate alkalinity was measured as alkalinity according to Standard Method 2320B (APHA, 1992). The sludge sample was centrifuged in a Dupont Instrument stainless steel

tube at a RCF of 2000g for 50 minutes or at 7000g for 20 minutes. The variation of centrifuge speed and duration was due to the availability and capacities of centrifuge machines. A sample of supernatant was tested for alkalinity. At each measurement, a certain amount of supernatant was placed in a 100mL beaker and titrated by 0.2~0.4N sulfuric acid dispensed through a 50-mL Kimax® burette. A Thermiz stirrer model 120 MR was used to ensure added sulfuric acid reacted with alkalinity substances immediately by putting a stirring rod in the beaker and setting the stirring at speed #3. pH value change was measured with a Fisher Accumet® Model 750 pH/ion meter with the electrode of the pH meter inserted in the sample during the titration. The quantity of acid needed to reach pH of 4.5 was recorded. The titration endpoint of pH 8.3 was not tested as all samples presented a pH value below 8.3. The electrode of the pH meter was stored in a large volume of distilled water and thoroughly rinsed with distilled water and wiped with Kimwipes® task wipers before each use.

3.3.2 Ammonia

Standard Method 4500 NH_3-F (APHA, 1992) was employed to measure the dissolved ammonia ($NH_{3(aq)}$ and NH_4^+) concentration. The determination was applied to supernatant prepared by the same method as that for alkalinity measurement as described in 3.3.1. Equipments used for the measurement were an Orion ammonia electrode model 95-12 and a Fisher Accumet model 750pH/ion meter. 25 or 40mL samples (depending on availability of sample) were placed in an 80mL beaker with the ammonia electrode. One ml of 10N sodium hydroxide was added into the sample to raise the pH value to above 11 and release the ionic ammonia into free (gas) ammonia prior to measurement. The electrode of a Fisher Accumet® Model 750pH/ion meter was inserted into the sample to ensure the pH value of 11 was reached. The sample beaker was shaken slightly after adding alkaline to accelerate completion of the chemical reaction.

Calibration curve was prepared prior to ammonia concentration reading of samples to verify proper electrode operation. The standard ammonia concentration points chosen were 10, 100, and 1000 mg/L based on the range of ammonia concentration in the samples examined. If the calibration curve showed a linear relationship a ten-fold change

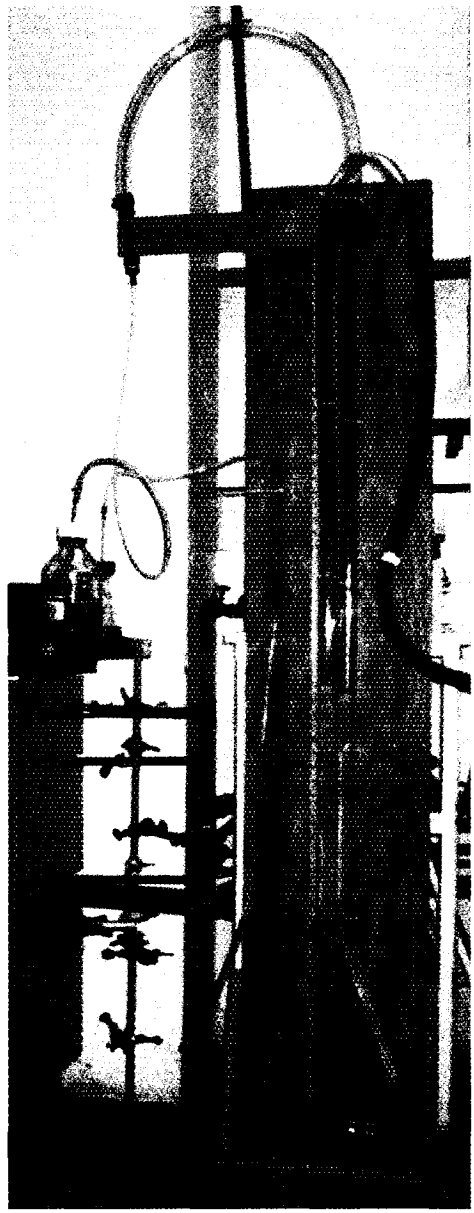
from an ammonia concentration of 0.1 M presented an electrode reading change of –54 to –60 mV, the measurement was accepted and the calibration curve used for ammonia concentration determination.

3.3.3 Biogas Composition

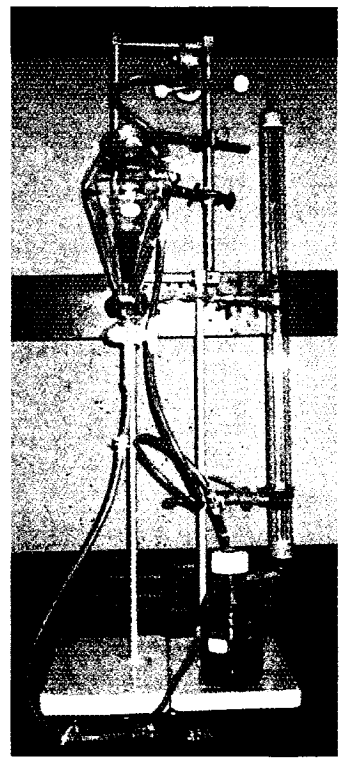
A 0.7-mL biogas sample was collected by inserting the 27-gauge needle of a 1-mL Turberculine syringe through the stopper of the BMP bottles. Before final sampling, the syringe plunger was worked in and out twice to ensure a representative sample. Then the needle was punched into a rubber stopper to seal the biogas samples immediately. 0.5mL sample was injected into the inlet port of a Hewlett Packard model 5710A gas chromatograph (GC) equipped with a thermal conductivity detector using helium as the carrier gas. National Instrument^{TM} LabVIEW version 6.0 was installed in the GC terminal computer. The composition of the biogas in terms of nitrogen, methane, and carbon dioxide was recorded from the computer monitor before proceeding to the next analysis.

3.3.4 Biogas Production

Two manometers were employed to measure biogas production. During the exponential phase, measurement was performed with a customized U-tube manometer that was capable of measuring up to 350 mL. A water displacement manometer with less capacity was used otherwise. A manometer-connected 27-gauge needle was punctured through the rubber stopper of the batch bottle. For the water displacement manometer, the volume of biogas production was recorded by reading the difference corresponding to water level in the column. Biogas volume measured by the U-tube manometer was calculated by multiplying the water level change with the transverse area of manometer tubing. The setup of biogas production measurement is shown in Figure 3.4.



U-tube manometer



Water replacement manometer

Figure 3.4 Biogas production measurement setup.

3.3.5 Dewaterability

Dewaterability of digested sludge was measured as capillary suction time (CST) according to Standard Methods 2710G (APHA, 1992). A Fann® capillary suction timer was used. Samples were placed at room temperature 2 hours before the test to ensure the sample temperatures were 20°C for all testing. Sample temperature was ensured with a Mercury-filled Celsius thermometer. A piece of CST paper was placed between

contacting sensors and a stainless steel reservoir was put on top of the sensors. 5 mL of sample was slowly injected into the reservoir from the top opening. The timer would count the time required for sludge water to flow from the first sensor to the second sensor. Measurements were performed in duplicate.

3.3.6 pH

pH was measured with a Fisher Accumet® Model 750 pH/ion meter equipped with a glass electrode according to Standard Methods 4500-H^+B (APHA, 1992). After microwave pretreatment, a fresh sample was cooled down to 20°C with a water bath. pH measurement was performed immediately to minimize contact of the sample with air. During the BMP assay, pH of fresh samples from batch bottles were measured immediately after the sample was taken. The electrode was rinsed with distilled water and dried with Kimwipes® task wipers before each measurement.

3.3.7 Total and Soluble Chemical Oxygen Demand

Total and soluble chemical oxygen demand were measured using the colorimetric technique based on Standard Methods 5220D (APHA1992). Preparation of soluble COD samples started by centrifuging sludge samples at an RCF of 7000g for 20 minutes or 2000g for 50 minutes. The resulting supernatant was filtrated through 0.45μm filter paper and filtrate was collected for soluble COD analysis. Preparation of total COD samples necessitated pre-dilution of sludge. The pre-diluted sludge sample was shaken and turned upside down 10 times before each sampling. Sample sludge was then added into volumetric flask, weighed on a Mettler PC4400 balance, and diluted to the mark on the bottle neck with distilled water. The weight of the sludge sample was recorded. The weight of sampled sludge and the size of volumetric bottle were used to determine the dilution factor.

COD determination was performed in Kimax and Pirex culture tubes (25×150mm) with Teflon-line bakelite screw caps. 10mL mixture of prepared sample and distilled water, 6mL of digestion solution, and 14mL of catalyst solution were added to the culture tube in order and mixed on a Fisher vortex Genie 2^{TM} tube mixer for 2 minutes prior to

digestion in a 150°C oven for 3 hours. The prepared samples and distilled water were measured and transported with serological pipets. The tip of pipets for total COD sampling was carefully cut off to avoid selective sampling and the pipets were recalibrated. Digestion solution and catalyst solution were prepared according to Standard Methods 5220D and added with bottle top calibrated dispensers. The proper sample volume out of the 10mL sample-distilled-water mixture was estimated using previous experimental results. A process of trial and error was required on the dilution of some samples.

Digested samples were taken out of the oven, cooled in a dark cabinet overnight, and read on a Coleman Perkin-Elmer spectrophotometer model 295. The spectrophotometer was turned on the night before COD reading and set to a light absorbance wavelength of 600nm. Before each reading, the COD tube was wiped with a wet towel and dried with Kimwipes® EX-L wipes. The spectrophotometer was calibrated with standard COD tubes that were prepared monthly and stored in a dark cabinet. Soluble COD analysis and Total COD analysis of the first set of experiment were performed in duplicates. Total COD analysis of the second set of experiment was performed in triplicate to minimize experimental error caused by the non-uniform nature of primary sludge.

Before each use, COD tubes were soaked in dishwasher detergent solution for 2 days, brushed, rinsed thoroughly, and placed on shelf upside down to dry. After no more than 5 uses, COD tubes were placed in a 20% sulfuric solution overnight washed with detergent and rinsed with distilled water.

3.3.8 Total and Volatile Solids

Total and volatile solids were measured according to Standard Methods 2540G.3a (APHA, 1992) with a slight modification. Due to the non-homogenous nature of primary sludge, the volume of sample was desired to be 50~100g instead of 25~50g as described in Standard Methods.

Before each use, porcelain crucibles were soaked in detergent solution for 1 day, scrubbed, submerged in 20% sulfuric acid overnight, scrubbed, rinsed with distilled water. The cleaned crucibles were conditioned in a Thermolyne muffle furnace model F62730 at 550°C for 1 hour based on Standard Methods 2540G.3a (APHA, 1992). Conditioned crucibles were cooled down in a dry 103-105°C oven for 30min. then placed in desiccators for 30 min, weighted on a Sartorius model 2001-MP balance (W), and then store in desiccators until ready for use.

At each measurement, a prepared crucible was placed on a Mettler PC4400 balance and 50~100g of well-mixed sludge were poured into the crucible. The weight of sludge (W_0) and the number of the crucible were recorded. Sample was dried in 103-105°C oven for 24 hours. The evaporation residue and crucible were cooled down in desiccator for 30 minutes and weighted on a Sartorius model 2001-MP analytical balance (W_1). Weighed evaporation residue with crucible were then placed in a Thermolyne muffle furnace model F62730 at 550°C for 40 minutes to ignite all organic matters in the sludge sample. Similar to crucible preparation, ignited sample was cooled in a dry 103-105°C oven and a desiccator, then weighed (W_2). Percentage total and volatile solids were calculated according to equations 3.1 and 3.2.

$$\%TS = 100 \times \frac{W_1 - W}{W_0} \tag{3.1}$$

$$\%VS = 100 \times \frac{W_1 - W_2}{W_0} \tag{3.2}$$

3.3.9 Suspended and Volatile Suspended Solid

To simplify the measurement techniques, the determination method of total and volatile suspended solid employed in this study was modified based on Standard Methods 2540D.2a (APHA, 1992). In the modified method, after centrifuging a 30g sample at an RCF of 7000g for 20 minutes, the pellet was directly taken to measure total and volatile suspended solid without filtration. (Filtration tests indicated that the amount of suspended

solids in the supernatant was neglibible). The pellet was taken out of the centrifuge tube with a specula after carefully pouring away the clear supernatant. By adding small volume of distilled water and vigorously shaking the centrifuge tube, remaining pellet suspended solids were also washed out.

The sampled precipitate was placed in prepared crucible. The drying and ashing procedure was the same as in measurement of TS and VS described before. The weight of sludge samples before centrifuge was weighed on a Mettler PC4400 balance (W_0). The weight of the prepared crucible was recorded as W, the weights of sample after treated in 103-105°C and 550°C were recorded as W_1 and W_2, respectively. Percentage total and volatile suspended solids were calculated according to equations 3.3 and 3.4.

$$\%TSS = 100 \times \frac{W_1 - W}{W_0} \tag{3.3}$$

$$\%VSS = 100 \times \frac{W_1 - W_2}{W_0} \tag{3.4}$$

3.3.10 Volatile Fatty Acids (VFAs)

Concentrations of VFA were determined in a Hewlett-Packard 5840A GC was equipped with a flame ionization detector, a 250°C injection port, a chromosorb 101 packed column, an oven temperature of 180°C, a model 5840 integrator, and an automatic sampler. Helium gas saturated with formic acid served as GC carrier gas at a flow rate of 15 mL/min.

One ml of sludge sample was centrifuged at speed of 12,000 rpm for 4 minutes. Each sample was prepared by transferring 0.5 mL of the resulting supernatant and 0.5 mL of Internal Standard Solution (ISTD) into a clean glass vial with a 500μL model 4700 Eppendorf ejector pipette. Prepared samples were covered with parafilm and stored in 4°C refrigerator and run in the GC with in 24 hours.

Calibration was carried out before each use with standard samples that consisted of 0.5 mL ISTD and 0.5 mL VFA standard mixture. The ISTD contained 2000 mg/L isobutyic acid. The VFA standard mixture contained 2000 mg/L of each acetic, propionic, and butyric acids. The process of measuring and calibration were repeated until the reading for each VFA reached 2000 ± 50 mg/L.

3.4 Preservation

Preservation of samples for each analysis was done in accordance with Standard Methods Table 1060:1 (APHA, 1992). All storage bottles and glass apparatus were soaked, scrubbed, and rinsed with distilled water. Table 3.3 presents the preservation methods employed.

Table 3.3 Preservation methods summary.

Analysis	Material of storage bottle	Sample type	Preservation	Max. storage time
Alkalinity	Plastic	Supernatant	4°C Refrigerated	24hours
TCOD				
pH	Glass	Sludge	Room temperature	15 Minutes
TS	Plastic	Sludge	4°C Refrigerated	7 days
VS				
TSS				
VSS				
CST				
Ammonia	Glass	Sludge	Added concentrated H_2SO_4 to PH< 2	7 days
SCOD	Plastic	Filtered with 0.45μm filter paper	Added concentrated H_2SO_4 to PH< 2	7 days
VFAs	Glass	Mixed with ISTD	4°C Refrigerated	1 day

CHAPTER 4
RESULT AND DISCUSSION

The results of the experiment are presented and discussed in the following sections. The methodology concerning this research is described in more detail in chapter 3. To begin with, the determination of a method to estimate the ultimate solubilization of primary sludge is evaluated and discussed. The second part of this discussion deals with the MW effect on the characteristics of the primary sludge. The sequential BMP assay of primary sludge after the MW pretreatment is discussed next. A further investigation involving the BMP assay on the soluble portion of primary sludge, untreated and MW pre-treated is also discussed.

4.1 Alkaline Pretreatment as An Estimate for Ultimate Solubilization of Primary Sludge

"Ultimate sludge solubilization" was examined to assess the maximum sludge solubilization obtained from pretreatment of sludge (Muller, *et al.,* 1998, Tiehm, *et al.,* 2001, and Tiehm, *et al.,* 1997). The measurement method was defined as 'aqueous phase COD obtained by chemical sludge solubilization in 0.5 mol/Lsodium hydroxide for 22 hours at 20°C (Tiehm, *et al.,* 1997). No further information about this measurement method was available. Thus, the determination of proper alkaline dosage and duration is open to question. To estimate the ultimate solubilization of the primary sludge used in this research, the recommended measurement method was modified and then used to examine the solubilization level of the primary sludge after being pretreated at varied alkaline exposure times and alkaline dosages at 20°C. Table 4.1 shows detailed experimental factors and the resulting soluble COD values determined after the alkaline pretreatment. Data are also plotted in Figure 4.1 and Figure 4.2 to show the influence of duration and alkaline dosage on the primary sludge solubilization level in terms of SCOD concentration and SCOD/TCOD ratios, respectively. It should be noted that all alkaline incubated tests and corresponding control tests were conducted in duplicates.

Table 4.1 Maximum sludge solubilization via alkaline pretreatment

Duration time	Alkaline dosage (N)	Average SCOD value (mg/L)
Fresh raw primary sludge *	0	2528
24 hours	0.5	5914
	1	5686
	2	5971
48 hours	0.5	6429
	1	9757
	2	12100

* Original fresh raw primary sludge had 4% TS concentration and 51244mg/L TCOD concentration, SCOD concentration 2528 mg/L.

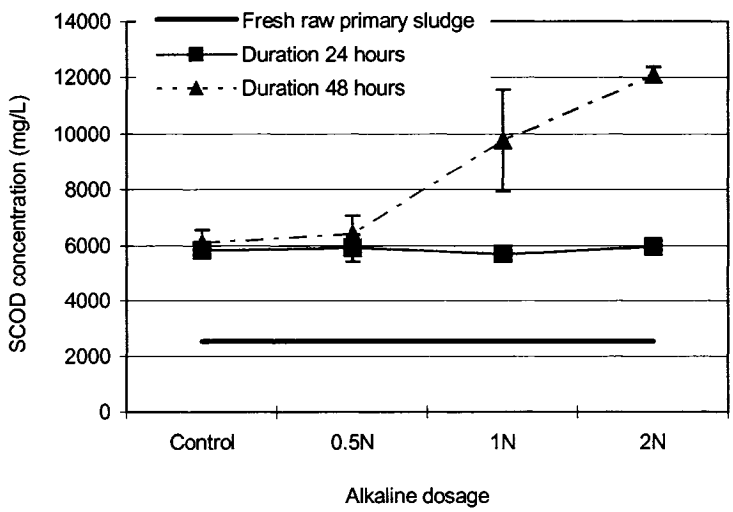


Figure 4.1 Influence of alkaline pretreatment on SCOD concentration

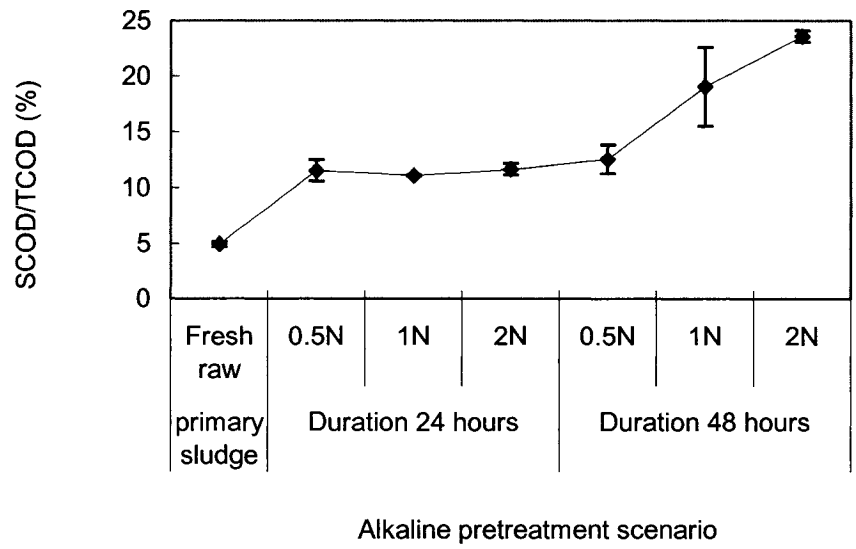


Figure 4.2 Influence of alkaline pretreatment on SCOD/TCOD ratio

After a pretreatment period of 24 hours, increasing the alkaline dosage from 0.5N to 2N did not improve the solubilization of the sludge. However, after 48-hour contact with alkaline, SCOD concentrations of pretreated sludge started to increase linearly with the increased concentration of alkaline and at the highest alkaline dosage of 2N reached 12100 mg/L, which comprised 23.6% of the TCOD (51,244 mg/L) of the sludge sample,. The linear relationship of the SCOD concentration increase with the increase of alkaline dosage at 48 hour-duration tests was described by:

$$[SCOD] = 0.0003 \times alkaline\ dosage - 1.2548$$

$$(R^2 = 0.9182)$$

Due to the non-uniform nature of primary sludge and the relatively small volume of each sludge sample (V=90 mL), SCOD values showed relatively low levels of agreement between duplicate treatments at experimental elapsed times of 48 hours and alkaline dosage 1N. However, the SCOD concentration of the chemically treated primary sludge samples did not reach the ultimate level (100%) in all of these experimental conditions.

From Figure 4.2 it can be seen that the greatest solubilization of 23.6% was obtained at the highest alkaline dose and longest exposure time. This condition was termed the maximum primary sludge solubilization (specific to ROPEC primary sludge) and was used to compare the effects of MW pretreatment.

4.2 Influence of Microwave Pretreatment on Characteristics of Primary Sludge

4.2.1 Design of Microwave Pretreatment Scenarios

Three MW pretreatment factors were investigated in the study of MW pretreatment on the characteristics of primary sludge and sequential BMP assay (separately discussed in section 4.3. These factors were primary sludge temperatures achieved during MW irradiation, MW irradiation intensity, and solid concentration of irradiated primary sludge. Sludge solid concentration was varied from 1% to 4%, final sludge temperature from 35 to 90°C, and MW intensity from 40% (energy input 9.73J/min) to 80% (energy input 19.47J/min). It should be noted that, for each solid concentration at each experimental setting, a portion of raw sludge was used as a control sample. The characteristics of raw fresh primary sludge used in the two sets of experiments were slightly different. Table 4.2 further details the factor studied and characteristics of corresponding undiluted raw primary sludge. Analysis of TCOD, SCOD, TS, VS, TSS, and VSS were performed in duplicate and experimental errors are presented. Bicarbonate alkalinity, ammonia, and pH were analyzed as single sample.

Table 4.2 Experimental factors evaluated to determine MW influence on characteristics of primary sludge and sequential BMP assays

	Intensity	Sludge solid concentration	Temperature (°C)	Characteristics of undiluted raw primary sludge
1st Experiment set	80%	1%	Control	TS = 4.16% VS = 3.38% TCOD = 52614 mg/L SCOD = 1289 mg/L Ammonia concentration = 145 mg/L Alkalinity concentration = 220 mg/L Total VFA concentration = 914 mg/L
			35°C	
			65°C	
			90°C	
	80%	2%	Control	
			35°C	
			65°C	
			90°C	
	80%	3%	Control	
			35°C	
			65°C	
			90°C	
2nd experiment set	80%	4%	Control	TS = 4.09% VS = 3.42% TCOD = 50942mg/L SCOD = 1249 mg/L Ammonia concentration = 108mg/L Alkalinity concentration = 462 mg/L Total VFA concentration = 905 mg/L
			35°C	
			65°C	
			90°C	
	40%	2%	Control	
			35°C	
			65°C	
			90°C	
	40%	3%	Control	
			35°C	
			65°C	
			90°C	
	40%	4%	Control	
			35°C	
			65°C	
			90°C	

*MW intensity 80% is equal to energy input level 19.47J/min, MW intensity 40% is equal to energy input level 9.73J/min.

The theory of MW heating mechanisms and the research results of MW nonthermal effects were reviewed in section 2.5.2 and 2.5.4. As discussed, in concentrated sludge, more dielectric molecules are involved in electromagnetic alignment per volume unit. On

the other hand, due to the greater density of particles, rotation inhibition from the molecules surrounding the rotating dielectric molecules may also increase. Both effects bear the potential to create higher final temperatures from MW irradiation per unit of energy. Furthermore, for sludge with a higher solid concentration, selective heating might lead to more intensive influence on the chemical aspects of dielectric molecules. Microwave intensity was deemed of interest as it affects the required irradiation time required for the sludge to reach the high temperature conditions. The effect of temperature on characteristics of sludge was deduced from the thermal nature of the MW treatment.

4.2.2 Microwave Pretreatment Influence on Concentration of SCOD and TVFA

SCOD and VFA concentrations are the indicator of the level of solubility of organic matter in sludge and are widely accepted as indicators of macromolecule disintegration. Data collected for each MW pretreatment scenario and each raw sludge sample formed the basis of evaluation of MW irradiation on the eventual concentration of SCOD and VFA in primary sludge.

Figure 4.3, Figure 4.4, and Figure 4.5 show the influence of MW irradiation on the SCOD concentration, SCOD concentration increase, and SCOD/TCOD ratio, respectively.

As may be seen in Figure 4.3, in raw primary sludge, most COD is associated with the solid phase rather than being in a soluble phase, as evidenced by the rather low SCOD concentration with no MW pretreatment. Based on the initial conditions, the increase of soluble COD concentration after MW pretreatment of raw primary sludge was caused by aggregate deagglomeration and a transfer of organic substances from non-soluble material into soluble material. For sludge pretreated at a solid concentration of 4% and MW intensity 80%, SCOD concentration increased linearly 1.4 fold from 1390 mg/L in raw sludge to 3304 mg/L in sludge pre-treated to 90°C. Other MW scenarios bear a strong similarity in terms of SCOD concentration improvement. This is further clarified later in Figure 4.6 regarding SCOD concentration in untreated and treated primary sludge

as a function of the MW pretreatment temperature and Figure 4.7 showing SCOD concentration in untreated and treated primary sludge as a function of sludge solid concentration.

The increase of solubility of primary sludge is further clarified as the ratio of SCOD of MW pretreated sludge over SCOD of the control in Figure 4.4. Microwave pretreatment achieved similar improvements at all MW intensities and sludge concentrations tested. Generally, pretreatment of samples to 35°C increased SCOD concentrations 10-70% while pretreatment to 90°C increased SCOD concentrations 140-190%. The fact that the intensity levels tested had little effect on solubilization suggests that exposure time to achieve a given temperature was not that important. Influence of MW intensity, temperature and concentration are discussed later.

Likely because of the mild nature of treatment at the low MW temperatures used in this study, the disassociation of organic matter from the solid phase to the liquid phase only increased from 2.5-2.7% to a maximum of 6-7% in all cases, as shown in Figure 4.5. It is readily apparent that most of the suspended organic compounds were still not directly available as soluble substrate for subsequent anaerobic reactions.

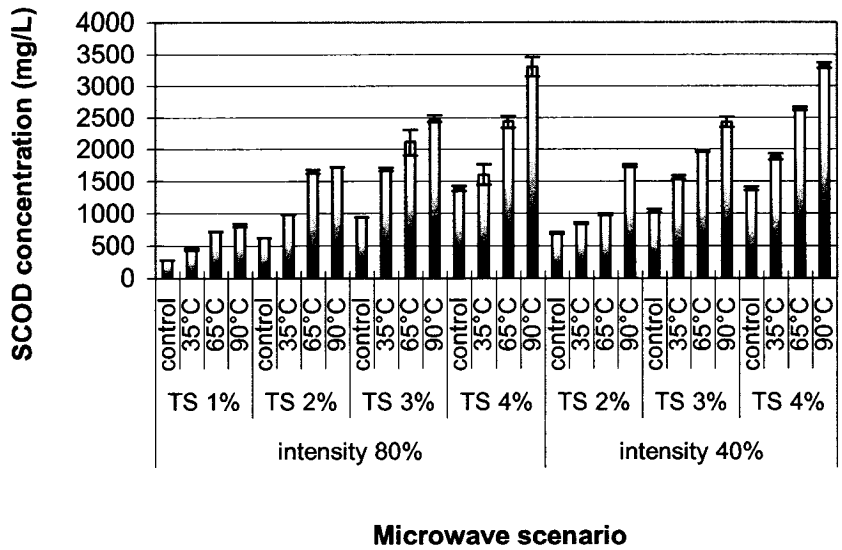


Figure 4.3 Influence of MW intensity, TS concentration and pretreatment temperature on SCOD concentration

(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

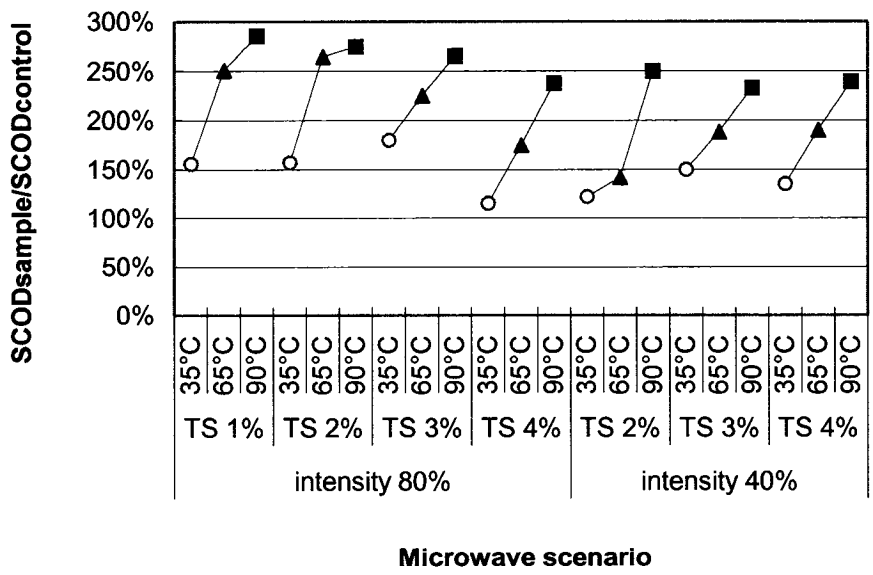


Figure 4.4 Increase of SCODsample/SCOD control ratio after MW pretreatment

(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

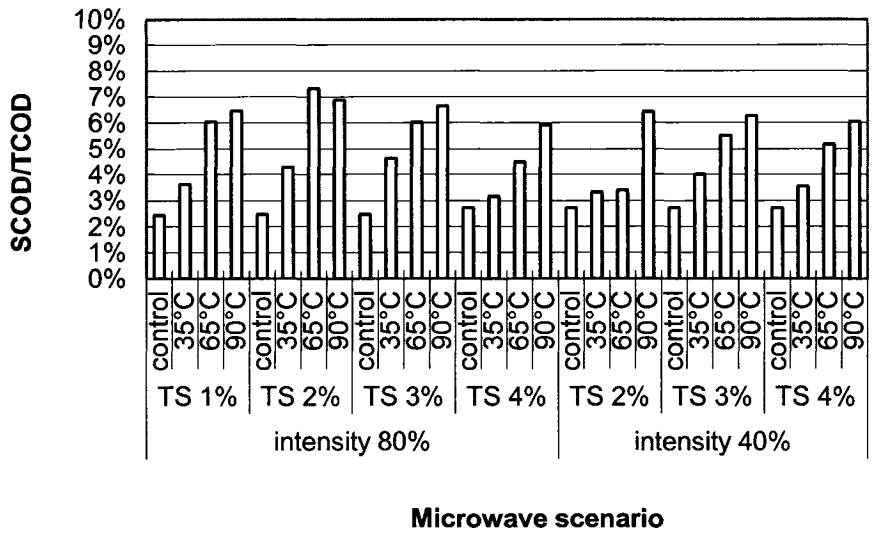


Figure 4.5 Influence of MW intensity and pretreatment temperature on SCOD/TCOD ratio(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

To explore the linear relationship between SCOD increase and MW irradiation scenarios, in Figure 4.6 SCOD concentrations are plotted as a function of the MW irradiation temperature at seven MW irradiation scenarios (sludge solid concentration 2, 3, 4% at MW intensity 40% and sludge solid concentration 1, 2, 3, 4% at MW intensity 80%). In comparison, in Figure 4.7 SCOD concentrations are plotted as a function of the sludge solid concentration at the six different MW irradiation scenarios (MW irradiation temperature 35, 65, 90°C at MW intensity both 80 and 40%).

The results of linear regression analysis between SCOD concentration and sludge solid concentration or MW temperatures are presented in Table 4.3 and Table 4.4.

Undoubtedly, the MW intensities and the resulting MW irradiation time and heating speeds were different in MW scenarios of intensities 40 and 80%, but on the whole the influences of intensity on the SCOD concentration of primary sludge is not significantly different. The slope and intercept values obtained at two different MW intensities appeared to be reasonably close, taking into account the characteristic differences in primary sludge used in the first and second experimental sets. It thus suggested that the

increase of SCOD concentration from primary sludge is independent of the MW irradiation intensities but depends on the final temperature achieved.

Comparison of linear relationships versus MW temperature (presented in Table 4.3) and linear relationship versus sludge solid concentration (presented in Table 4.4) reveals that both sludge solid concentration and the MW irradiation temperature are important parameters affecting primary sludge floc disintegration.

As described in Table 4.3, at MW intensity 80%, slope values obtained in linear regression of SCOD concentration vs. temperature increased from 7.6 in MW scenario at 1% TS to 27.3 in MW scenario at 4% TS. This means that for a given energy dissipated, the disintegration of solid organic matters will be much greater with concentrated sludge than with diluted sludge. This fact is important because, from the industrial application standpoint, it is better to apply the process to concentrated sludge to consume less energy and achieve greater solubilization.

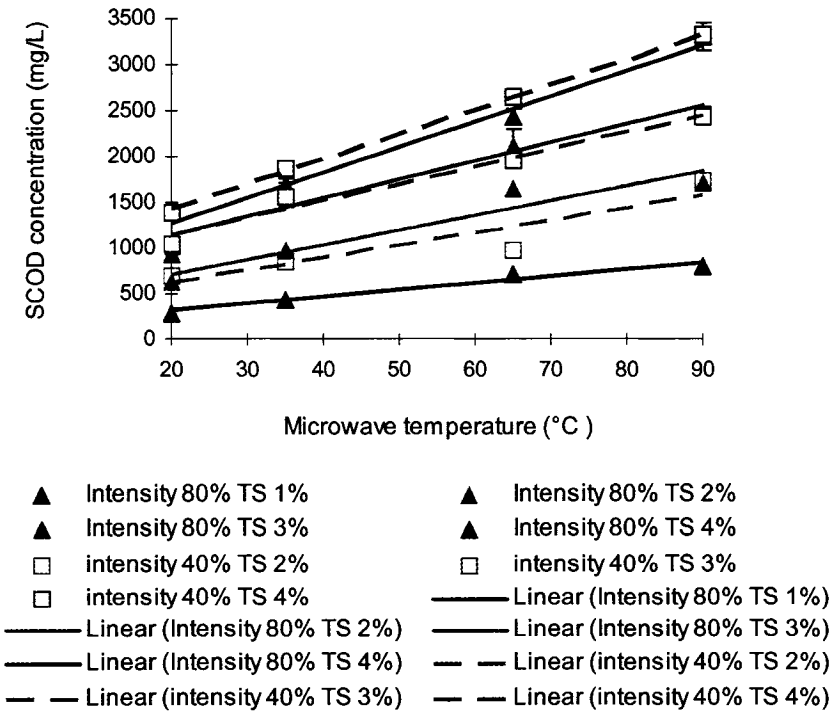


Figure 4.6 Influence of MW temperature, MW intensity and sludge solid concentration on SCOD concentration

(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

Table 4.3 Linear relationships between SCOD concentration and temperature achieved at each MW intensity and primary sludge solid concentration

Microwave scenario		Linear relationship	
TS 1%	Intensity 80%	SCOD = 7.67×T (°C) + 161	$R^2 = 0.97$
TS 2%	Intensity 40%	SCOD = 13.7×T (°C) + 346	$R^2 = 0.85$
	Intensity 80%	SCOD = 16.3×T (°C) + 389	$R^2 = 0.92$
TS 3%	Intensity 40%	SCOD = 18.6×T (°C) + 771	$R^2 = 0.97$
	Intensity 80%	SCOD = 20.3×T (°C) + 733	$R^2 = 0.92$
TS 4%	Intensity 40%	SCOD = 27.3×T (°C) + 878	$R^2 = 1.00$
	Intensity 80%	SCOD = 27.7×T (°C) + 727	$R^2 = 0.98$

*MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min

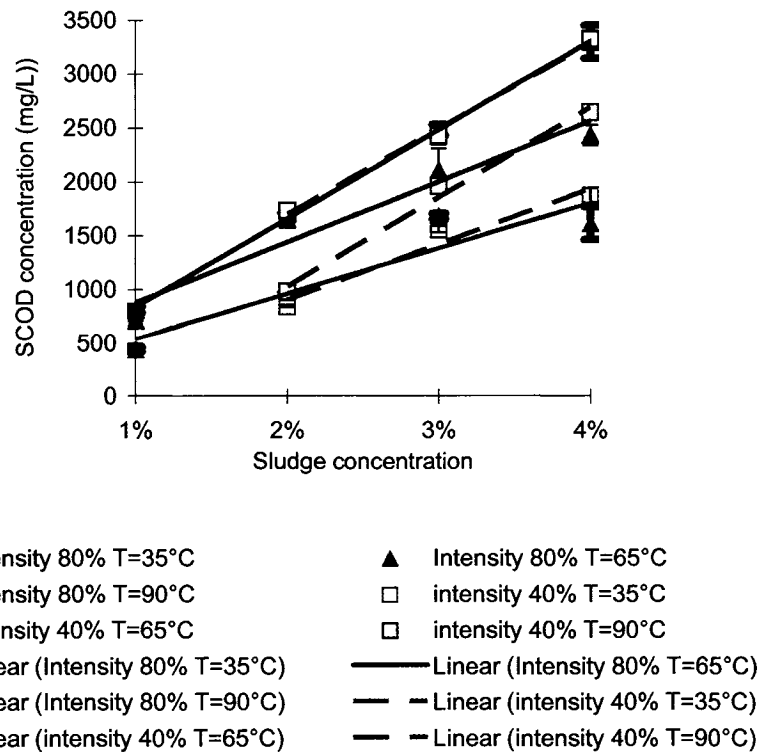


Figure 4.7 Influence of sludge solid concentration on SCOD concentration at each MW intensity and MW temperature
(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

Table 4.4 Linear relationship between SCOD concentration and primary sludge solid concentration at each MW intensity and irradiation temperature

Microwave scenario		Linear relationship	
T=35°C	Intensity 80%	SCOD = 41850×C + 132	$R^2 = 0.86$
	Intensity 40%	SCOD = 51600×C - 118	$R^2 = 0.95$
T=65°C	Intensity 80%	SCOD = 56200×C + 324	$R^2 = 0.94$
	Intensity 40%	SCOD = 83100×C - 626	$R^2 = 0.99$
T=90°C	Intensity 80%	SCOD = 82380×C + 20	$R^2 = 1.00$
	Intensity 40%	SCOD = 79450×C + 116	$R^2 = 0.99$

*MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min)

To compare the SCOD concentrations after MW pretreatment at three temperatures and two intensities and those after a 2N alkaline pretreatment for 48 hours, for 4% TS samples are presented in Figure 4.8 and Figure 4.9. After high-alkaline-concentration and 48-hour-duration pretreatment, SCOD concentration reached ~12,000 mg/L. In comparison, 12-minutes of mild MW pretreatment achieved a SCOD concentration of 3,300mg/L, which was 27% of the ultimate SCOD concentration based on alkaline treatment. Again, the similarity of the slope of the $SCOD/SCOD_{alkaline}$ vs temperature lines for the two intensities studied shown in Figure 4.9 suggest that MW temperature, instead of MW intensity, is the most crucial factor affecting ultimate solubilization. Considering the fact that the MW pretreatment in this study was conducted only in the relatively low temperature range, these values revealed that, in comparison to widely-accepted alkaline pretreatment, MW pretreatment to higher temperature may have the potential to produce relatively "clean" sludge product (no additional chemicals) that could lead to increased overall biogas yields or rates of biogas production that could result in smaller more efficient digestion facilities.

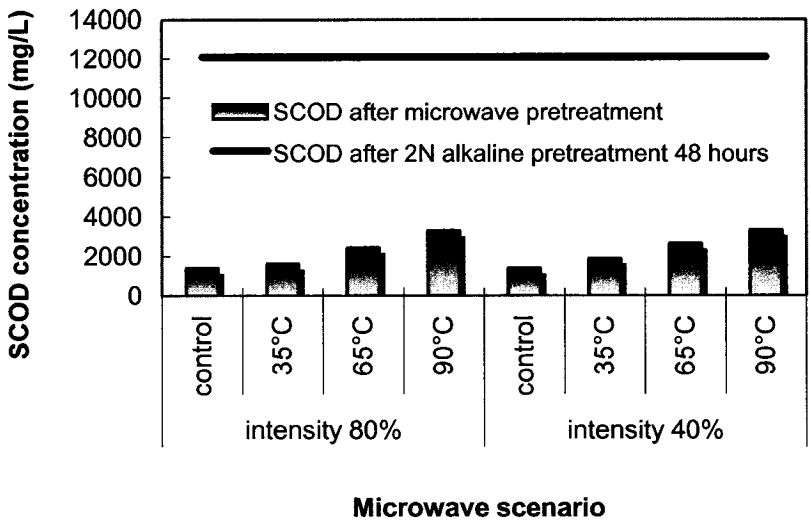


Figure 4.8 SCOD concentration after MW pretreatment and SCOD concentration after alkaline pretreatment (2N dosage for 48 hours duration for TS 4% samples)

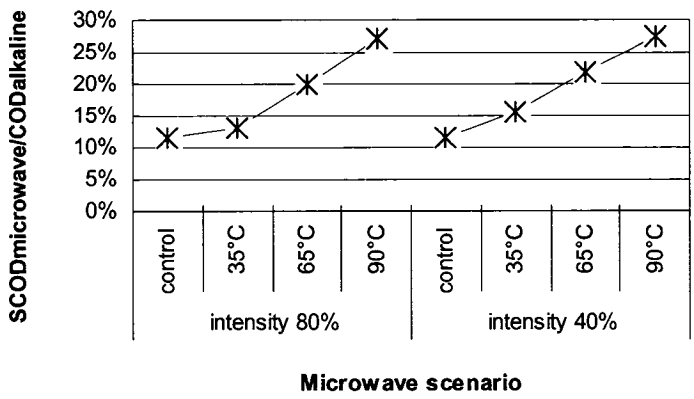


Figure 4.9 Comparison of SCOD concentration after MW pretreatment and SCOD concentration after alkaline pretreatment (2N dosage, 48 hours duration) for 4% TS samples

By plotting the values of solubilization (SCOD/TCOD ratio) obtained from all samples, Figures 4.10 and 4.11 separately describe the influence of MW irradiation on the disassociation of COD matter from the solid phase under MW intensity 80% and 40%, respectively. The SCOD/TCOD ratio is calculated on a percentage basis based on SCOD value and TCOD value determined for each MW pretreated sample and each corresponding control sample. As pointed out previously, under the 3-D view the surface shapes of SCOD climb consistently with the increase of temperature achieved.

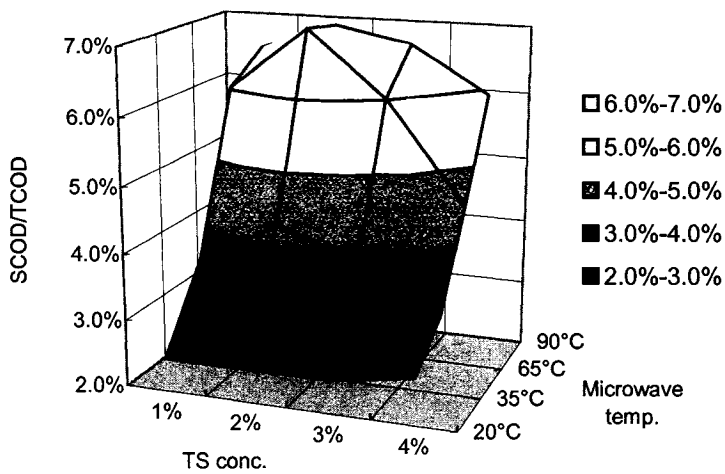


Figure 4.10 Microwave influence on solubilization rate (MW intensity 80% and energy input level 19.47J/min)(20°C represents control sample)

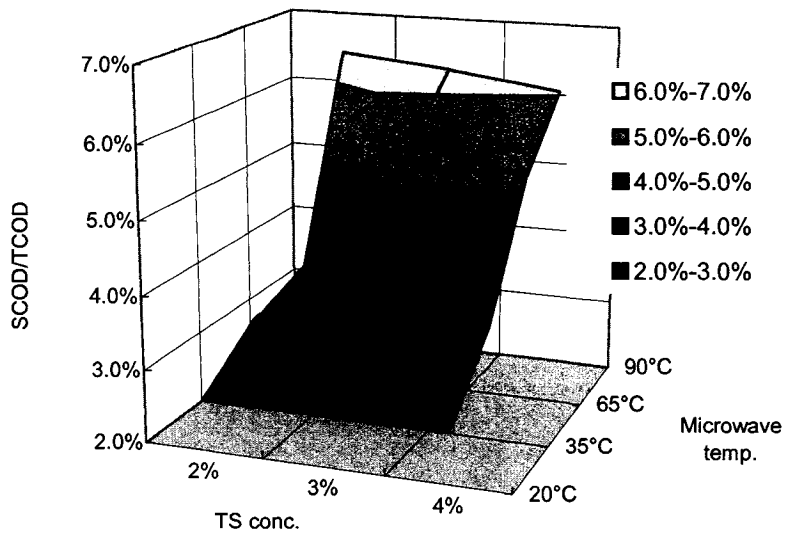


Figure 4.11 Microwave influence on solubilization rate (MW intensity 40% and energy input 973J/min)(20°C represents control sample)

Figure 4.12 and Figure 4.13 present the influence of MW irradiation of total volatile fatty acids (TVFA) concentration and TVFA concentration increases, respectively. It was believed that, smaller molecules, mainly VFAs, may be part of the final products of solubilization. Therefore, the TVFA concentration should increase with increase of hydrolysis of the primary sludge. In this study, TVFA concentration did not yield similar increasing ratios to those observed in SCOD concentration. From Figure 4.13, most of the TVFA concentrations of MW pretreated sludge only increased 5 ~ 35% above untreated samples, representing a rather low enhancement compared with the increases in SCOD concentration. As pointed out later in the discussion of TCOD concentration in section 4.2.3, no obvious mineralization of total organic matter was achieved during MW pretreatment, thus this overall poor enhancement of TVFA concentration suggested that MW irradiation solubilized macro-molecules to smaller particulate and soluble compounds, but these compounds were most likely simple sugar and protein compounds. However, the observation that the greatest improvement in TVFAs occurred at 35°C rather than 90°C implied the evaporation of VFA molecules at relatively higher temperatures (65 and 90°C) may also have been occurring.

The strength of MW irradiation decreases from the surface of the irradiated object to its center. To define the non-uniform irradiation of MW on an object exposed in the MW electromagnetic field, penetrating depth is defined as the distance at which the power density decreases to $1/\alpha$ of its initial value at the material surface as referred to in section 2.5.3. For pure water, penetrating depth decreases from about 5.7cm at 95°C to about 1.4cm at 25°C. During MW irradiation, the phenomenon of relatively high local temperatures on the surface of the sludge was also observed. High local temperatures near the surface would enhance the evaporation of various volatile substances dissolved in the water solution. Once the temperature of irradiated sludge reached 65°C, evaporation caused notable weight loss (1% of original weight) and became one of the affecting factors that may have to be accounted for.

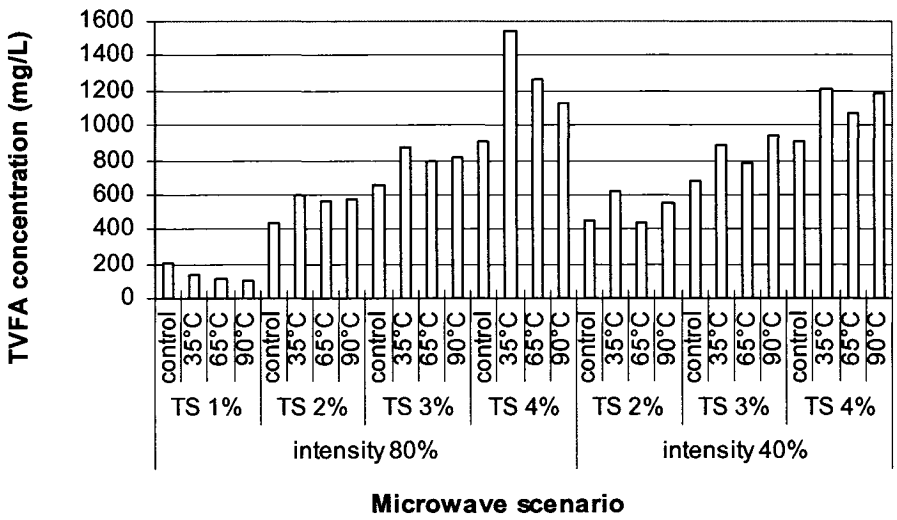


Figure 4.12 Influence of MW intensity and pretreatment temperature on TVFA concentration

(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

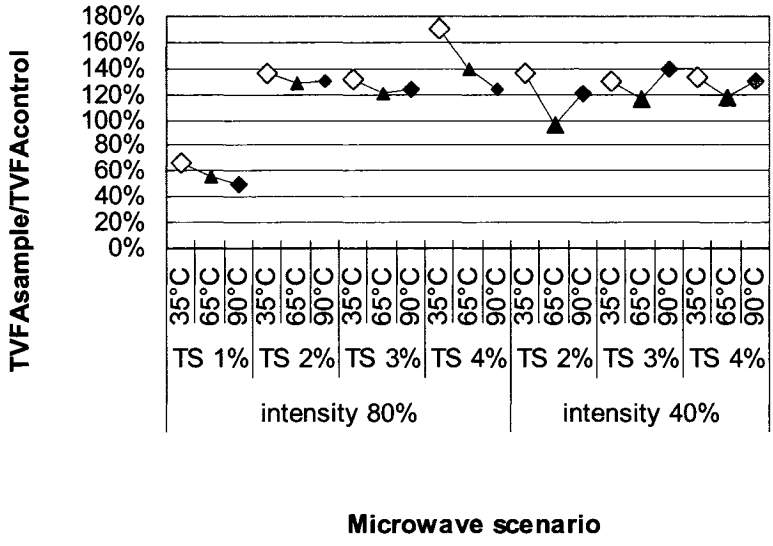


Figure 4.13 Comparison of sample and control TVFA concentration after MW pretreatment

(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

4.2.3 Microwave Pretreatment Influence on Concentration of TCOD, TS, VS, TSS, and VSS

Levels of TCOD concentration for each sample pretreated at different MW scenarios and each corresponding control sample were determined and plotted graphically in Figure 4.14. This formed a visual representation of how mild MW pretreatment affects the quantity of total organic matter in primary sludge. Relatively bigger sizes of particles and agglomeration of particles one would expect to see in primary sludge caused difficulty in representative sampling, and resulted in fluctuation in the collected data. In general, it can be seen in Figure 4.14 that there didn't seem to be any substantial difference in TCOD concentration among all experimented MW situations at each sludge solid concentration. This overall minimal influence indicated the minor MW irradiation caused no mineralization of organic compounds.

The exception to this was a slight increase of TCOD concentration values in all samples at the pretreatment temperature of 90°C over the control samples. This was likely the result of a decrease in sludge volume caused by evaporation during the MW heating process. Data collected for sludge mass before and after MW irradiation indicated that there was up to 5% weight loss during the process of raising the sludge temperature from 20°C (control) to 90°C. But it has to be noted that the volume change resulting from evaporation is not considered in the following data calculation and presentation in section 4.2 and section 4.3.

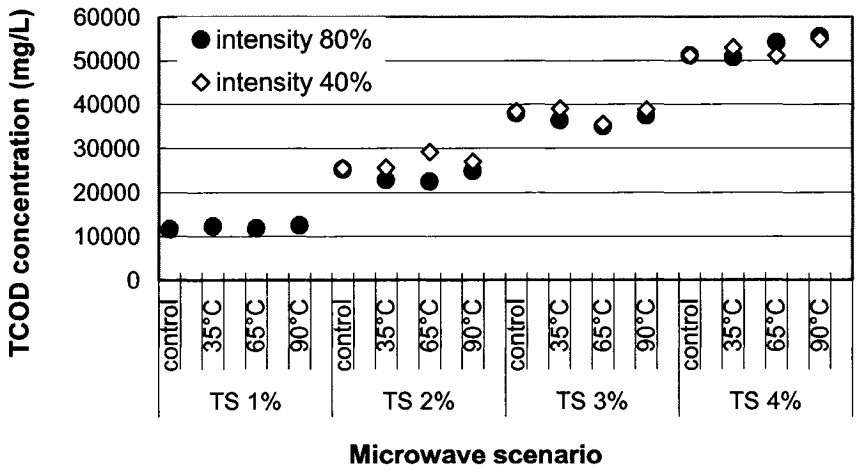


Figure 4.14 Influence of MW intensity and pretreatment temperature on TCOD concentration
(Agreements for duplicate samples are equal or less than 6% of the average values)
(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

In contrast with the concentration of SCOD and TVFA, the study of TS, VS, TSS, and VSS values focuses on transferring of substances from the solid phase into the non-solid phase and revealed another effect of MW irradiation.

The concentration results are shown for TS in Figure 4.15, VS in Figure 4.16, TSS in Figure 4.17, VSS in Figure 4.18. As expected, concentrations of TS and VS were not changed by the MW irradiation temperature for both MW intensities. Additionally, no significant change in the VSS or TSS concentrations with temperature and intensity

indicate that resistance of both TSS and VSS to solubilization is likely due to the low energy-input of the mild MW irradiation. And again, liquid evaporation led to the decrease of volume of the sludge and then a slight increase in TS and VS concentration values in most of the 90°C pretreatment. . Therefore, in terms of general performance of TSS and VSS concentration values under irradiation, the solubilization of non-soluble solid organic substances into the soluble substances is not large enough to be detected by the TSS and VSS determination methods used in this study. These results concur with the measured changes in SCOD.

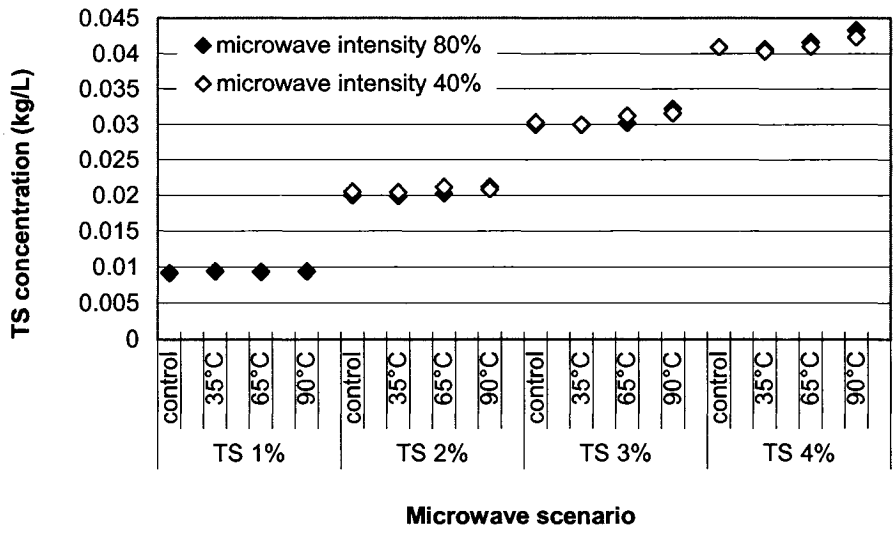


Figure 4.15 Microwave influence on TS concentration
(Agreements for duplicate samples are equal or less than 2% of the average values)
(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

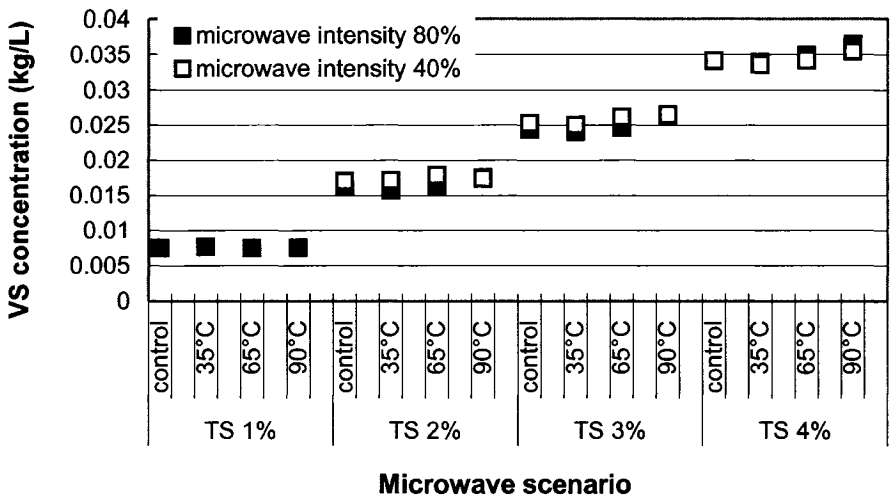


Figure 4.16 Microwave influence on VS concentration
(Agreements for duplicate samples are equal or less than 2.2% of the average values)
(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

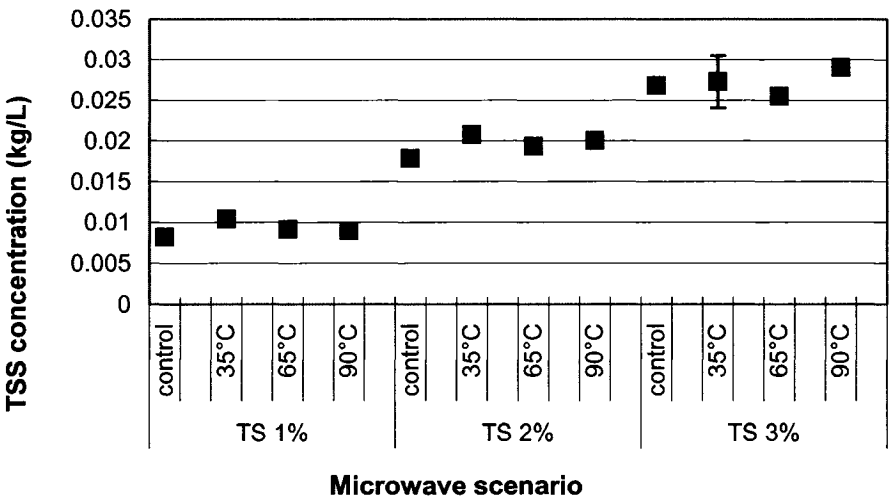


Figure 4.17 Microwave influence on TSS concentration
(MW intensity 80% and energy input level 19.47 J/min).

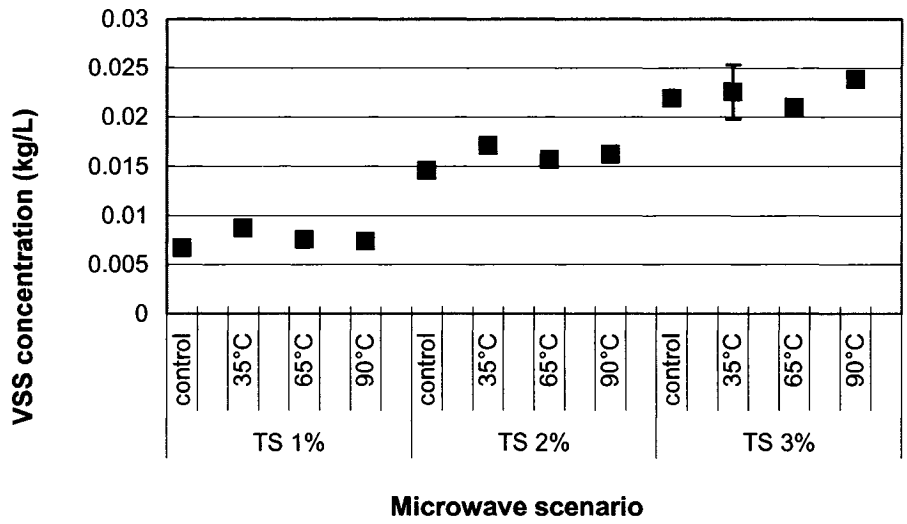


Figure 4.18 Microwave influence on VSS concentration (MW intensity 80% and MW energy input level 19.47 J/min)

4.2.4 Microwave Pretreatment Influence on Concentration of Bicarbonate Alkalinity, Ammonia Concentration, and PH Value

Ammonia and bicarbonate alkalinity are potential products of solubilization and hydrolysis of organic substances and their concentration levels can represent the degree of pretreatment of primary sludge. Ammonia concentrations for samples pretreated at each MW scenario and corresponding control samples are summarized in Figure 4.19. Bicarbonate alkalinity concentrations for samples pretreated at each MW scenario and corresponding control samples are summarized in Figure 4.20 and Figure 4.21. The pH values were also determined for samples pretreated at a MW intensity of 80% and corresponding controls to confirm the observation of ammonia and alkalinity. Figure 4.22 presents all pH values collected.

Proteins, as one of the principal constituents of PS solids, contain a fairly high and constant proportion of nitrogen. Therefore, an increased value of ammonia concentration, apart from SCOD and TCOD concentration (ammonia is not detected by COD test), is the distinguishing characteristic of protein solubilization. In this investigation, irrespective of the fluctuation of ammonia concentration data under various MW

pretreatment situations, it is apparent for the data in Figure 4.19 that MW irradiation did not show any obvious influence on the ammonia concentration. This phenomenon may be attributed to either poor degradation of complex protein molecules at mild MW conditions or the evaporation of ammonia molecules due to the high temperature during MW pretreatment.

Alkalinity in sludge is contributed by the hydroxide, carbonate, and bicarbonate salts, as well as the phosphates, borates, silicates and similar ions. The presence of alkalinity helps resist change in pH values caused by the generation of acids and help maintain pH values near the neutral range. In this investigation, MW irradiation was not found to substantially increase the alkalinity level, as was the case for the ammonia concentration presented in Figure 4.19. Figure 4.21 indicates that MW temperatures of 65°C caused the highest alkalinity concentrations. This may also be related to the evaporation of carbon dioxide and free ammonia, which becomes more significant after sludge temperatures reach 60°C, which in turn eliminates alkalinity substances in further temperature increase.

The pH level is a combined result from various strong and weak bases and acids presented in the primary sludge. Hydrolysis and other chemical reactions could contribute to the variation of pH value with their non-neutral products, such as ammonia (weak base), carbon dioxide (weak acid), and VFA (weak acid). The pH values among all pretreated samples and control samples remained in the range between 5.68 and 6.06 as indicated in Figure 4.22. Allowing for experimental error, MW irradiation to temperatures between 35-90°C did not show any obvious influence on the pH level, which is in fair agreement with the performance of alkalinity and ammonia.

Overall, the effect of MW pretreatment on the solubilization of primary sludge was not observed in the values of alkalinity, ammonia, and pH, although it had a dramatic affection on SCOD concentration and a milder effect on TVFA concentration. This is likely a result of incomplete solubilization of COD substances and likely attributed to the relatively low MW temperatures used.

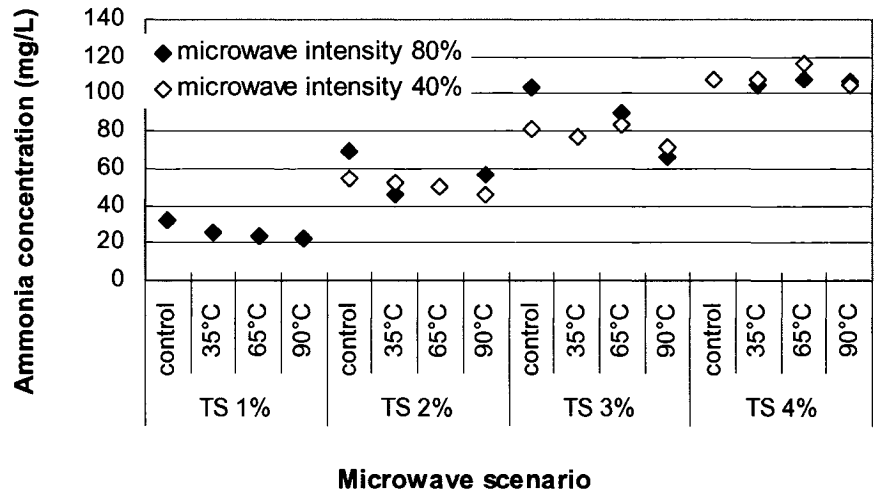


Figure 4.19 Microwave influence on ammonia concentration for different sludge concentration pretreated to various temperatures at 40 and 80% MW intensity.
(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

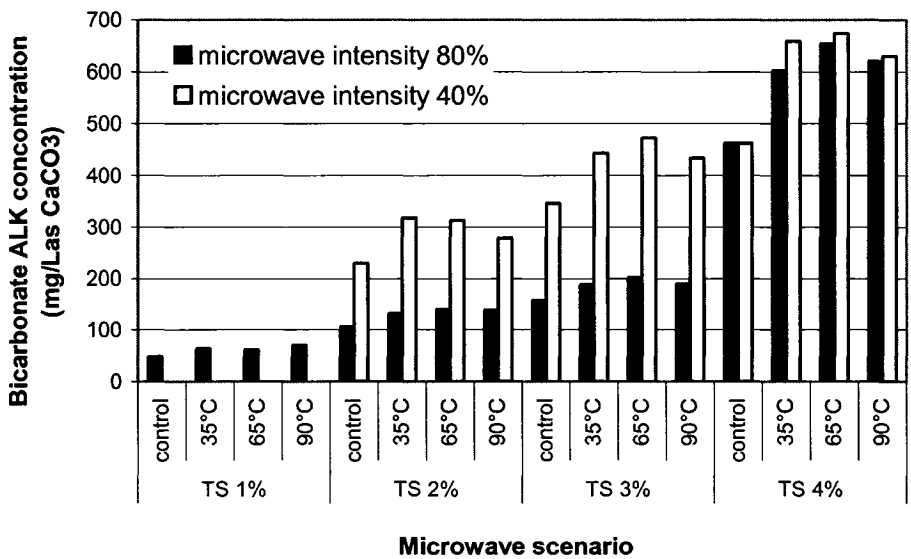


Figure 4.20 Microwave influence on ALK for different sludge concentrations pretreated to various temperatures at 40 and 80% MW intensity.
(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

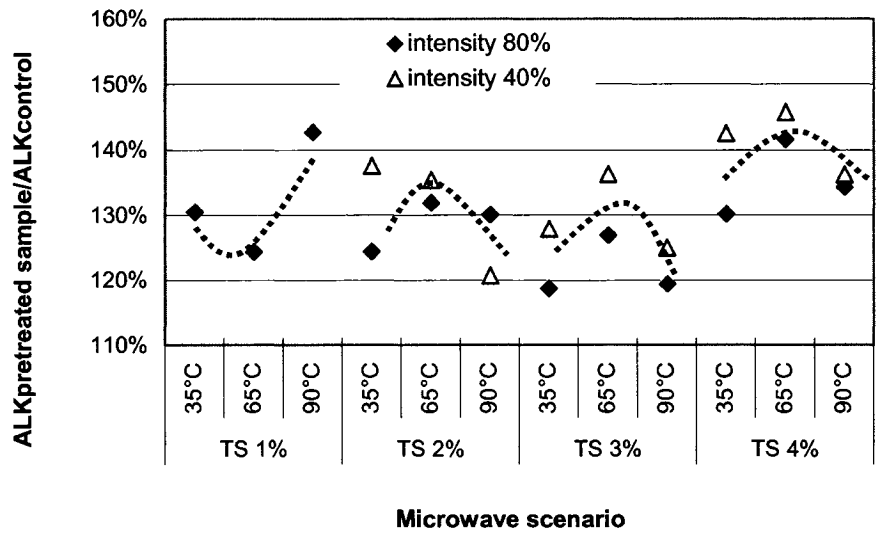


Figure 4.21 Increase of biocarbonate alkalinity compared to control with trend lines for different sludge concentrations pretreated to various temperatures at 40 and 80% MW intensity.

(MW intensities 80% and 40% are equal to energy input level 19.47 and 9.73J/min).

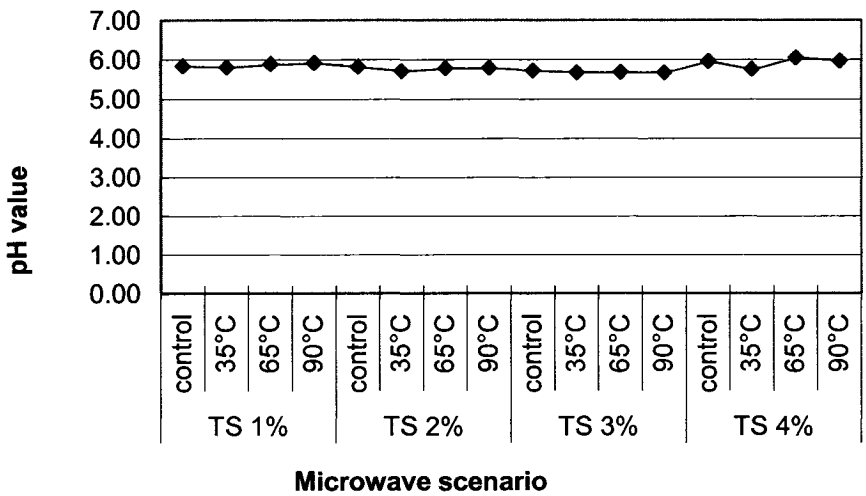


Figure 4.22 Microwave influence on pH value

(MW intensity 80% and MW energy input level 19.47 J/min).

4.3 Biochemical Methane Potential (BMP) Assays on Primary Sludge

The mesophilic BMP Biochemical methane potential assay was employed for the purpose of determining the biodegradability examination of pretreated primary sludge. The variables investigated in the BMP test are were the sludge temperature reached, the sludge solid concentration, and the MW intensity. The experimental factors are the same as described in section 4.2.1. The experimental methods are presented in chapter 3. Contribution of digestion seed was considered in the calculations, presentation and discussion of biogas production, TCOD, TS, VS, TSS, and VSS. All BMP assays were preformed in duplicated reactors.

4.3.1 Microwave Influence on Biogas Production

Generally, biogas production was measured daily and the time of measurement was recorded to the moment hour. Two methods were employed to assess the change in biogas production rate for all pretreated samples and the corresponding control samples. Cumulative biogas production at a specific time was calculated by summing up all of the biogas production. Daily biogas production rate is equal to biogas production at a specific time divided by the time interval between this measurement and the last measurement. Both cumulative biogas production and daily biogas production rate are expressed as biogas volume per 500mL sludge sample. As examples, the cumulative biogas productions obtained with the BMP test to sludge pretreated at MW scenarios of 1% TS and 80% MW 1%, intensity is provided in Figure 4.23, cumulative biogas productions for 4% TS 4% and MW intensity 80% and 40% are provided in Figure 4.24 and Figure 4.25, respectively. Corresponding daily biogas production rates were plotted in the Figures 4.26, 4.27, and 4.28, respectively. These figures are discussed in the following subsections. The figures of cumulative biogas production of all microwave scenarios are presented in appendix B-1. The figures of daily biogas production rate of all microwave scenarios are presented in appendix B-2. All data presented in these figures are average values of duplicated reactors. The following is a general discussion of the observations based on biogas production of all samples with time.

4.3.1.1 Cumulative biogas production

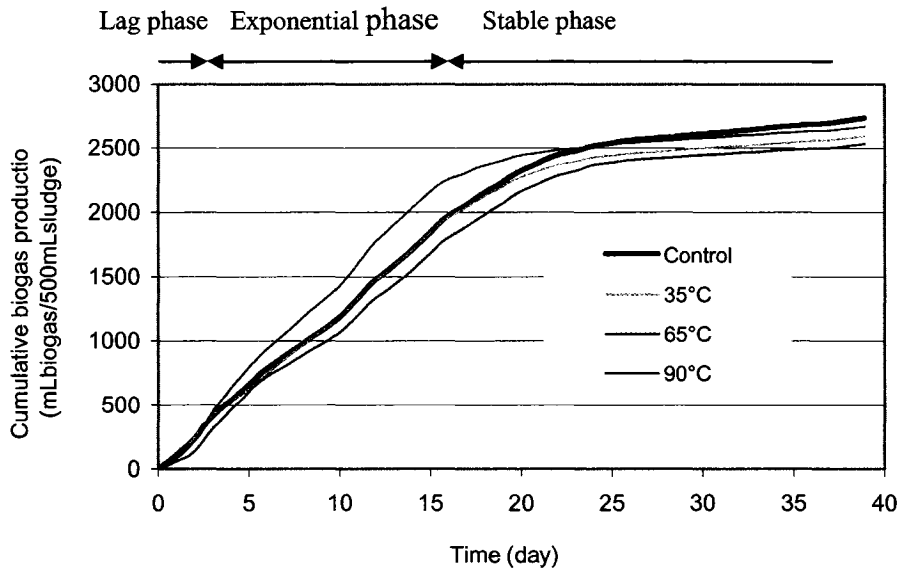


Figure 4.23 Cumulative biogas production (1% TS, MW intensity 80% and MW energy input 19.47J/min)

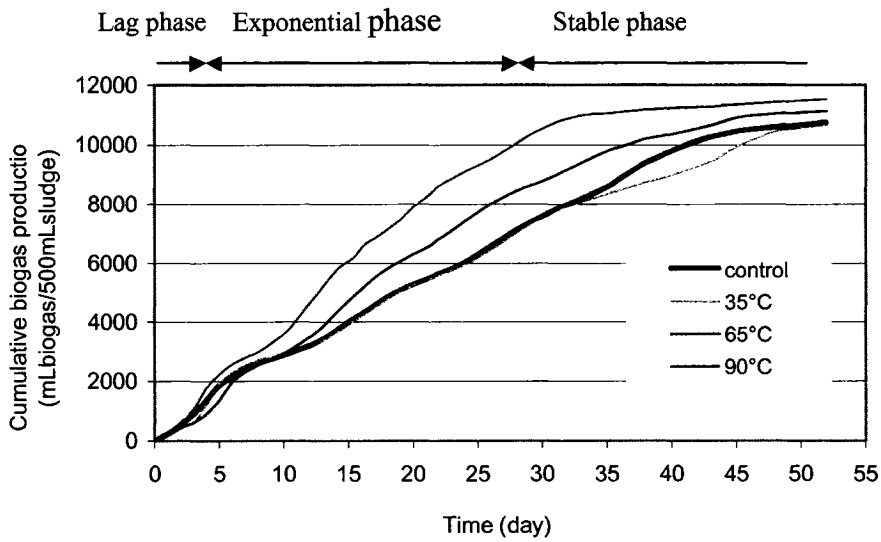


Figure 4.24 Cumulative biogas production (4% TS, MW intensity 80% and MW energy input 19.47J/min)

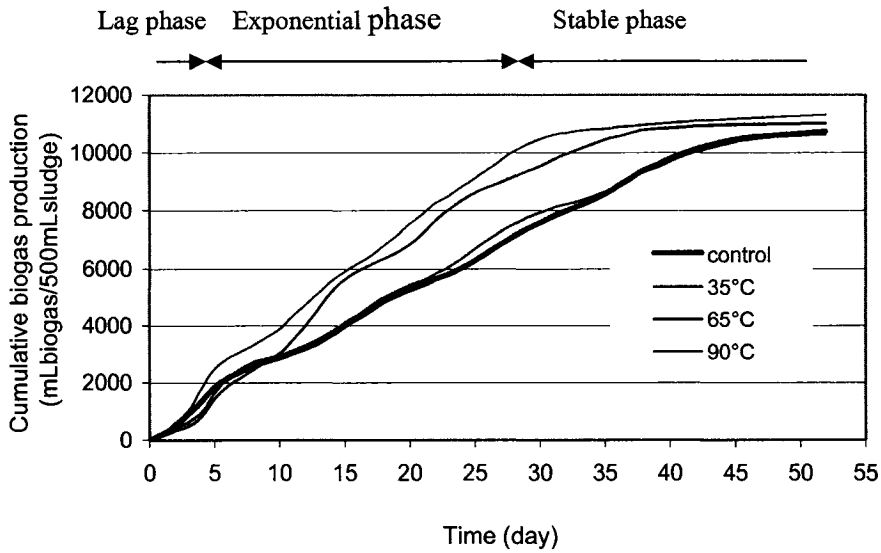


Figure 4.25 Cumulative biogas production (4% TS, MW intensity 40% and MW energy input 9.73J/min)

As shown in Figure 4.23, 4.24, and 4.25, and further in appendix B-1, two different MW intensities (80% and 40%) of sludge pretreatment did not significantly affect biogas production from the BMP test.

The basic shapes of curves for each of the MW pretreatment scenarios are similar. They were characterized by a very short lag phase at the beginning of digestion (2-3 days for 90°C sludge) followed by the exponential phase. Then biogas production curve slowed off and reached the stable phase when the readily degradable portion of the sludge was utilized. The short-lag-phase phenomenon is attributed to the acclimation of digestion seed to the pretreated primary sludge (about 85°C) for more than 2 months. This advantage suggested that, at mild MW irradiation, the production of toxic compounds seemed to be marginal and, if produced, could be effectively tolerated by acclimating the anaerobic digestion bacteria consortium.

A comparison between the cumulative biogas production obtained during the exponential stage with or without the MW pretreatment at different solid concentrations and MW irradiation intensities shows that:

- For sludge samples pretreated at 90°C, there were substantial improvements from raw sludge. After the 3rd or 4th day of digestion, the cumulative biogas production from the 90°C sludge sample increased consistently faster than the control sample. The differences in cumulative biogas productions reached their peaks on the 15th to 30th day of digestion for samples at solid concentrations of 1% to 4%; and then gradually decreased with time in the rest of the digestion. This improvement in biogas production was greatest in the digestion of the 4% sludge sample.
- Generally, the curves presenting cumulative biogas production from the 65°C sludge were some where place between the 90°C sample curve and the control sample curve.
- The cumulative biogas production from 35°C sludge present no obvious improvement compared to the untreated samples in most cases. The observation of inconsistent improvement of biogas production of the 35°C and 60°C curves is related to the non-uniform nature of the PS and the minor improvement.
- Due to the higher biogas production in the earlier exponential phase, for most of the pretreated sludge samples, the required digestion time to achieved 85% of stabilization (i.e. reach stable phase) was shorter than that for the untreated sludge. The required digestion time for 90°C sludge were 4 to 11 days less than that for the corresponding control at sludge solid concentration 1 to 4%.
- From Figure 4.23, 4.24, and 4.25, allowing for the sufficient digestion time, all sludge samples showed no substantial improvement in biogas production at the end. This indicates no overall improvement in VS stabilization. It is a result of the fact that, in the latter phase of the digestion, the untreated samples produced more biogas than pretreated sludge samples.

The results of the cumulative biogas production suggested that the MW irradiation at to 65 and 90°C enhanced the solubilization of anaerobic digestion in of primary sludge by

improving COD solubility as discussed in section 4.2.2. It in turn increased the biogas production rate in the first half of digestion for the pretreated samples. Obviously it means that the organic compounds released by MW pretreatment from the solid phase into the aqueous phase were readily biodegradable. But without fundamental improvement of the biodegradability, the pretreated sludge did not achieve higher digestion efficiency in terms of total biogas production, VS removal efficiency, and TCOD removal efficiency. In a study performed by Eskicioglu *et al.,* (2004), MW irradiation of wasted activated sludge (WAS) showed more overall improvement in terms of biogas production. In her study, at the end of the BMP test (34-days digestion), for WAS of 1.5% TS pretreated to 96°C ultimate biogas production increased by 12 % compared to the sludge for control WAS samples sludge. The poor improvement in terms of ultimate stabilization in both primary and secondary sludge suggested the limited influence on solubilization of primary and secondary sludge from WM pretreatment.

The comparison of cumulative biogas production from digestion of different sludge samples showed that samples with increased pretreated temperature and higher sludge solid concentration presented higher biogas production speed over the raw samples. This suggestion is further clarified in the following discussion regarding the daily biogas production (section 4.3.1.2).

4.3.1.2 The Microwave influence on daily biogas production rate

As presented in Figure 4.26, 4.27, and 4.28, daily biogas production rate curves clearly reflect the influence of the MW disintegration on the speed of primary sludge digestion. An increase of daily biogas production rate was observed in the reactor receiving disintegrated the most solubilized sludge as pointed out previously in the discussion of cumulative biogas production.

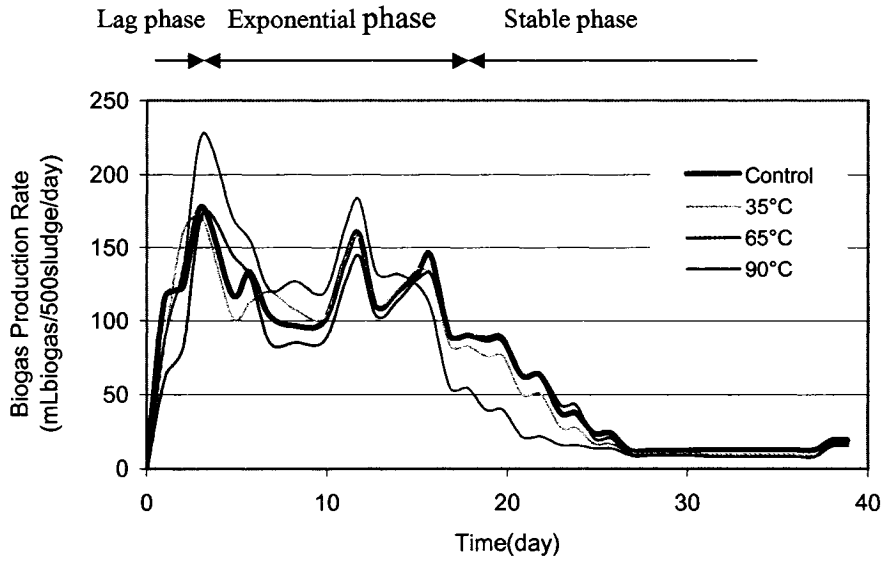


Figure 4.26 Daily biogas production rate (1% TS, MW intensity 80% and MW energy input 19.47J/min)

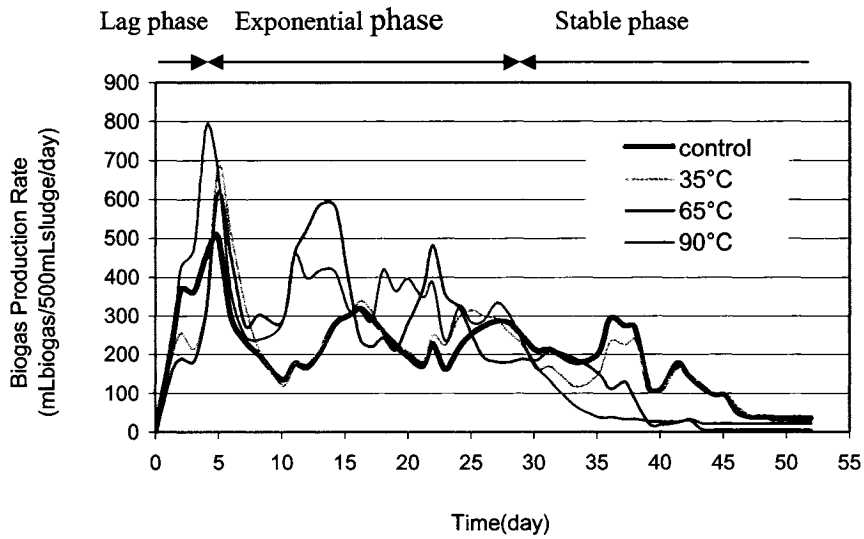


Figure 4.27 Daily biogas production rate (4% TS, MW intensity 40% and MW energy input 9.73J/min)

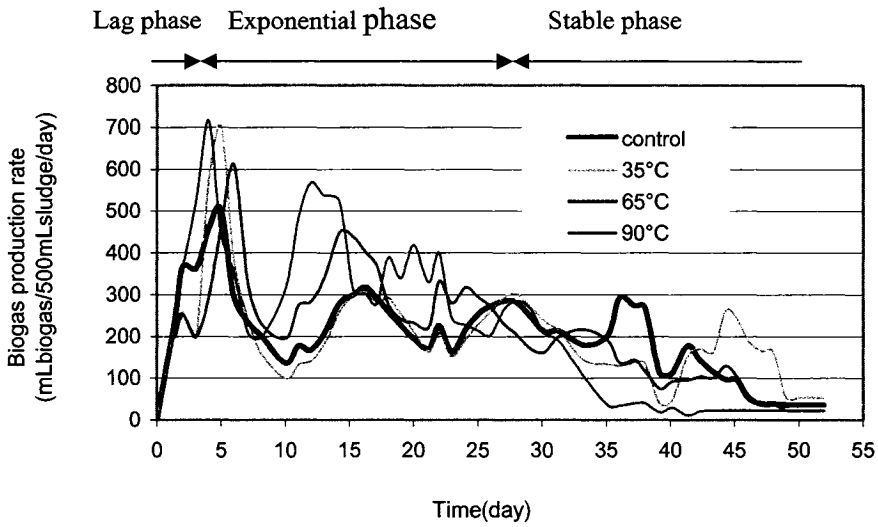


Figure 4.28 Daily biogas production rate
(4% TS, MW intensity 80% and MW energy input 19.47J/min)

Curves describing the daily biogas production bear similarity in shape. Digestion of all sludge samples at solid concentrations of 1, 2, and 3% experienced two groups of peaks, each of which consisted of several fluctuations. For sludge at a solid concentration of 4% the second peak group lasted about 30 days and the sub-peaks became heavier.

After a short lag phase, the highest peak of the first group was reached by the 90°C sludge first, then control and sludge irradiated at 35 and 65°C. Usually this peak is the highest peak during the entire digestion. But the later analysis of pH, VFA, and biogas composition suggested that the first peak resulted from the neutralization of a large amount of low-molecule-weigh acid by base-form alkalinity substances in the sludge. In fact it shows the high strength of hydrolysis that was happening in the digested sludge at that moment. The second peak group began 1-2 days after the first peak group ended. The fluctuation in the second peak group is due to the complex nature of primary sludge and the multiple steps of digestion metabolism.

Generally speaking, in the first half of the digestion period, peaks for the 90°C sludge appeared earlier and were stronger than that for the control. Again, the digestion performance of 65°C sludge was between that of control and 90°C sample. The curve for 35°C sample was close to the curve for the control for most of the digestion period.

4.3.2 VFA, pH, and Gas Composition

The VFA, pH and gas composition were measured concurrent with the biogas production at an interval of about 5 to 7 days. Data collected over the entire BMP assay study period formed the profile of the VFA, pH and biogas composition for sludge pretreated under all MW scenarios. Profiles for 4% TS sludge and MW intensity of 80% and 40% are presented in Figure 4.29 and 4.30, respectively. Profiles for all MW scenarios are presented in appendix B-3. Average values of duplicate reactors are presented in this section. The following is a general discussion of the observations based pH/biogas compositions/ TVFA obtained from all sludge samples.

The results obtained in the determination of pH, VFA, and gas composition require consideration from many perspectives in order to clearly see the interrelation.

The initial period of digestion showed a relatively neutral environment in all BMP reactors. Values of pH reached their lowest value of 6.9-7.1 in the initial period of the 4^{th} to 12^{th} day of digestion, then increased gradually to a pH value 8.0 to 8.1, and then maintained this level until the end of digestion. This was attributed to the addition of a mixture of potassium bicarbonate and sodium bicarbonate (equal to bicarbonate alkalinity concentration), which served as buffering against possible acidification of the reactors. The final pH value was slightly higher than optimal for methanogenic bacteria (pH6.4 to 7.8); but still within good digestion conditions. Lin *et al.* (1997) observed a similar high pH value in continuous sludge digester operation. In Lin *et al.*'s research, three digesters were run at pH 7.09 to 7.55 and one was run at pH value of 7.78 to 7.96. Operation at a pH level of 7.96 did not present any disadvantages over the operation under normal pH situation in terms of biogas production and organic matter removal, but the high- pH-

level-operation did increase the methane percentage of biogas produced from 71-76% to 84%.

Interestingly, if we compare the daily biogas production rate with the percentage of carbon dioxide in the biogas, pH level, and TVFA concentration, there was a strong correlation between the values obtained. In the 4^{th} to 12^{th} day of BMP operation, each reactor reached its peak of TVFA concentration and CO_2 percentage in biogas (some 55-90%) and the lowest pH levels. Correspondingly, the initiation of the increase in pH levels and the decrease of CO_2 percentage in the biogas happened when the TVFA concentration started to decline. The initiation and decline of the first peak in the daily biogas production rate curve also reflected this change. This was consistent throughout the experimental study period for all the investigated MW scenarios.

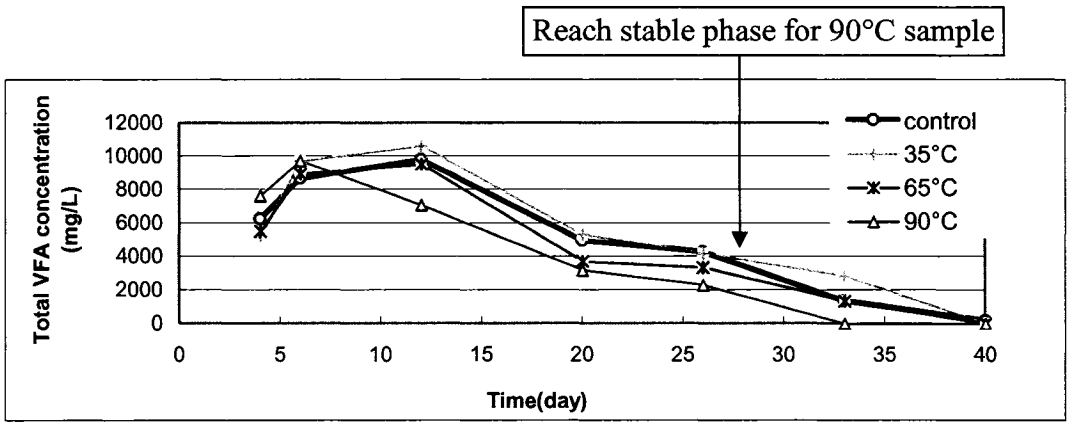
Combined with the consideration of the large amount of alkalinity dissolved in digested sludge (~9000 mg/L), comparisons with these parameters also revealed that biogas produced in the first group of daily rate biogas production peaks, consisted mainly of CO_2, which was likely from the neutralization of acid and alkalinity substance.

Research conducted by Zhang and Zhang (1999) on digestion of rice straw with an anaerobic-phased solids digester system also observed a carbon dioxide content of biogas as high as 50-80% with the absence of methanogenic bacteria in a hydrolysis reactor. In Zhang's research, as acids were transferred to the biogasification reactor and consumed, the pH level in the hydrolysis reactor increased to around 7. Zhang and Zhang indicated that the high carbon dioxide content of the biogas detected in the initial phase of BMP digestion was attributed to the overwhelming intense hydrolysis and acidogenic activity.

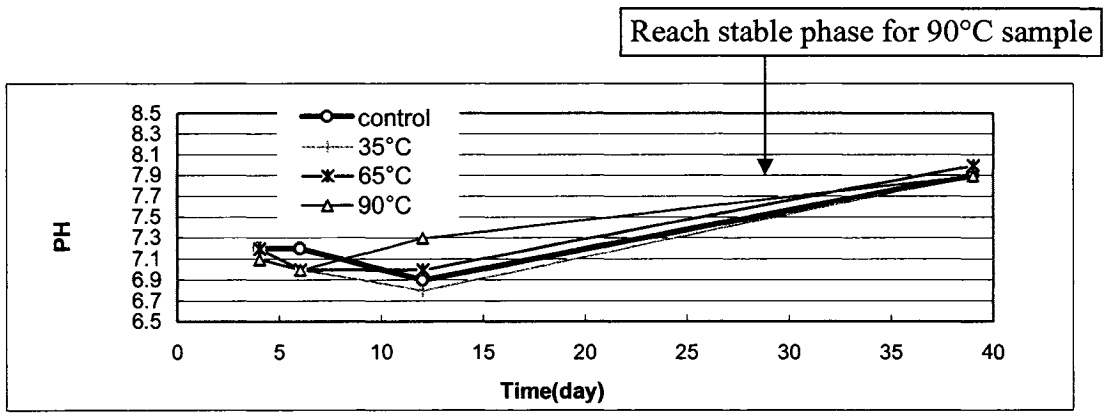
According to Jimenez and Borja (1997), if the VFA/alkalinity ratio is less than 0.3-0.4, the digestion process is considered to be operating without risk of acidification. In this study, ratio was lower than the suggested limit value in the digestion of all sludge samples, except for 1% TS sludge. During the experiment, one BMP bottle, which contained the 90°C sludge at 4% TS and MW intensity 40%, showed initial signs of

excess loading and digestion failure (acidification) at the beginning of the BMP assay as indicated by a decreased pH value as low as 6.6 on the 6th day of digestion. The recovery of pH value to a more neutral value was much slower and cumulative biogas production was substantially less than the duplicate bottle. This result indicated the possible risk from high strength acid production in the digestion of sludge pretreated at high solid concentration and high temperature.

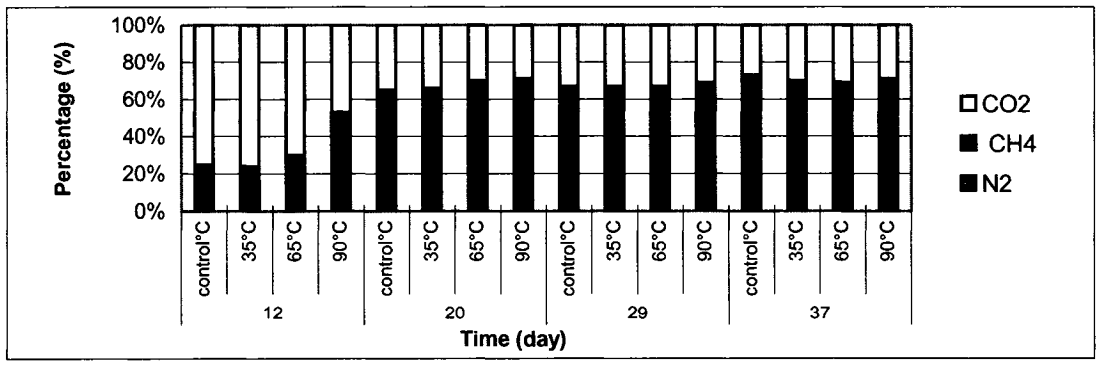
Generally speaking, allowing for the inaccuracies caused by the measurement interval, comparison between data for sludge pretreated with different MW scenarios shows that sludge with greater solid concentrations and higher MW pretreatment temperatures experienced more intensive and earlier onset of acidogenic peaks. MW pretreatment of sludge solubilized a large amount of organic material into solution (increased SCOD), which can be utilized by anaerobic bio-system immediately with no requirement or less requirement for hydrolysis. Additionally, it can be speculated that the exposure to MW pretreatment may cause some of the organic matter to be hydrolyzed more readily by hydrolyzing enzymes in the digester although the MW temperature used was insufficient to fully disrupt the flocs and effectively release the organic substances from the solid phase. Thus, it is likely that rapid degradation of a large amount of soluble organic matter and partially solubilized organics (more readily biodegradable) into short-chain fatty acid can potentially contribute to an unstable digestion situation in the initial phase of BMP digestion if sufficient buffer capacity is not available.



Total VFA profile

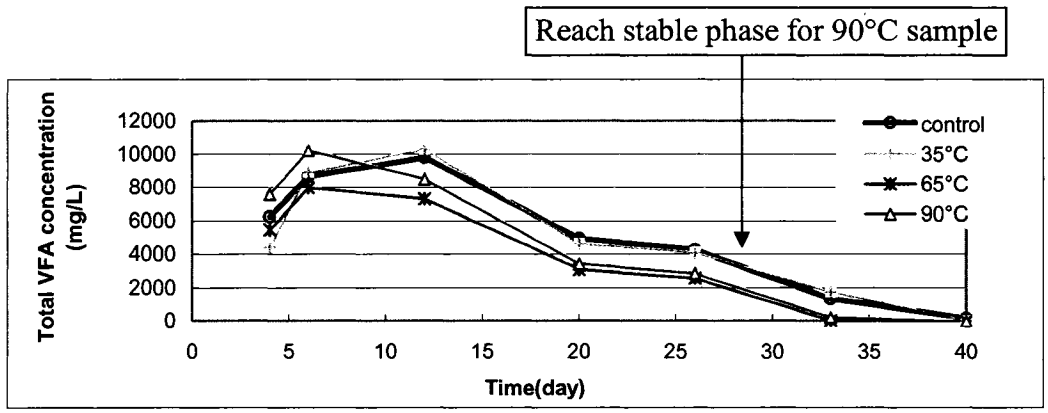


pH profile

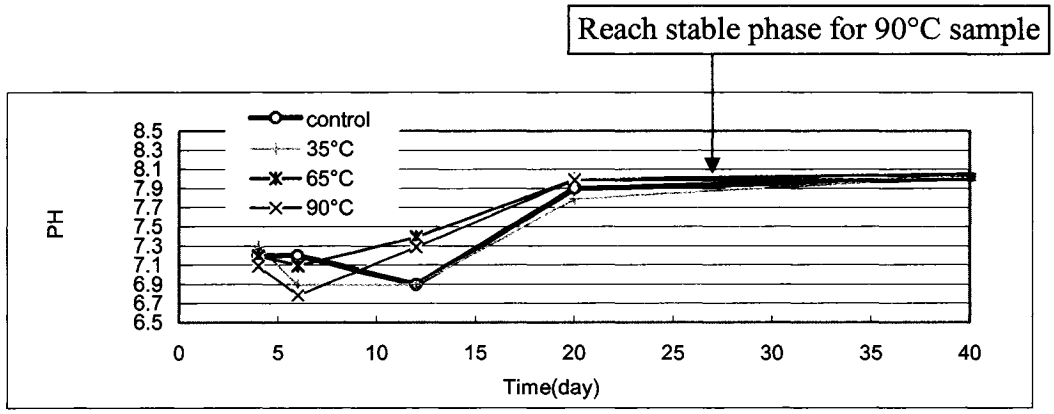


Biogas composition profile

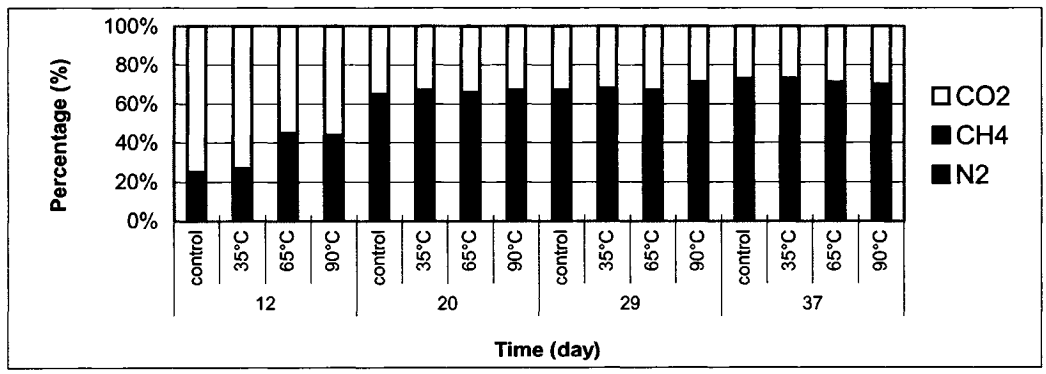
Figure 4.29 Time profiles of TVFA, pH, and biogas composition for BMP assay for primary sludge (TS 4%, MW intensity 80% and MW energy input 19.47J/min)



Total VFA profile



pH profile



Biogas composition profile

Figure 4.30 Time profile of TVFA, pH, and biogas composition for BMP assay for primary sludge
(TS 4%, MW intensity 40% and MW energy input 19.47J/min)

4.3.3 Ammonia Concentration

During the anaerobic digestion of primary sludge, ammonia is generated by the degradation of nitrogen compounds, primarily structural proteins and enzymes. Generation of ammonia, which is a natural pH buffer, also increases the alkalinity level. The ammonia concentrations measured before and after the BMP assay are plotted and presented in Figure 4.31 and Figure 4.32. Unsurprisingly, the data presented indicate no significant difference of the ammonia levels between the MW pretreated sludge and those without pre-treatment. The fact that at the end of the BMP assay overall extent of primary sludge degradation (based on cumulative biogas) did not change without or with MW pretreatment was not unexpected. It can also be observed that final ammonia concentrations increased in proportion to the TS concentration which was again expected based on the relatively high biodegradability of primary sludge as indicated by cumulative biogas production.

Due to ammonia released during digestion and the addition of alkalinity at BMP reactor start-up, digester's pH reached values around 8.0. At this pH level, only about 10% of the total ammonia was in un-ionized form (NH_3). Research shows that free un-ionized ammonia is more toxic than ionized ammonia (NH_4^+) and often causes inhibition. Speece (1996) reported that the maximum allowable free ammonia concentration for batch digestion is about 100 mg/L, while ionized ammonia concentration began to inhibit at much higher level of around 3000 mg/L. During this study, the highest ammonia level, of 882-960mg/L, was found in the BMP assays treating 4% TS. The calculated free ammonia concentration of 88-96mg/L was slightly lower than the threshold of inhibition, which is coincident with the observation of little inhibition in digestion. Thus in this experiment, the elevated level of ammonia did not inhibit the methane forming bacteria in the anaerobic digesters.

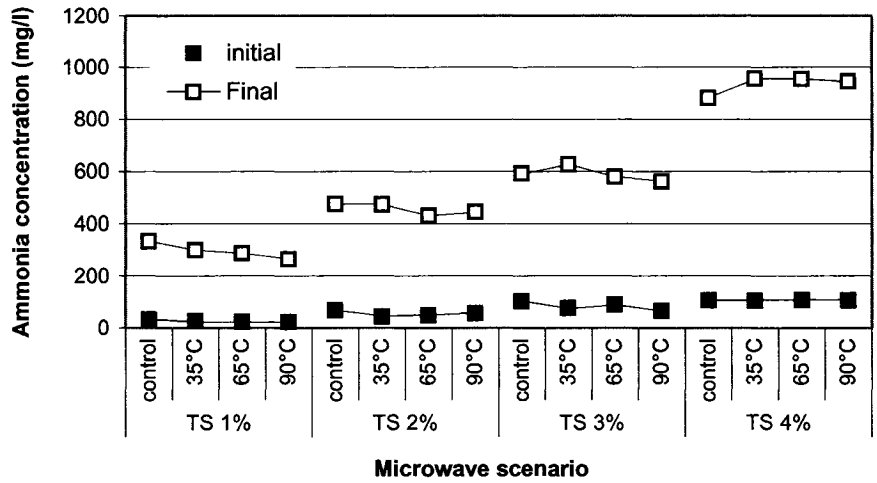


Figure 4.31 Ammonia concentration in BMP test at various TS and temperatures. (MW intensity 80% and MW energy input 19.47J/min)

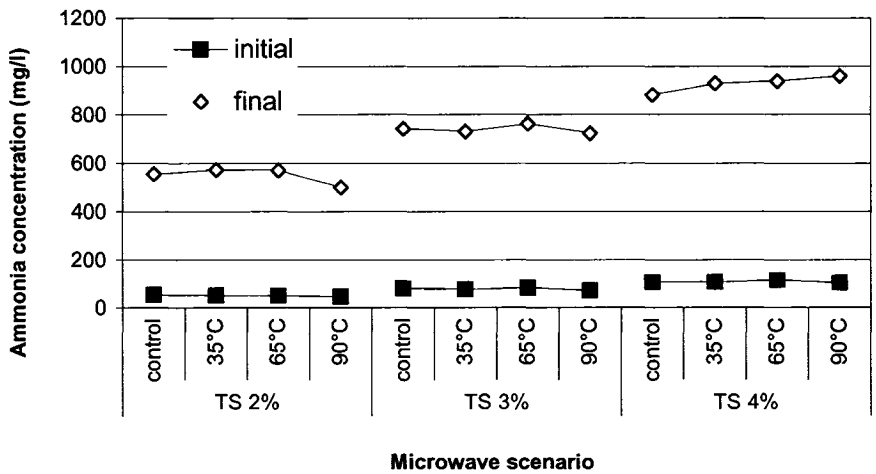


Figure 4.32 Ammonia concentration in BMP test at various TS and temperatures. (MW intensity 40% and MW energy input 9.73J/min)

4.3.4 SCOD Concentration

Data presented in Figure 4.33 and 4.34 indicate (perhaps surprisingly) that, at the conclusion of the BMP assay, no significant difference of SCOD levels existed between pretreated-sludge-fed digesters and those without pre-treatment even through there was a tremendous increase in SCOD concentration for pretreated sludge before digestion. This result combined with biogas results suggests that mild MW irradiation increased the rate of hydrolysis but did not enhance the degree of hydrolysis. Additionally hydrolysis products formed at a faster rate and may have been degraded at a faster rate but overall were not any more or less degradable without or with MW pretreatment.

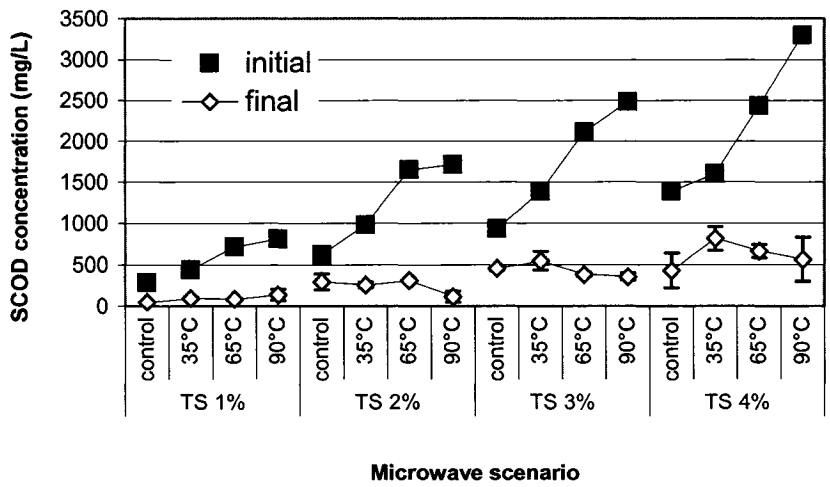


Figure 4.33 SCOD in BMP test at various TS and temperatures. (MW intensity 80% and MW energy input 19.47J/minand MW energy input 19.47J/min)

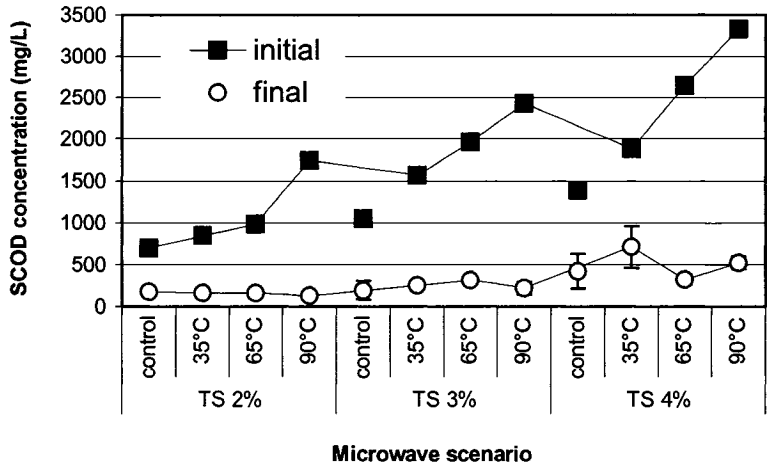


Figure 4.34 SCOD in BMP test at various TS and temperatures. (MW intensity 40% and MW energy input 9.73J/min)

4.3.5 Specific Biogas Production

The biogas yield for anaerobic digestion is commonly expressed as a function of mass reduction of VS (specific biogas production). The specific biogas production values based on entire digestion for all the sludge samples are presented in Figure 4.35. The result of the regression of all these values is shown in Figure 4.36.

Nominally each gram of VS reduced produces 1000 mL of biogas. In this study, the specific biogas production values for most sludge samples were quite consistent with the nominal value. Through linear regression between mass of VS removed versus volume of biogas production, the square of the correlation coefficient of determination (R^2) was 0.9754, which is close to "1". The biogas production volume per gram of VS destroyed from the BMP test averaged 926.8 mL biogas/gVS removed. The good agreement in biogas yield for all tests gives further confidence in the accuracy of the overall BMP results.

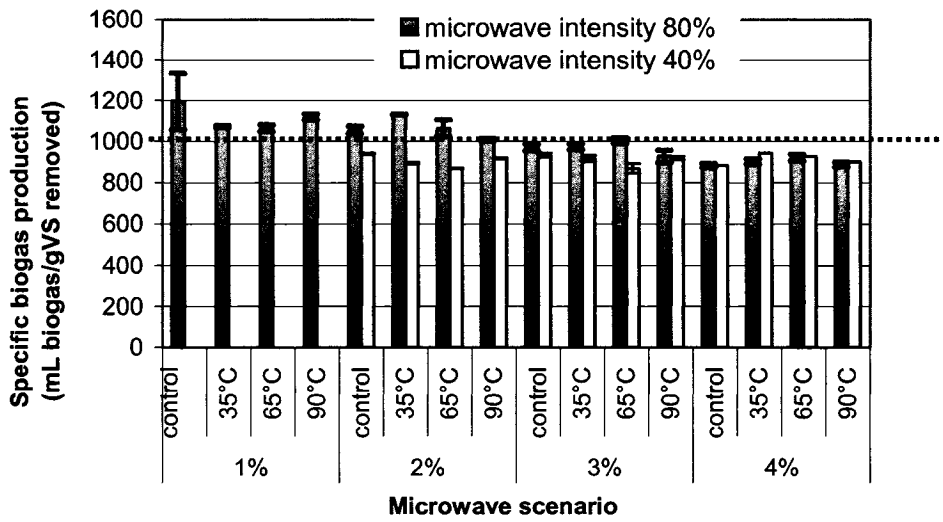


Figure 4.35 Specific biogas production yield at various TS, temperatures, and MW intensities

(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

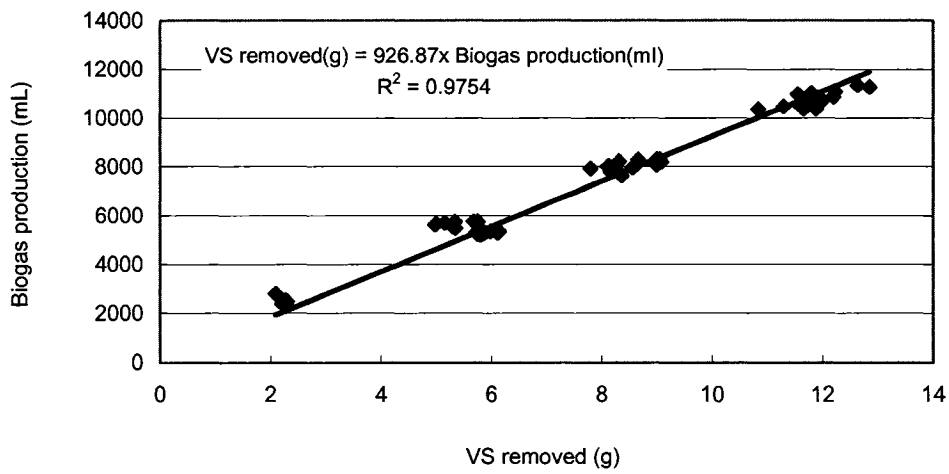


Figure 4.36 Relationship between biogas production versus VS removal (n=28).

4.3.6 VS and TCOD Removal

As with any batch sludge digestion study, VS reduction and biogas production are the two main parameters to evaluate digester performance. Overall comparisons of VS and TCOD removal efficiency for the digestion of all sludge samples pretreated in various MW scenarios appear in Figure 4.37 and Figure 4.38, respectively. The values from duplicated bottles are presented in Appendix C. These two parameters were calculated by dividing the decrease of VS (or TCOD) during the entire digestion process by the mass of the original VS (or TCOD) before digestion. Obviously, from Figures 4.37 and 4.38 there was no indication of any form of efficiency improvement for batch digestion characterized by increased VS and TCOD removal efficiency at the end of the BMP assays. This coincides with the BMP performance based on overall biogas production for MW pretreated sludge and those without pretreatment. Ultimate VS removal efficiencies of 60-70% measured in this study are within the typical range of VS removal value of 40-70% reported for primary sludge (Metcalf & Eddy 2003).

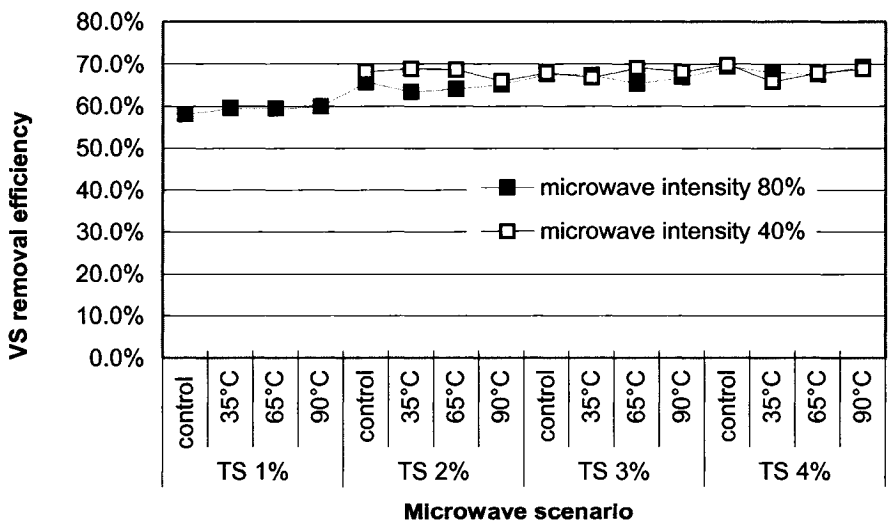


Figure 4.37 VS removal efficiency in BMP test at various TS, temperatures, and MW intensities.

(Agreements for duplicate samples are equal or less than 2.2% of the average values) (MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

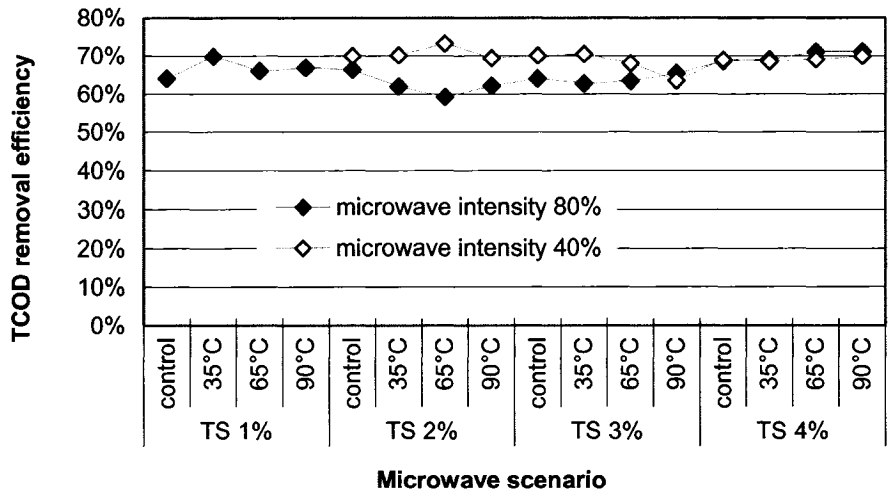


Figure 4.38 Total COD removal efficiency in BMP test at various TS, temperatures, and MW intensities.

(Agreements for duplicate samples are equal or less than 1.5% of the average values) (MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

4.3.7 Dewaterability

Anaerobic digestion tends to improve the dewaterability of sewage sludge by preferential removal of small particles, which leads to a consequent loss of specific surface area of sludge (Lawler *et al.,* 1986). This theory was confirmed by visual observation of the settlability difference between the digested sludge and undigested sludge. As one of the three most important considerations in sludge reuse and disposal, potential sludge volume reduction is defined by the dewaterability of sludge without addition of polymer in the present application.

Capillary suction time (CST) of the digested sludge (without addition of polymer) was measured at the end of the BMP test to study the influence of MW pre-treatment on dewaterability of primary sludge. Data in Figure 4.39 illustrates that MW irradiation slightly reduced the CSTs for the stabilized primary sludge in this experiment. By

comparing sludge pretreated at 90°C and those without pretreatment, the reduction of CST was around 5%. The only exception to this was observed in the sludge sample pretreated at MW intensity 80%, temperature 35°C, and sludge solid concentration 3%.

Research on the influence of MW pretreatment on enhanced anaerobic digestion and dewaterability of wasted activated sludge (WAS) was conducted by Eskicioglu (2004). Her analysis of CST of digested sludge at the end of mesophilic BMP tests indicted substantial improvement for MW pretreated WAS compared to untreated WAS. For WAS at 1.5% TS , MW irradiation to 95°C reduced CSTs by 37%. Neither of these results (primary sludge or WAS) guarantee an improvement or decrease in dewaterability in practice if polymer is added that could affect water loss. However, the results seem to suggest that primary sludge showed no potential improvement in dewaterability following MW pretreatment and anaerobic digestion compared to controls.

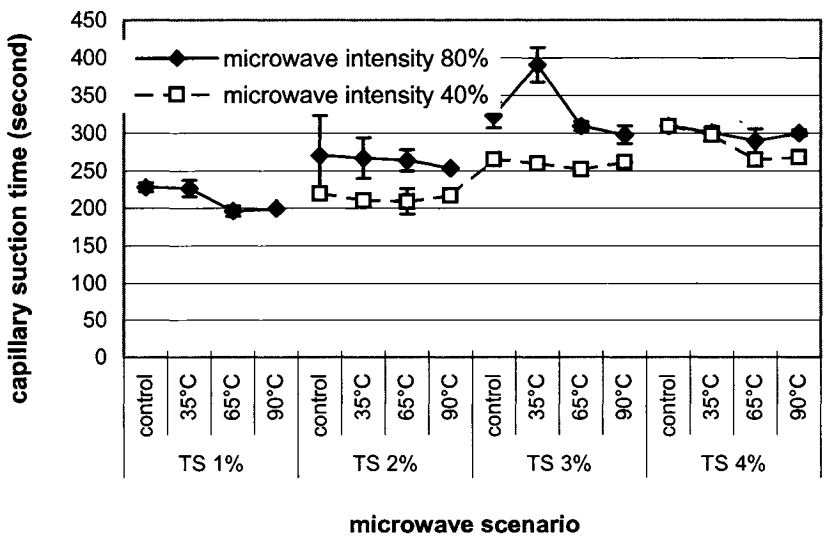


Figure 4.39 Result of capillary suction test after BMP test at various TS, temperatures, and MW intensities.

(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

4.3.8 Digestion Improvement

Three methods were employed to assess improvement in anaerobic digestion of primary sludge by MW pre-treatment for each specific MW irradiation scenario. They were: decrease of required digestion time, improvement of digestion rate, and improvement of the ultimate digestion at the end of the digestion of the pre-treated sludge.

The required digestion time was the digestion time from the reactor's setup until the end of the exponential phase. The end of the exponential phase was determined based on achieving 85% of the ultimate biogas production. Ultimate biogas production, in this discussion, was represented by the total biogas production achieved at the very end of the BMP assay. The digestion rate was equal to the total biogas production during required digestion time divided by the value of the required digestion time, and expressed as the biogas volume per 500mL sludge sample per day.

The decrease of required digestion time was calculated as:

$$\%\ decrease\ of\ required\ digestion\ time = 100 \times \frac{required\ digestion\ time\ of\ control - required\ digestion\ time\ of\ pretreated\ sample}{required\ digestion\ time\ of\ control} \quad (4.1)$$

The improvement of digestion rate was calculated as:

$$\%\ increase\ of\ digestion\ rate = 100 \times \frac{digestion\ rate\ of\ pretreated\ sample - digestion\ rate\ of\ control}{digestion\ rate\ of\ control} \quad (4.2)$$

Values of required digestion time and the corresponding decrease required digestion time compared to controls obtained with BMP assays for all MW pre-treatment scenarios are

provided in Figure 4.40 and 4.41, respectively. The corresponding levels of digestion rate and improvement are presented in Figure 4.42 and 4.43, respectively.

Generally speaking, both digestion time improvements and digestion rate improvements with MW pretreatment increased with an increase of sludge solid concentration. This observation is attributed to the higher organic loading rate in the reactor fed with concentrated sludge. Among the sludge samples that shared the same solid concentration, a higher pretreatment temperature also led to less required digestion time and a higher digestion rate. No difference in required digestion time and digestion rate was observed between various MW intensities pretreated to at similar temperatures.

The biogas production rate from sludge samples pretreated at 90°C and solid concentration of 4% was 350 mL biogas/500mL sludge/day, which was 37% higher than that from the untreated sludge. The digestion of this sample required 27 days to the end of the exponential phase, which was about 30% less than the control sample.

Plotting the values described in Figure 4.43 into 3-dimensional views, Figure 4.44 and 4.45 visually present the influence of MW irradiation on the anaerobic digestion of primary sludge in terms of the digestion rate at MW intensities of 80% and 40%, respectively. As discussed in Figure 4.43, the similar shape of these two surfaces reflects the little difference in influence of different MW intensities on the digestion of primary sludge. The shapes of the 3-D surface reemphasizes the importance of sludge solid concentration and MW temperature on the BMP digestion performance of primary sludge which increased from lower sludge solid concentration and lower pretreatment temperature to the higher sludge solid concentration and higher MW temperature.

The calculation of digestion improvement at the end of the exponential phase of pretreated sludge reflects the combined improvement of required digestion time and digestion rate. This measurement compares the cumulative biogas production for a specific pretreated sludge sample until the end of its exponential phase to that for the

corresponding control sample over the same period of time. The calculated results are shown in Figure 4.46.

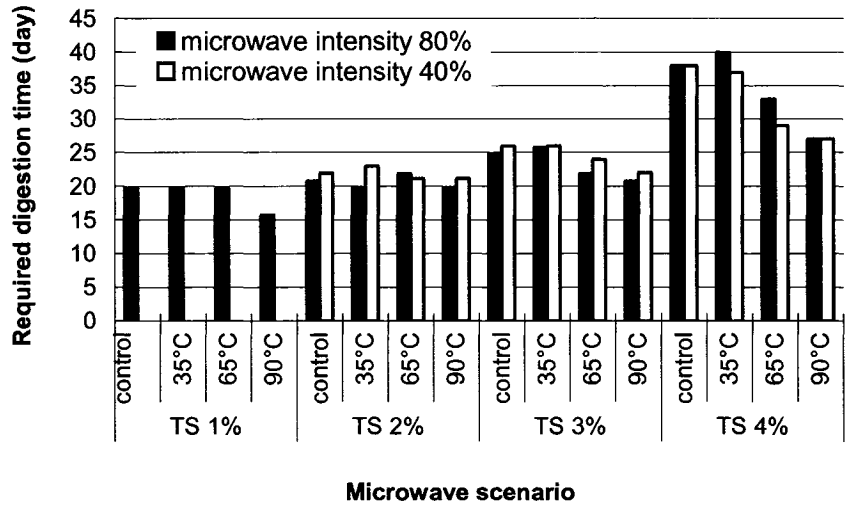


Figure 4.40 Required digestion time in BMP test at various TS, temperatures, and MW intensities.(experimental errors are equal or less than 1 day)
(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

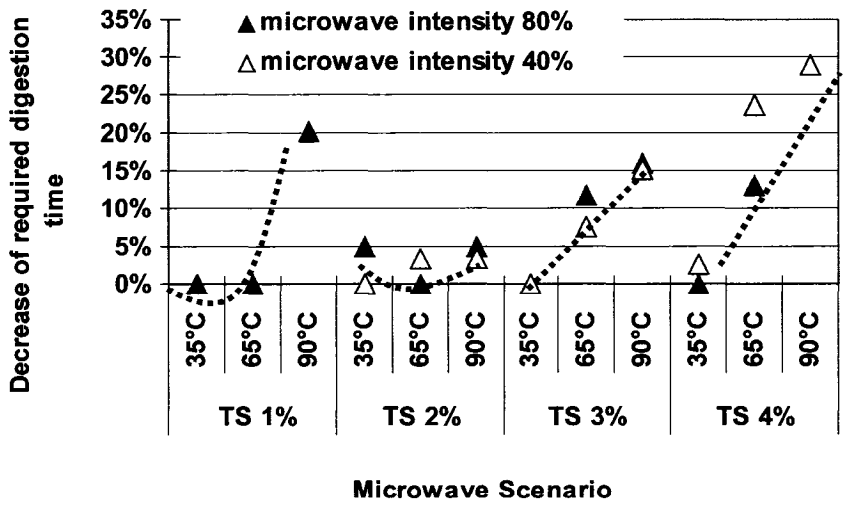


Figure 4.41 Decrease of required digestion time in BMP test at various TS, temperatures, and MW intensities.
(Agreements for duplicate samples are equal or less than 5% of the average values)
(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

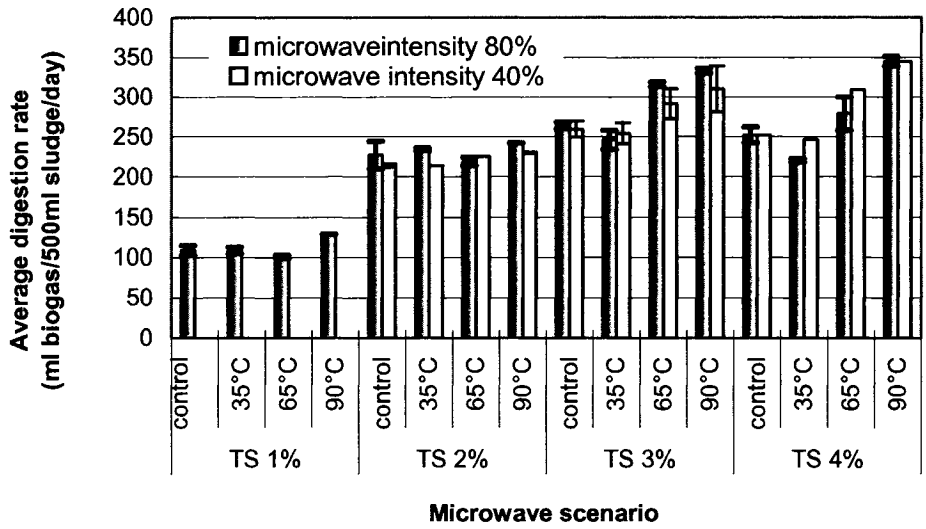


Figure 4.42 Digestion rate in exponential phase of BMP test at various TS, temperatures, and MW intensities.
(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

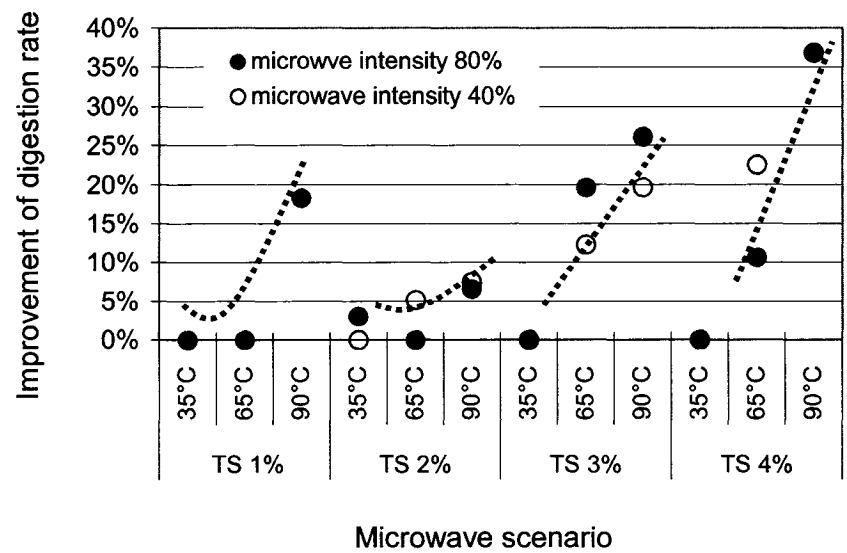


Figure 4.43 Improvement of digestion rate in the exponential phase of BMP test at various TS, temperatures, and MW intensities.
(Negative values are presented as zero)
(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

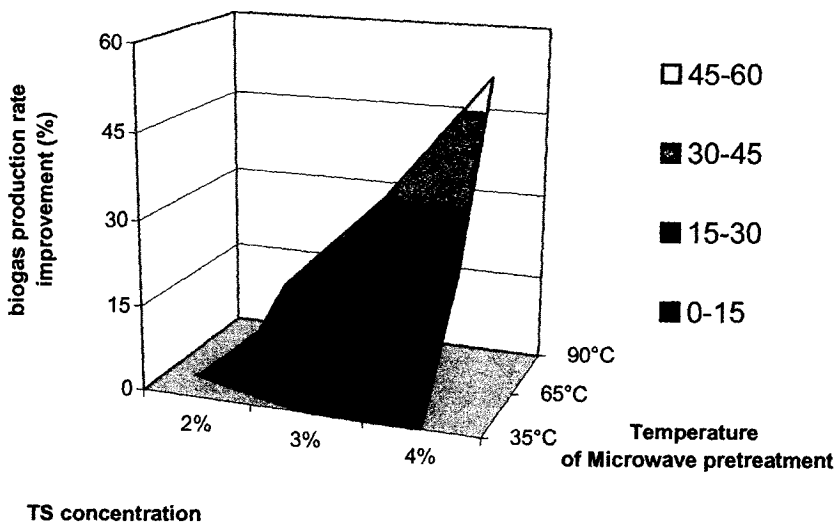


Figure 4.44 Improvement of digestion rate at various TS and temperatures. (Microwave intensity 80% and MW energy input 19.47J/min)

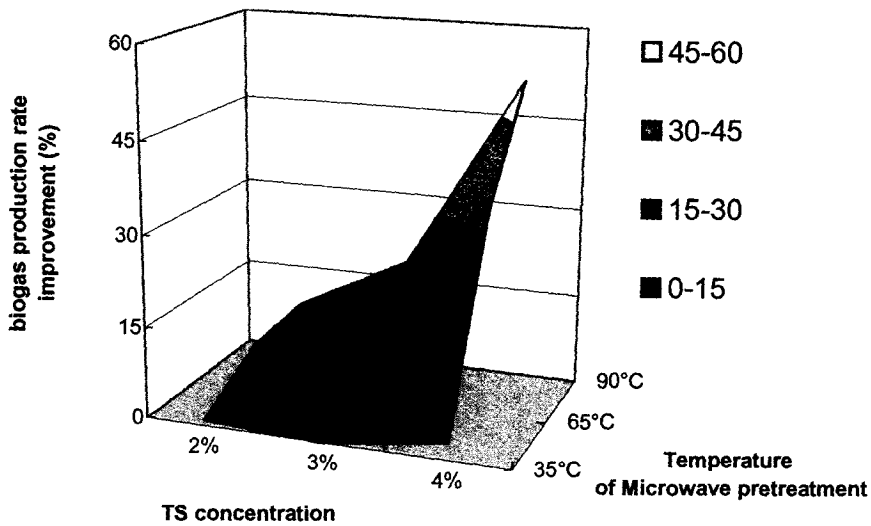


Figure 4.45 Improvement of digestion rate at various TS and temperatures (Microwave intensity 40% and MW energy input 9.73J/min)

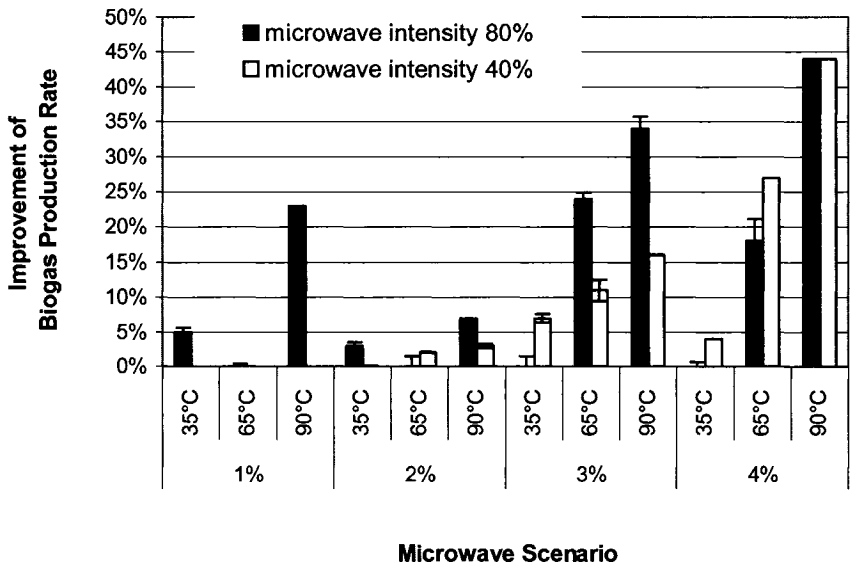


Figure 4.46 Improvement of biogas production at the end of digestion of MW pretreated sludge at various TS, temperatures, and MW intensities.

(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

4.3.9 Kinetics study

In a batch culture system, based on the simplification that the concentration of essential substrates and nutrients for bacterial cell growth are not present in limiting amounts, anaerobic digestion can be generally described as a first-order reaction (Metcalfe& Eddy 1991):

$$r_g = dX / dt = \mu X \qquad (4.3)$$

r_g – *Rate of bacterial growth* (*mass / unit volume · time*)

X – *Concentration of microorganism* (*mass / unit volume*)

μ – *Specific growth rate of bacterial cells* ($time^{-1}$)

t – *Digestion time* (d)

As the growth rate of bacteria cells has been observed to show a linear relationship with the rate of substrate utilization, the equation 4.3 can be expressed as

$$dX/dt = -a\frac{dS}{dt} \qquad (4.4)$$

$$Thus\ \ \gamma_{su} = -b\frac{dS}{dt} \qquad (4.5)$$

γ_{su} – *Substrate utilization rate* (*mass / unit volume · time*)
S – *Concentration of substrate* (*mass / unit volume*)
a – *Maximum yield coefficient* (*mass / mass*)
b – *Substrate ultization coefficient* (*mass / mass*)

After integration, equation 4.6 can be rearranged as

$$S = S_{\mu}(1 - e^{-kt}) \qquad (4.6)$$

S_{μ} – *Ultimate concentration of substrate* (*mass / unit · volume*)
k – *Substrate reduction rate coefficient* (d^{-1})

Parameter values were converted from mass of VS removed to the volume of biogas produced by using the experimental value of 927.87ml biogas /gVS removed obtained in this study as discussed in section 4.3.5.

$$Y = Y_{\mu}(1 - e^{-kt}) \qquad (4.7)$$

Y – *Cumulative biogas production* (*mL biogas* / 500*mLsample*)
Y_{μ} – *Ultimate cumulative biogas production* (*mL biogas* / 500*mLsample*)
k' – *Biogas production rate coefficient* (d^{-1})

By assuming that maximum stabilization levels reached in this experiment represent the ultimate stabilization levels, the VS reduction rate constant can be estimated according to equation 4.7.

Using the "Solver" function of MS Excel software, the values of k', Y_μ, and R^2 for the MW pretreated and un-pretreated sludge are calculated and listed in Table 4.5. The influence of MW pretreatment on ultimate biogas production Y_μ, first-order reaction coefficient k', and correlation coefficient of determination R^2 for all MW scenarios are presented in Figures 4.47, 4.48, and 4.49.

As can be seen, consistency is good and R^2 values are greater than 0.90 except for the 65°C sludge pretreated at 3% TS and 40% intensity, 3% TS and 80% intensity, and 2% TS and 80% intensity. So equation 4.7 and its calculated results can be used to compare different treatment scenarios.

As pointed out previously, the measured ultimate biogas production reached in this study did not change significantly with MW pretreatment, as seen in Figure 4.47. Thus the slight difference between ultimate biogas production values will not affect the following discussion on the first-order reaction coefficient k'.

As shown in Figure 4.48, for the first-order reaction coefficient k' obtained in this study, there was a significant correlation between MW pretreatment and digestion rate. Generally speaking, k' value improved with the MW temperature, which is consistent with the increase of digestion rate presented in section 4.3.8. The only marked exceptions to this were sludge samples pretreated at a MW intensity of 80%, TS concentration 1% and 2%. In both cases, k' values of 65°C sludge samples were slightly lower than those of control samples, which might be caused by the non-homogenous nature of primary sludge. The increased reaction coefficient value further indicated that the MW pretreatment was effective in solubilizing the particulate organic matter and improving the biodegradability of the solubilized primary sludge.

Interestingly, if we compare k' values of control samples at different TS concentrations at a MW intensity of 80%, we see that there was a constant decrease of k' value as sludge concentration increased. Sludge samples at all MW pretreatment temperatures and intensities bear strong similarity. It showed that the improvements of actual biogas production rate were not as great as the increase of ultimate biogas production as sludge concentration increased.

As shown in Figure 4.49, among the control sludge samples, 65°C sludge samples, and 90°C sludge samples, the R^2 values for 90°C sludge sample were consistently the greatest suggesting that the solubilization effect of MW pretreatment improved the models ability to fit the data for digestion with the reaction model. Any potential inhibitory substances produced in MW pretreatment appeared to play an unimportant role in this study.

Comparisons were also made between the experimental cumulative biogas production values and those calculated by using ultimate biogas production Y_{μ}, and reaction coefficient k' for the kinetic model and presented in Table 4.5. The comparison for primary sludge pretreated at a sludge concentration 4% TS and MW intensity 40% are shown in Figure 4.50, 4.51, 4.52, others are presented in Appendix D. Visually the experimental curve and model output are pretty close to each other in each situation. Again, the primary sludge samples 90°C presented the best fit to the model output,

To assess the appropriateness of the 1st order reaction model applied in this kinetics study, the residual plots for 4%TS sludge pretreated at MW intensity 40% (MW energy input 9.73J/min), 65°C and 90°C, as well as corresponding control sample are presented in Figure 4.53, 4.54, 4.55. As can be seen, the residuals (Y_{model} - $Y_{experimental}$) are positive in the first half of BMP test and stay negative in the second half of BMP instead of the randomly scattering around the figure. It reveals that, even through the coefficients of determination (R^2) are very close to "1", there are some shortages in this model and further research could be conducted regarding this issue.

Table 4.5 Performance comparison of biogas production and model constants

			Yu	*k'*	R^2
Microwave Intensity 80%	TS 1%	Control	2737	0.082	0.96
		65°C	2537	0.079	0.93
		90°C	2671	0.097	1.00
	TS 2%	Control	5786	0.0732	0.92
		65°C	5741	0.067	0.81
		90°C	5911	0.0766	1.00
	TS 3%	Control	8046	0.058	0.90
		65°C	8139	0.07	0.86
		90°C	8335	0.074	1.00
	TS 4%	Control	10754	0.042	0.93
		65°C	11157	0.0468	0.91
		90°C	11541	0.0589	1.00
Microwave Intensity 40%	TS 2%	Control	5894	0.062	0.93
		65°C	5761	0.0659	0.91
		90°C	5703	0.071	1.00
	TS 3%	Control	8219	0.058	0.93
		65°C	8525	0.062	0.85
		90°C	8360	0.0667	1.00
	TS 4%	Control	10754	0.042	0.93
		65°C	11020	0.0553	0.94
		90°C	11333	0.06	0.96

*MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min

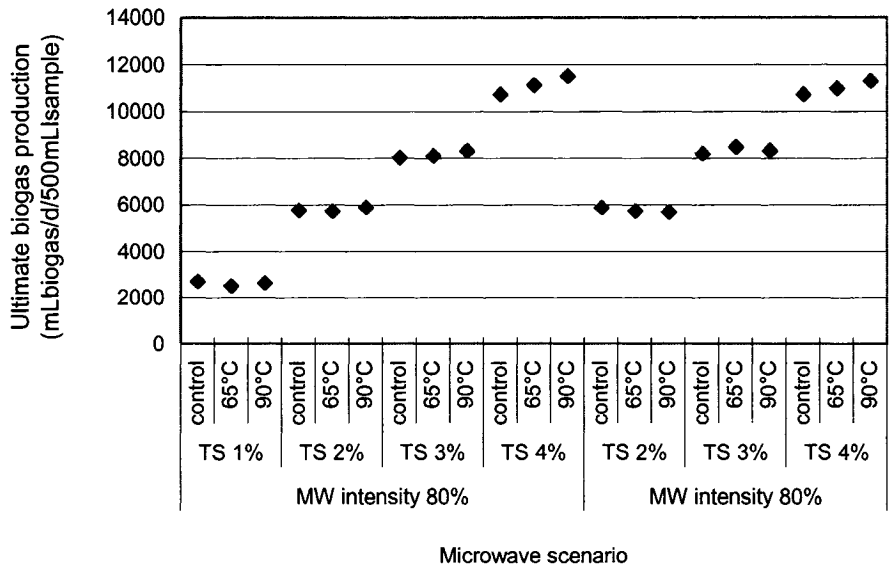


Figure 4.47 Comparison of measured ultimate biogas production (*Yu*) at various TS, temperatures, and MW intensities.
(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

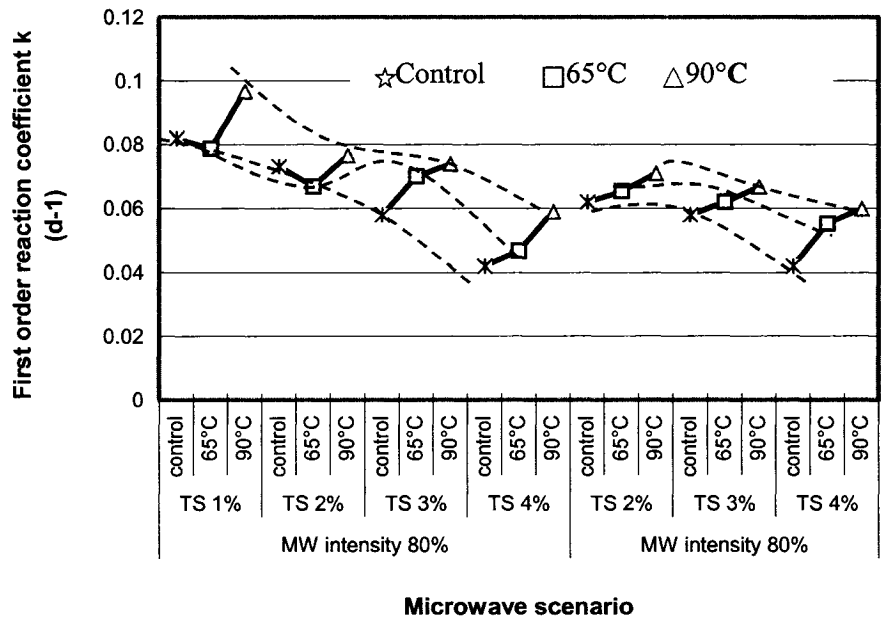


Figure 4.48 Comparison of reaction coefficient (*k'*) at various TS, temperatures, and MW intensities (dotted line shows similar temperatures and solid line shows similar TS)
(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

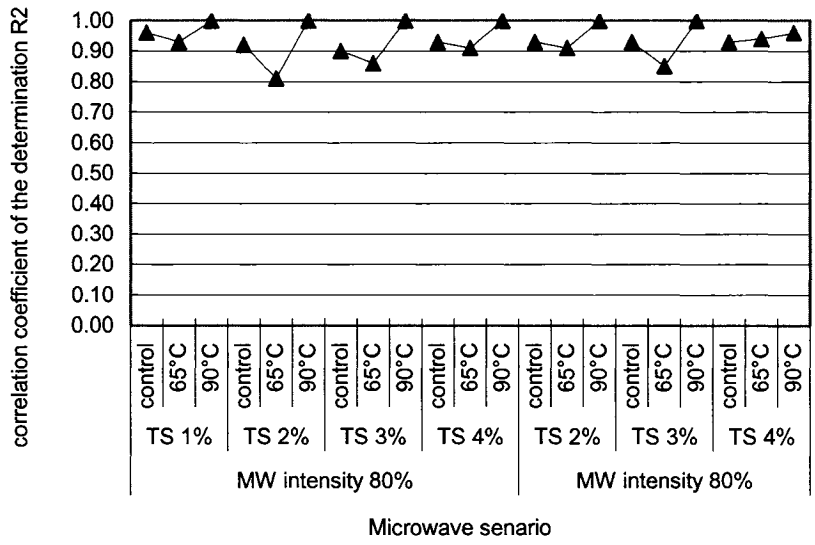


Figure 4.49 Comparison of R^2 at various TS, temperatures, and MW intensities.
(MW intensities 80% and 40% are equal to MW energy input 19.47 and 9.73 J/min).

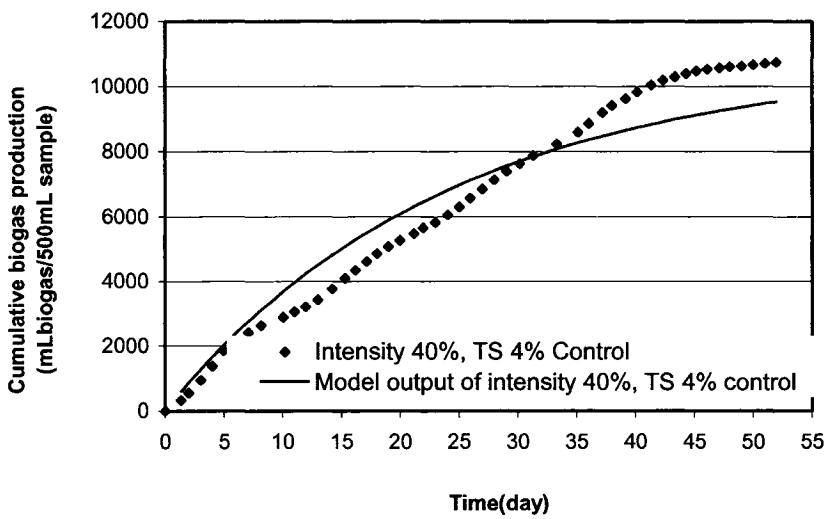


Figure 4.50 Comparison of experimental cumulative biogas production and model output for control at 4% and MW intensity 40% run.
(MW intensity 40% is equal to MW energy input 9.73 J/min).

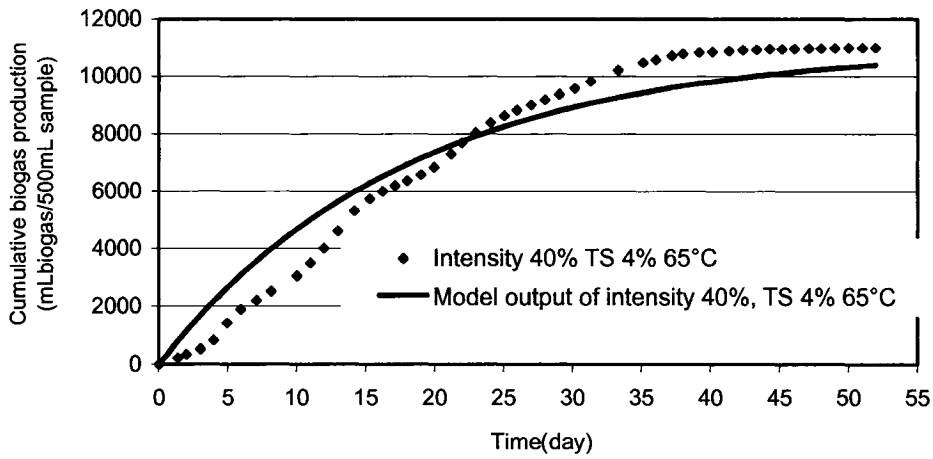


Figure 4.51 Comparison of experimental cumulative biogas production and model output for 65°C sludge at 4% TS and MW intensity 40%

(MW intensity 40% is equal to MW energy input 9.73 J/min).

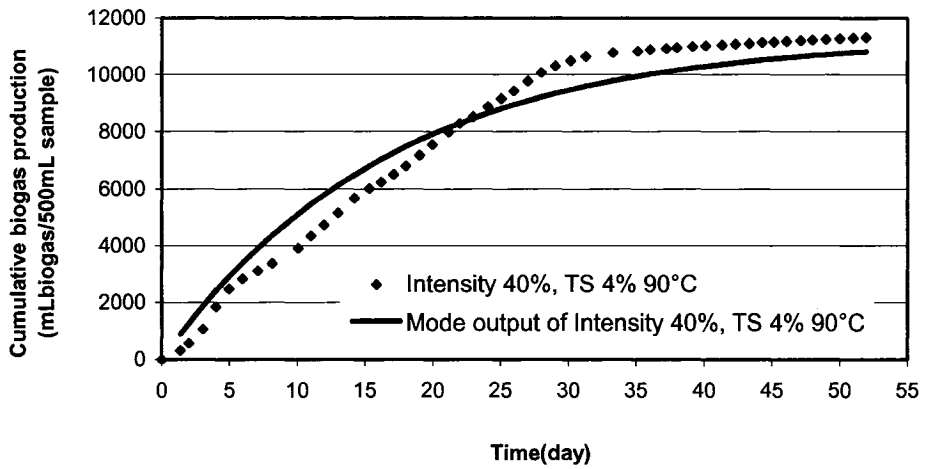


Figure 4.52 Comparison of experimental cumulative biogas production and model output for 90°C sludge at 4% TS and MW intensity 40%.

(MW intensity 40% is equal to MW energy input 9.73 J/min).

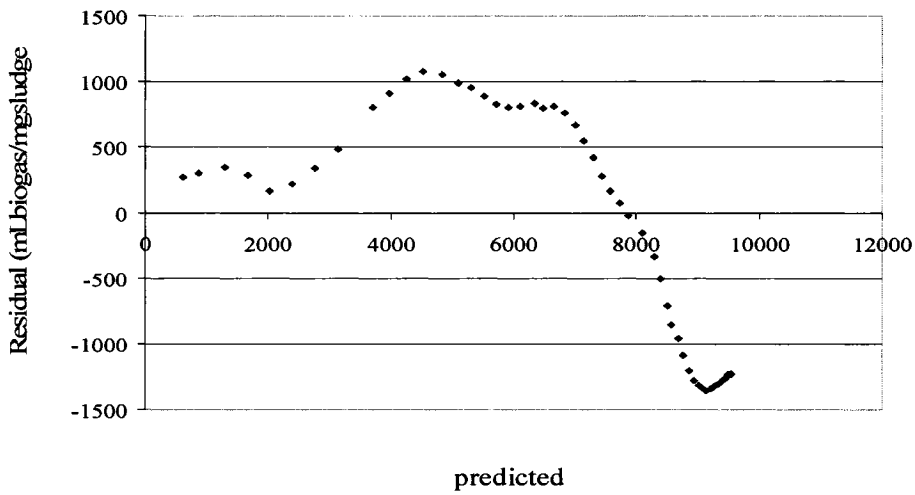


Figure 4.53 Residual plot for untreated sludge sample at TS 4%.

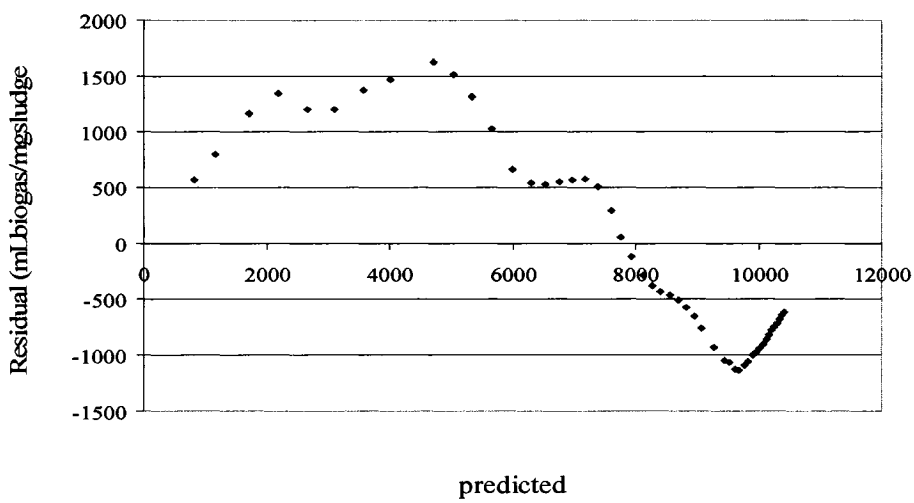


Figure 4.54 Residual plot for sludge sample at TS 4%, pretreatment temperature 65°C.

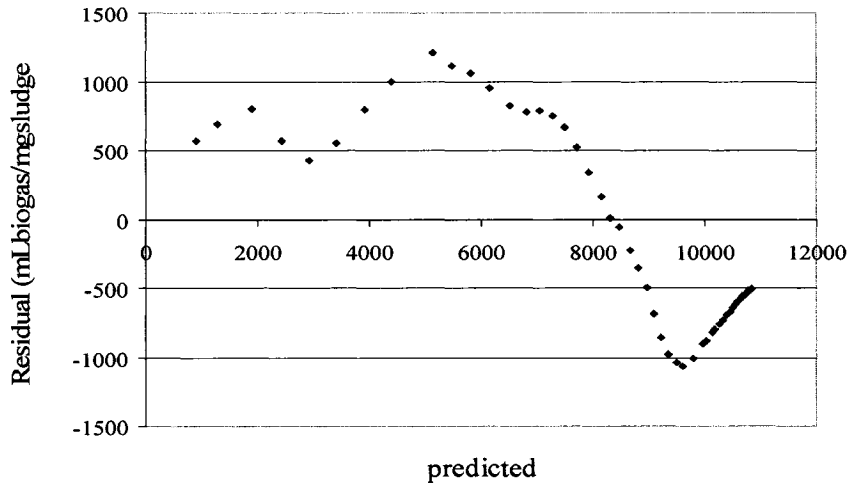


Figure 4.55 Residual plot for sludge sample at TS 4% and pretreatment temperature 90°C.

4.4 Biochemical Methane Potential Assay on Soluble Fraction of Primary Sludge.

This BMP assay was conducted to assess possible inhibition by soluble toxic compounds produced from MW irradiation, due to either thermal and athermal MW effects. As discussed in section 4.3, a short and light lag phase appeared at the very beginning of the sludge digestion. Hong (2002) found that, for MW pretreated primary sludge, the inhibition value was lower than the untreated sludge until the irradiation temperature reached 85°C; but he also speculated that even the 100°C pretreatment temperature would not affect the biogas production. It was not specified in his study if he used MW acclimated (as in this study) or unacclimated inoculum.

Two MW scenarios were chosen to perform this part of the study as they resulted in the greatest improvement in digestion during BMP tests. They were 4% TS, MW intensity 80% (energy input 19.47J/min), and temperatures 65°C and 90°C. The soluble portion of the 65°C and 90°C samples were run at both undiluted (SCOD concentration as produced from pretreatment) and samples diluted to the same SCOD concentration as the control sample prior to running the BMP assays (in duplicate). The volume of all sample used was 90mL Acclimated digestion seed was used to initiate the reactors. More details of the

experimental design were discussed in chapter 3. Biogas production, daily biogas production rate as well as starting and final SCOD concentration for the different diluted and undiluted sample, are shown in Table 4.6 and plotted in Figure 4.53 and Figure 4.54.

It should be noted that at the conclusion of the BMP assay all SCOD values were less than 100mg/L indicating that a majority of the SCOD was biodegradable in nature. Additionally, undiluted SCOD from pretreated sludge samples which were higher in concentration for higher pretreatment temperature conditions resulted in higher amounts of cumulative biogas production compared to the control sample which had a lower SCOD concentration. This makes sense based on the fact that all final SCODs in the BMP assay bottles were less than 100 mg/L indicating that almost all the SCOD was stabilized. In addition, both 65°C and 90°C of diluted MW pretreated samples produced a similar amount of biogas to the control sample. Based on Table 4.6 and Figure 4.53 methanogenic inhibition would seem to be negligible. A closer look at daily biogas production rates shown in Figure 4.54 indicates that for the diluted pretreated samples and the control the daily rates were quite similar indicting no inhibition. Additionally, comparison of the undiluted MW pretreated samples to the control indicates that in general the rate of biogas production increased in proportion to the increase in concentration. Again this is further evidence that MW pretreatment did not produce soluble components that were inhibitory to methanogenesis. It should be kept in mind that this result may be specific to PS and the conditions of the pretreatment used in this study. Higher temperatures or longer exposure times or WAS may result in a different result. While there was some very mild inhibition shown in the digestion of whole pretreated sludge (section 4.2.1; 2-3 day lag phase for 90°C sludge sample with acclimated digestion seed) this test would tend to indicate that this mild inhibition was not directly associated with the soluble components of pretreatment. If it is argued that mild inhibition of whole sludge digestion after pretreatment did occur that the inhibitory compounds caused by MW irradiation were part of the insoluble portion of the sludge or that rapid acidogenesis of the insoluble fraction causing an imbalance in the microbial consortia and VFA that may have caused the mild inhibition.

Table 4.6 Soluble COD concentration and biogas production of soluble samples

Sample	SCOD concentration before BMP assay (mg/L)	SCOD concentration after BMP assay (mg/L)	Biogas production (mL/90ml sludge)
Control	2528	< 100	82
65°C	4364	< 100	139
65°C diluted	2522	< 100	79
90°C	4800	< 100	157
90°C diluted	2528	< 100	80

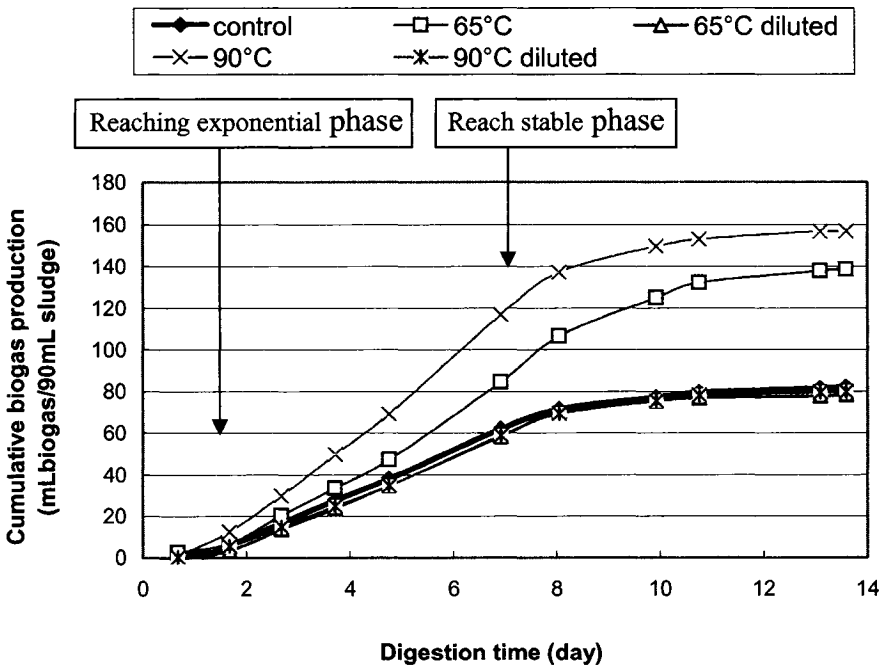


Figure 4.56 Cumulative biogas production of BMP assay on soluble portion of primary sludge

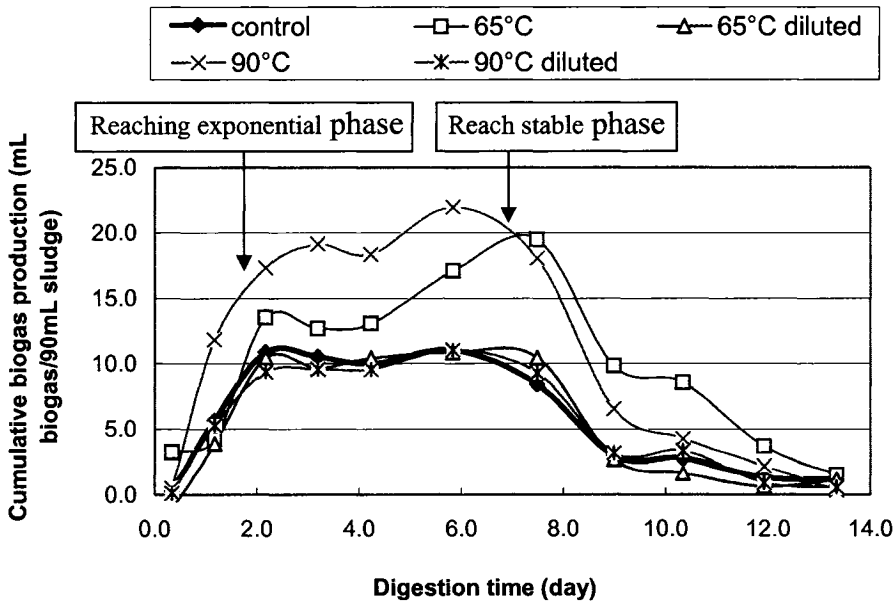


Figure 4.57 Biogas daily production rate in BMP assay of soluble portion of sludge

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

Research from this study indicated that MW irradiation indeed has a positive influence on the anaerobic biodegradation of primary sludge. Based on research conducted in this study, specific conclusions may be drawn:

1. Mild MW irradiation causes solubilization (SCOD) of non-soluble organic matter. Both sludge solid concentration and MW temperature achieved in irradiation are important in sludge solubilization parameters while the MW intensity parameter was insignificant

2. Severity of MW pretreatment conditions used in this research was too mild to solubilize a significant amount of the suspended organic substances in primary sludge.

3. Organic compounds solubilized by MW pretreatment were readily biodegradable and were not inhibitory to the methanogenic microbial consortium.

4. Higher MW irradiation temperature and higher TS concentration led to higher digestion rates (up to 37% higher) and less required digestion time (up to 27% less time) to achieve ultimate cumulative biogas production. MW pretreatment had no impact on ultimate primary sludge degradability (biogas production and VS removal efficiency) while MW intensity had no impact on digestion rate or ultimate degradability

5. At mild MW irradiation, production of mild toxicity distributed in both soluble portion and insoluble portion of sludge can be effectively tolerated by the cultivated digestion bacterial consortium

6. Microwave irradiation did not significantly change the CSTs of the stabilized primary sludge.

It would be beneficial to conduct further research focusing on higher temperature and higher sludge solid concentration to explore the possible application of MW irradiation on primary sludge. Production of potential inhibitory compounds combined with higher biodegradable soluble concentrations that can be easily converted to VFA could result in potential digester instability and should be fully monitored and evaluated prior to pilot testing.

Finally anaerobic treatment at both mesophilic and thermophilic conditions of combined, unpretreated and MW pretreated primary sludge with MW pretreated WAS should be undertaken to determine the overall improvements possible in a more real world scenario.

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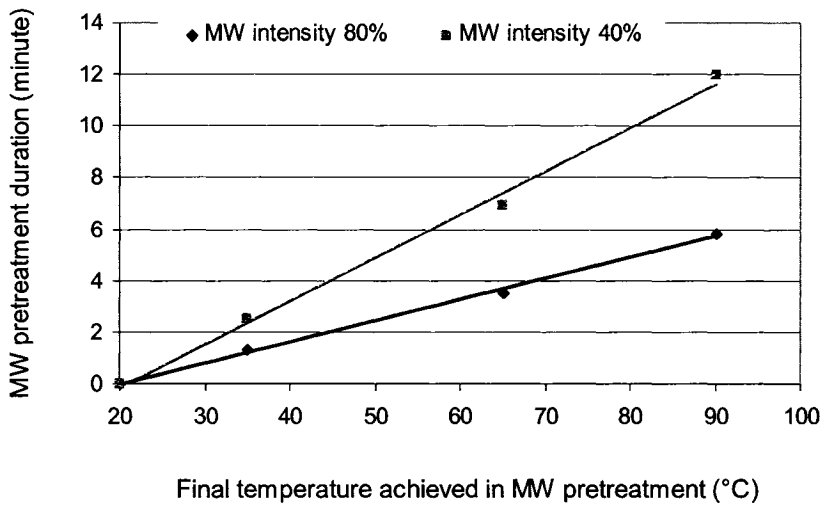
APPENDICES

Appendix A Calibration Result of Final Temperature Achieved in MW Pretreatment versus MW Pretreatment Duration

Appendix A-1 Relationship between MW Pretreatment Duration and Final Temperature Achieved in MW Pretreatment

Appendix A-2 Relationship between Energy Input during MW Pretreatment and Final Temperature Achieved in MW Pretreatment

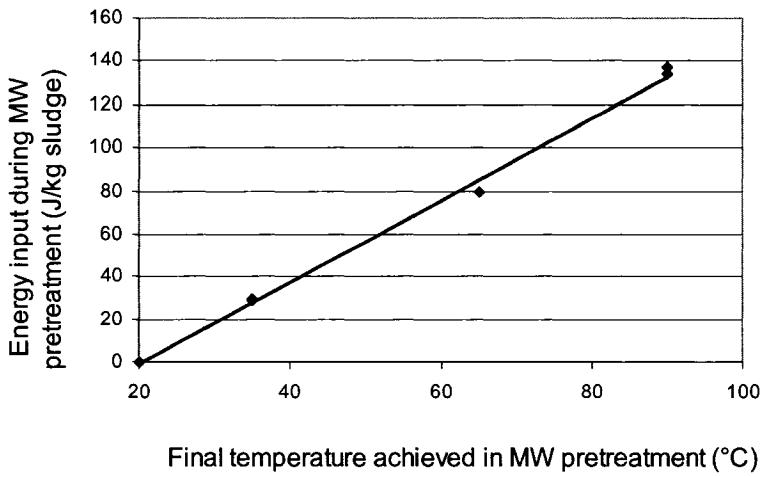
Appendix A-1 Relationship between MW Pretreatment Duration versus Final Temperature Achieved in MW Pretreatment



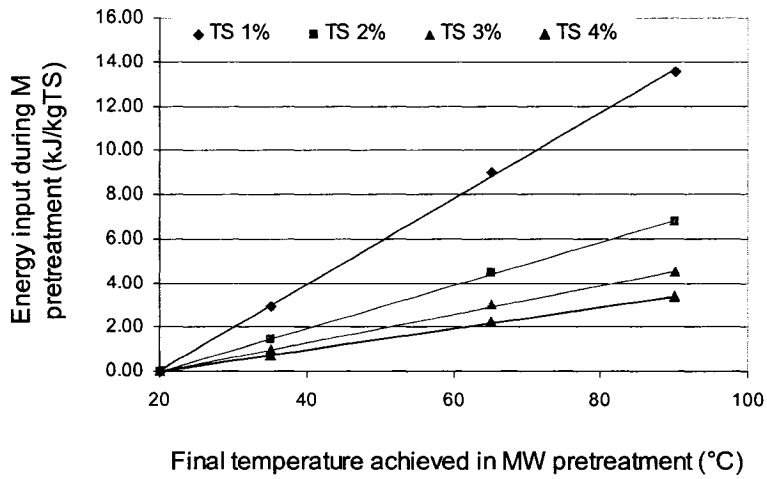
	Linear relationship	**R^2**
MW intensity 80%	MW pretreatment duration (min) = 0.0822×(final temperature achieved in MW pretreatment -20)	0.9959
MW intensity 40%	MW pretreatment duration (min) = 0.1688×(final temperature achieved in MW pretreatment -20)	0.9973

* MW intensities 80 and 40% represent energy input 19.47 and 9.73 J/min.

Appendix A-2 Relationship between Energy Input during MW Pretreatment versus Final Temperature Achieved in MW Pretreatment



Energy input during MW pretreatment (kJ/g sludge) =
1.9083 ×(final temperature achieved in MW pretreatment -20) (R^2 =0.9955)



	Linear relationship	R^2
Sludge TS 1%	Energy input during MW pretreatment (kJ/kgTS) = 0.1946×(final temperature achieved in MW pretreatment -20)	0.9995
Sludge TS 2%	Energy input during MW pretreatment (kJ/kgTS) = 0.0973×(final temperature achieved in MW pretreatment -20)	0.9995
Sludge TS 3%	Energy input during MW pretreatment (kJ/kgTS) = 0.0649×(final temperature achieved in MW pretreatment -20)	0.9995
Sludge TS 4%	Energy input during MW pretreatment (kJ/kgTS) = 0.0486×(final temperature achieved in MW pretreatment -20)	0.9995

*VS/TS ratio is 0.824 for the PS used in this research.

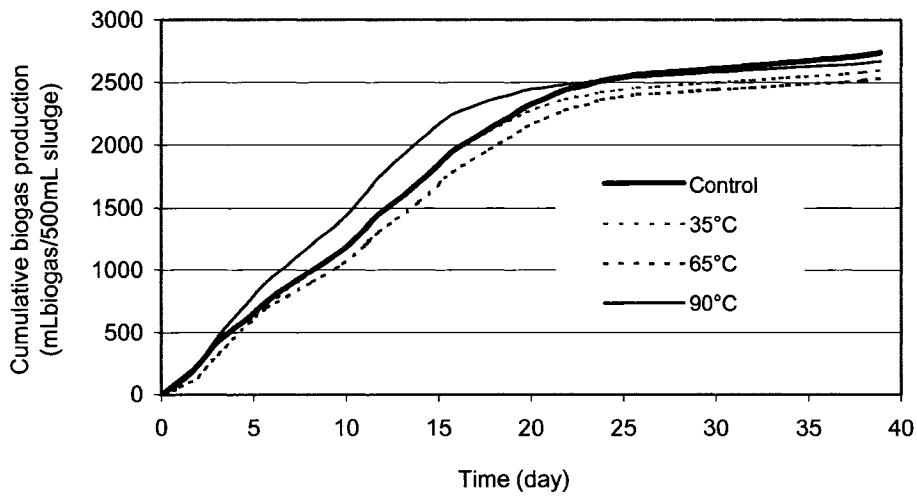
Appendix B Supplement Information of Biogas production, VFA Concentration, Biogas Composition, and pH in Duplicated BMP Reactors

Appendix B-1 Figures of cumulative biogas production

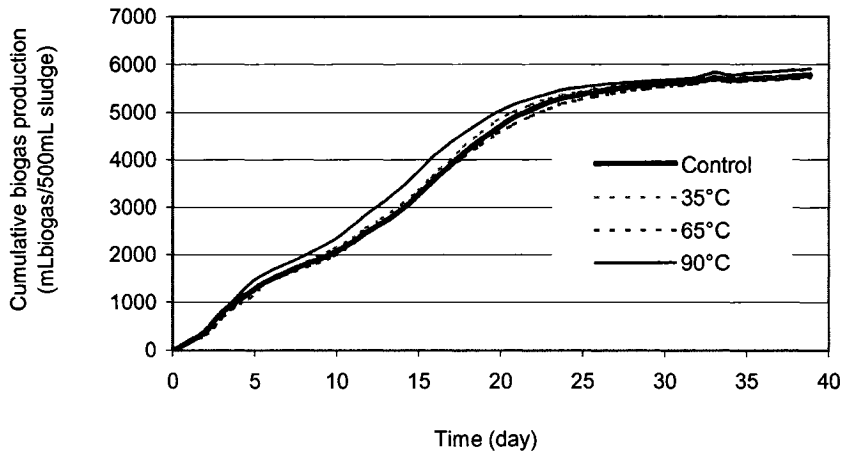
Appendix B-2 Figures of daily biogas production rate

Appendix B-3 Profile of VFA concentration, pH, and biogas composition in BMP assay

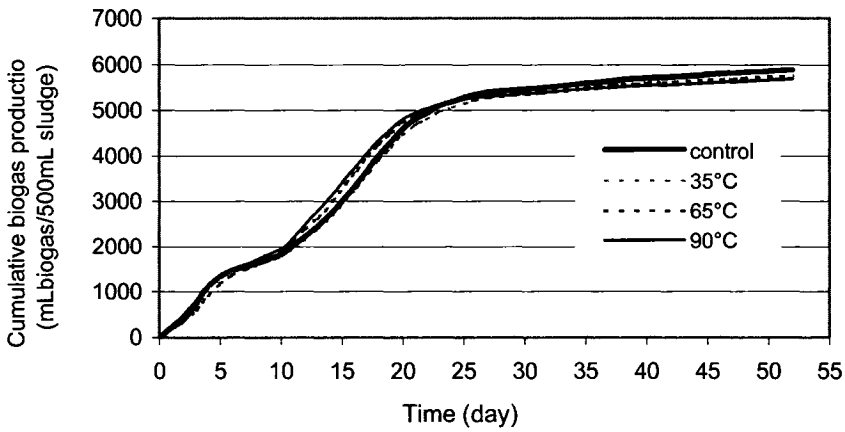
Appendix B-1 Figures of cumulative biogas production



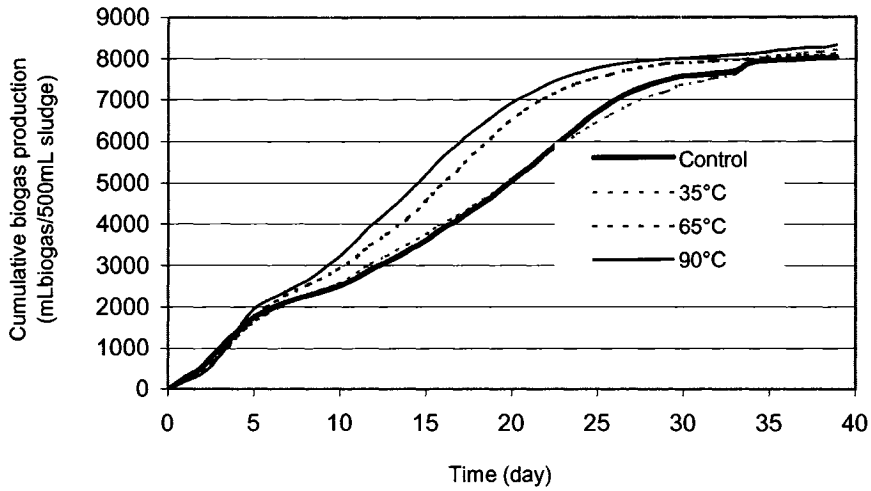
Cumulative biogas production
(sludge TS 1%, microwave intensity 80% and MW energy input 19.47J/min)



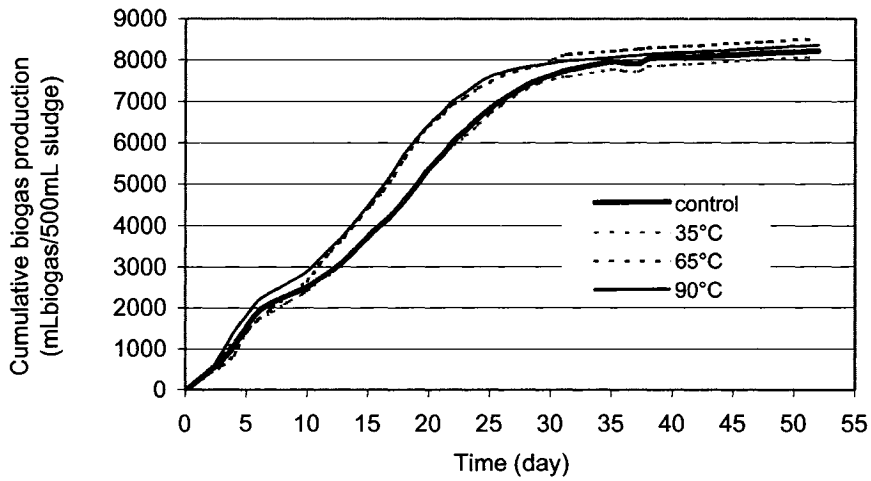
Cumulative biogas production
(sludge TS 2%, microwave intensity 80% and MW energy input 19.47J/min)



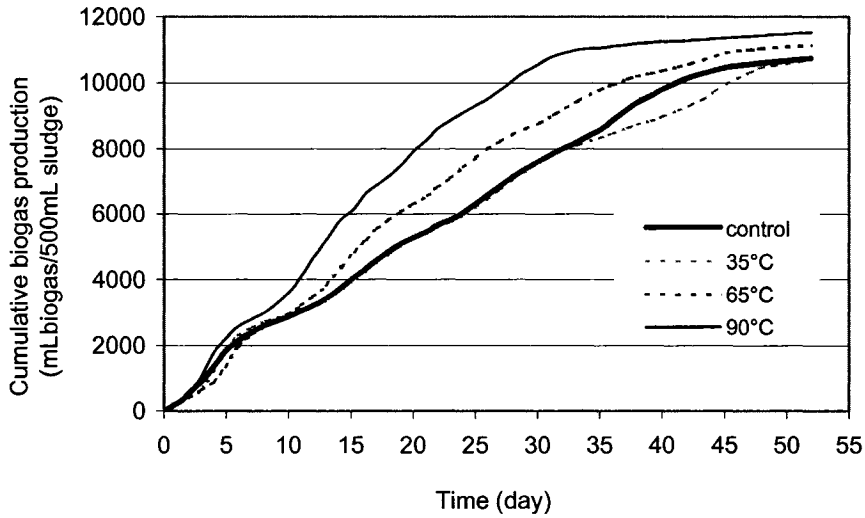
Cumulative biogas production
(sludge TS 2%, microwave intensity 40% and MW energy input 9.73J/min)



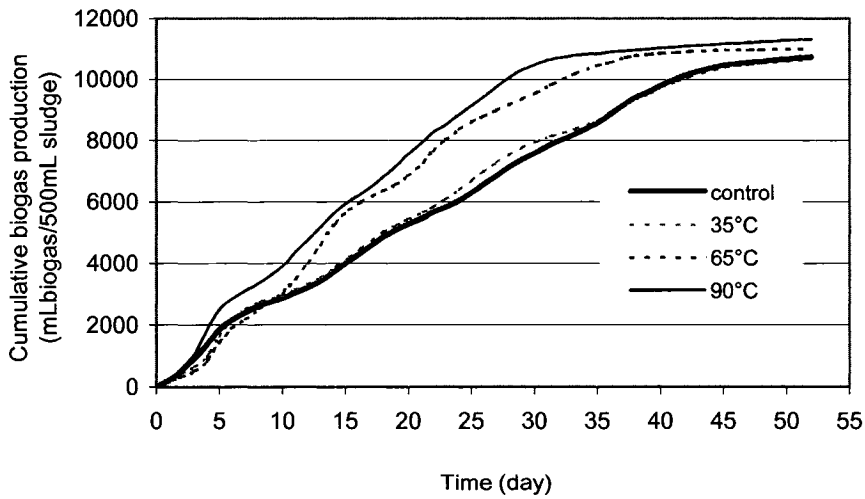
Cumulative biogas production
(sludge TS 3%, microwave intensity 80% and MW energy input 19.47J/min)



Cumulative biogas production
(sludge TS 3%, microwave intensity 40% and MW energy input 9.73J/min)

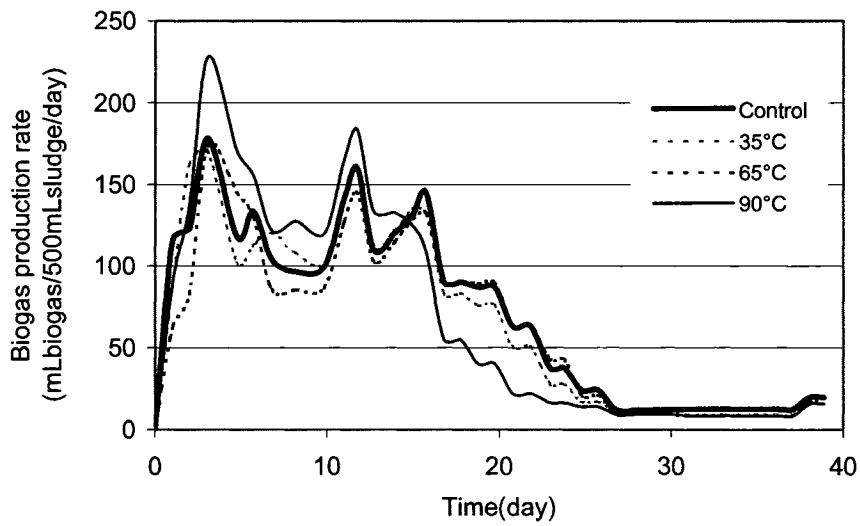


Cumulative biogas production
(sludge TS 4%, microwave intensity 80% and MW energy input 19.47J/min)

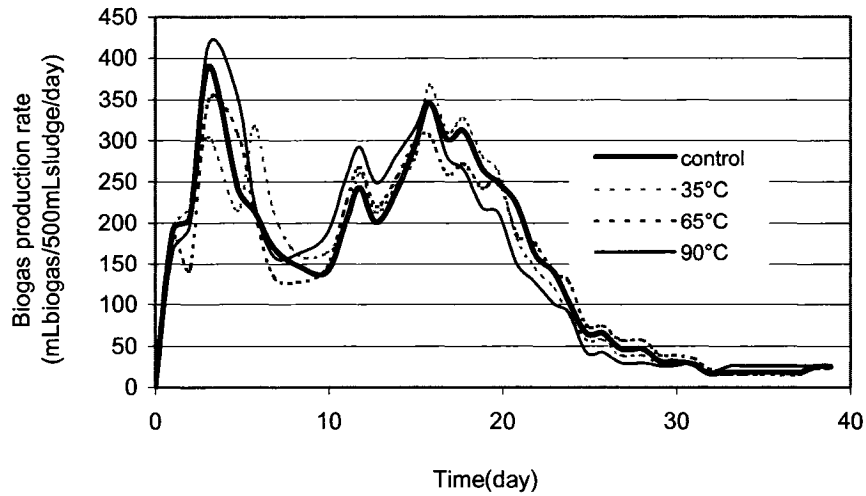


Cumulative biogas production
(sludge TS 4%, microwave intensity 40% and MW energy input 9.73J/min)

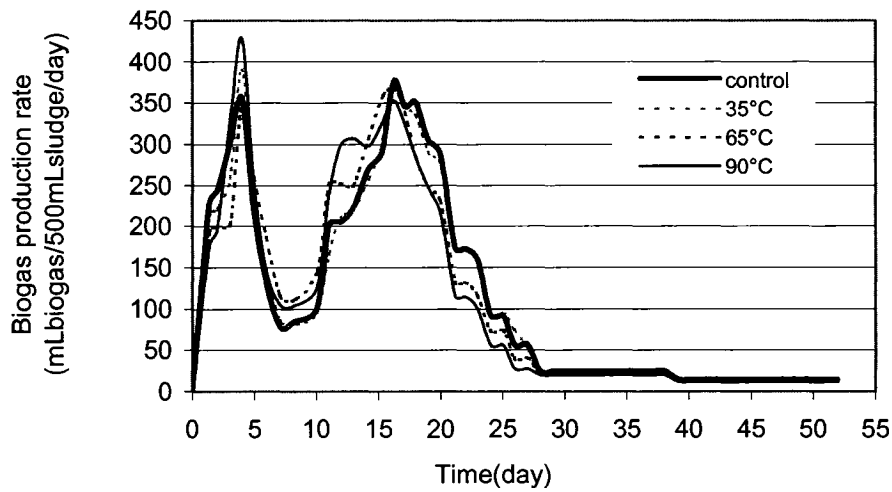
Appendix B-2 Figures of daily biogas production rate



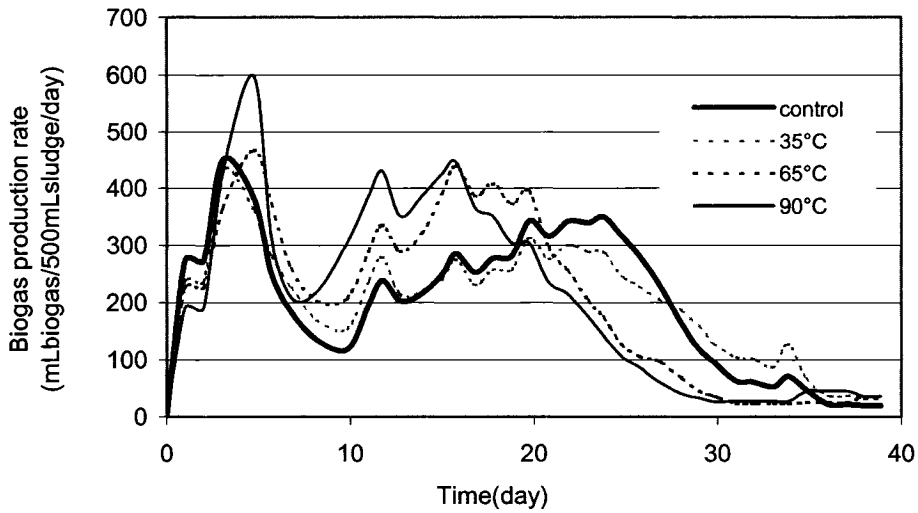
Biogas daily production rate
(sludge TS 1%, microwave intensity 80% and MW energy input 19.47J/min)



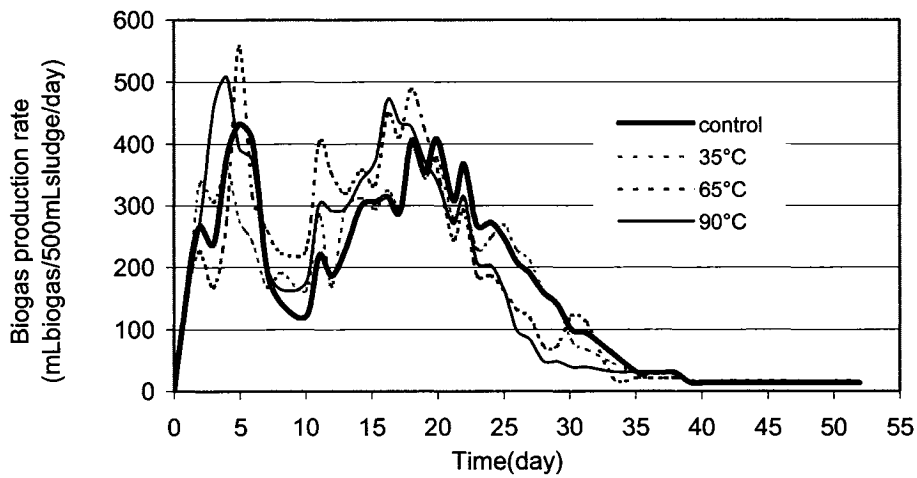
Daily biogas production rate
(sludge TS 2%, microwave intensity 80% and MW energy input 19.47J/min)



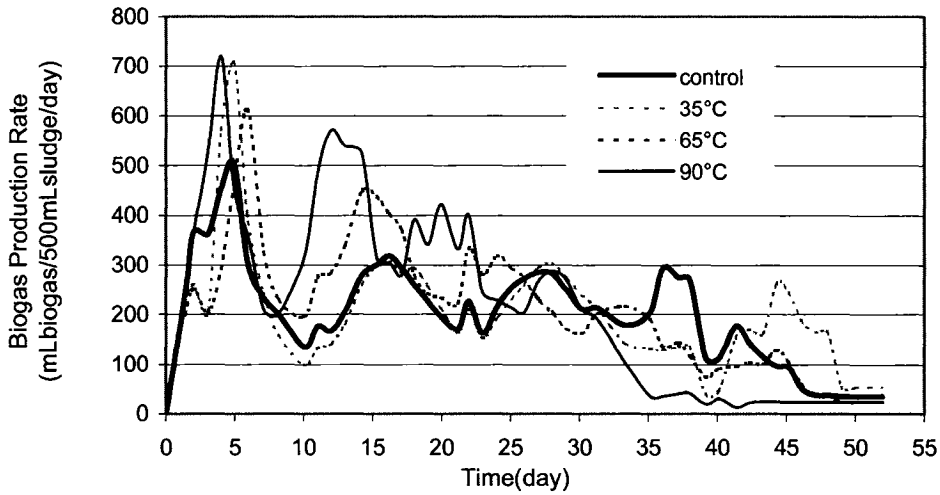
Daily biogas production rate
(sludge TS 2%, microwave intensity 40% and MW energy input 9.73J/min)



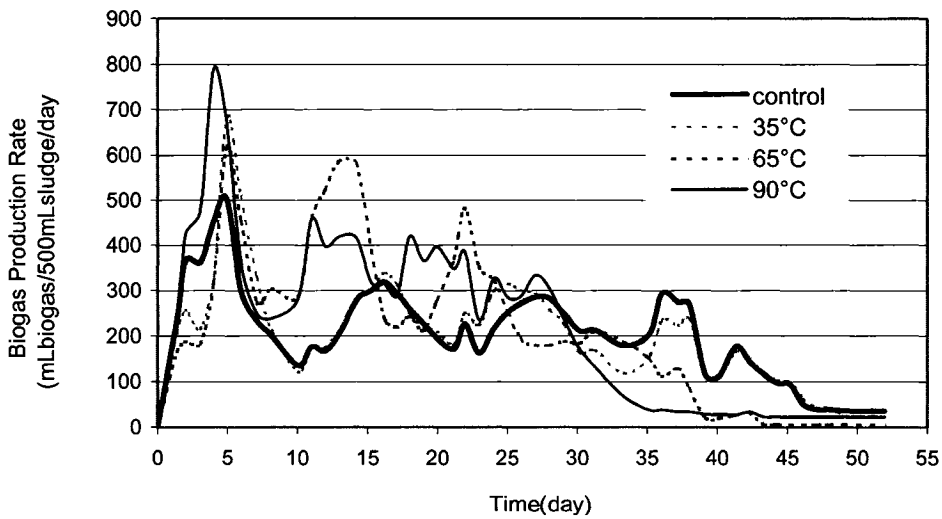
Daily biogas production rate
(sludge TS 3%, microwave intensity 80% and MW energy input 19.47J/min)



Daily biogas production rate
(sludge TS 3%, microwave intensity 40% and MW energy input 9.73J/min)

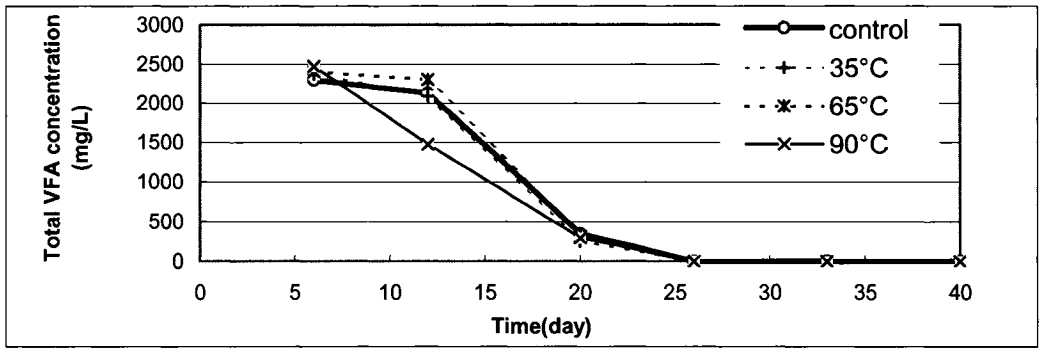


Daily biogas production rate
(sludge TS 4%, microwave intensity 80% and MW energy input 19.47J/min)

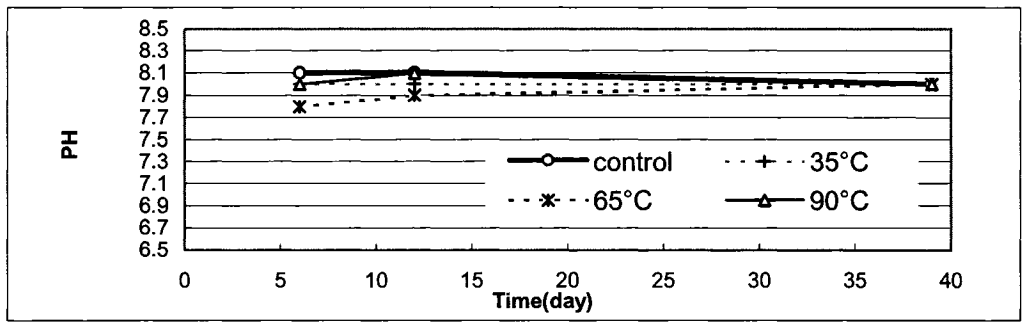


Daily biogas production rate
(sludge TS 4%, microwave intensity 40% and MW energy input 9.73J/min)

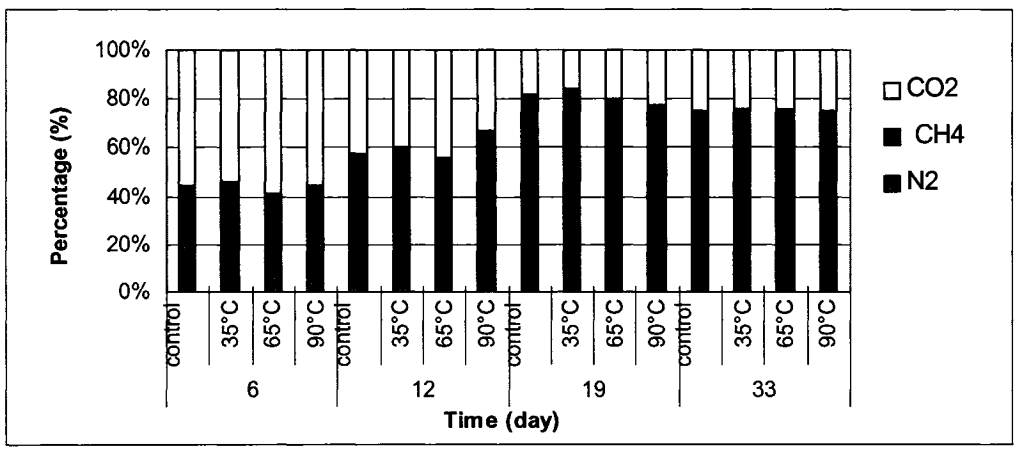
Appendix B-3 Profile of VFA concentration, pH, and biogas composition in BMP assay



Total VFA profile

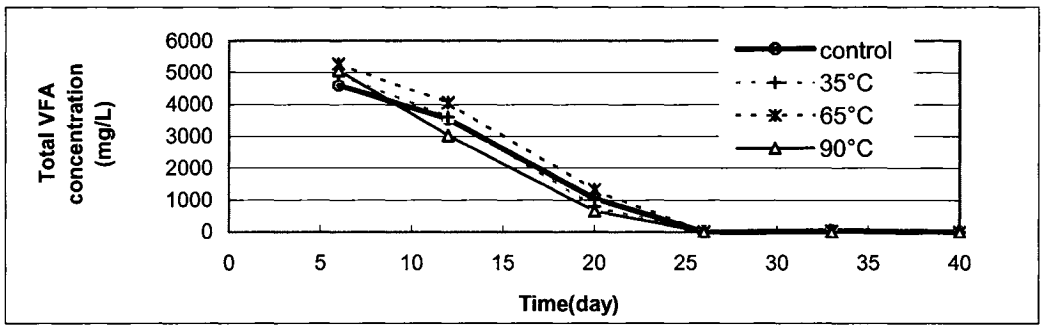


pH profile



Biogas composition profile

Profile of VFA concentration, pH, and biogas composition in BMP assay for sludge at solid concentration 1% and pretreated at microwave intensity 80% and MW energy input 19.47J/min



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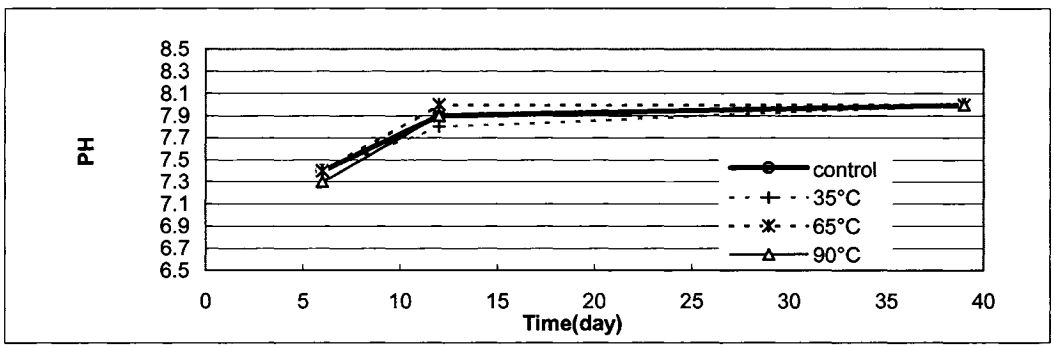

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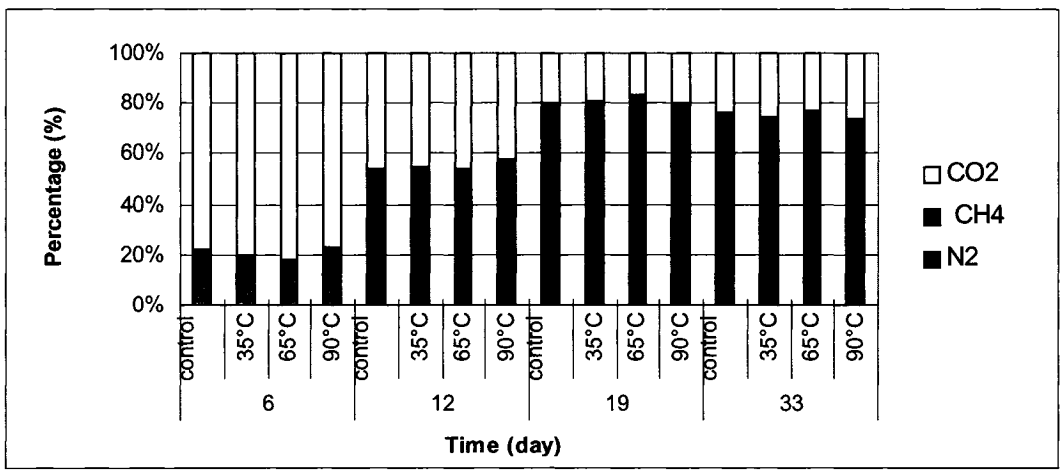
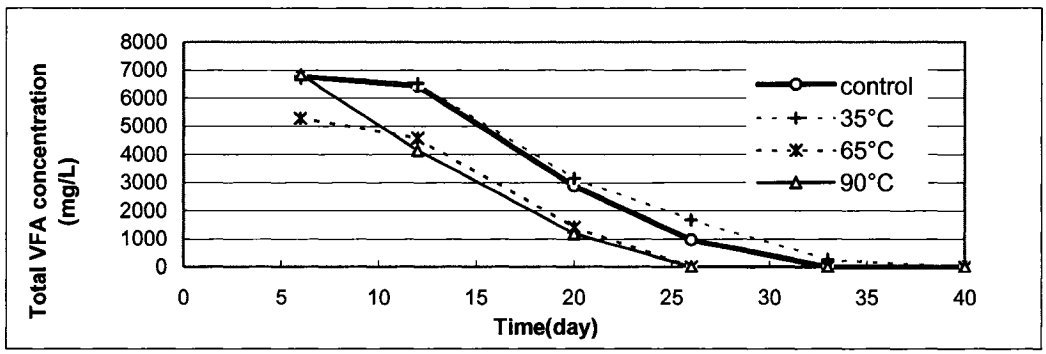


Biogas composition profile

Profile of VFA concentration, pH, and biogas composition in BMP assay for sludge at solid concentration 2% and pretreated at microwave intensity 80%, and MW energy input 19.47J/min



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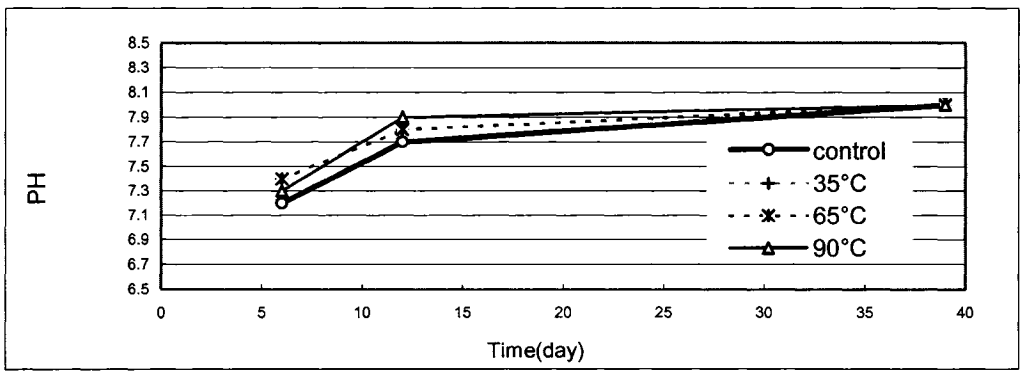

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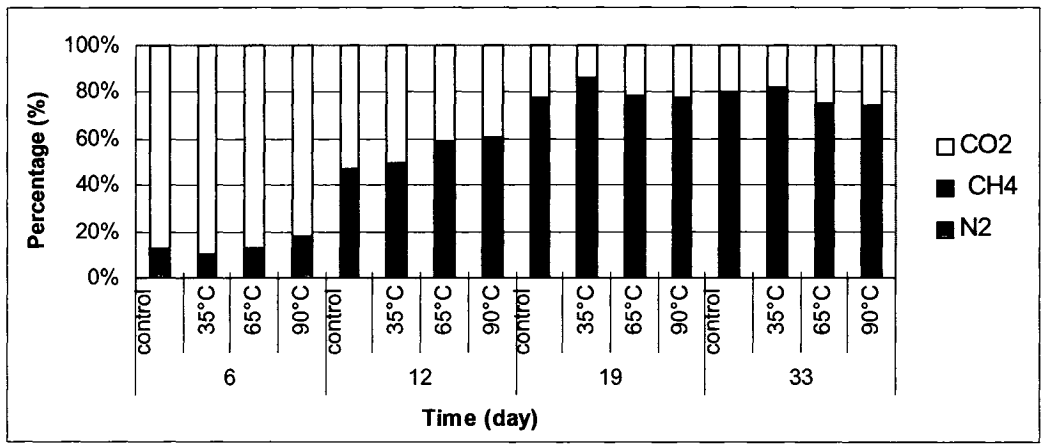
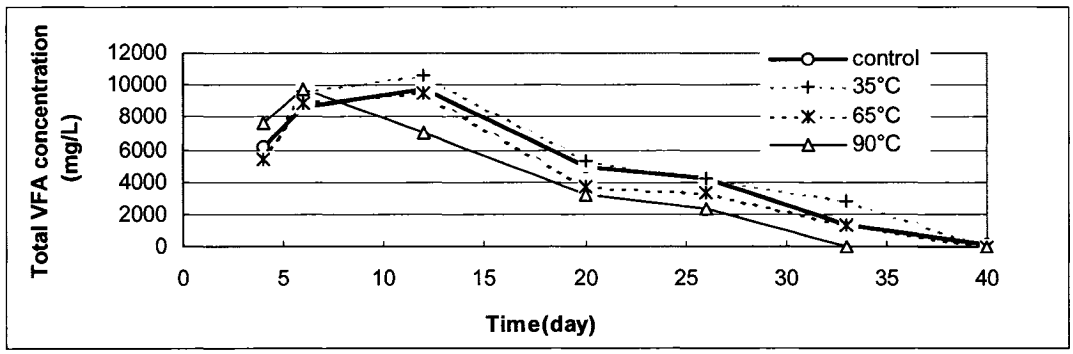


Biogas composition profile

Profile of VFA concentration, pH, and biogas composition in BMP assay for sludge at solid concentration 3% and pretreated at microwave intensity 80%, and MW energy input 19.47J/min.



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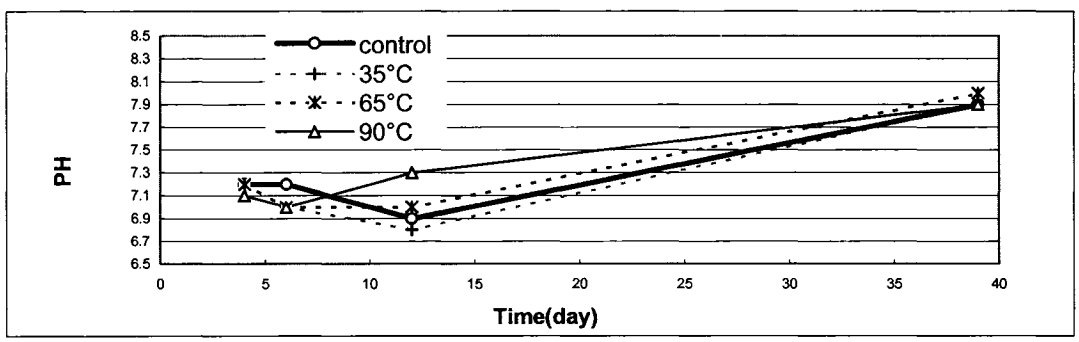

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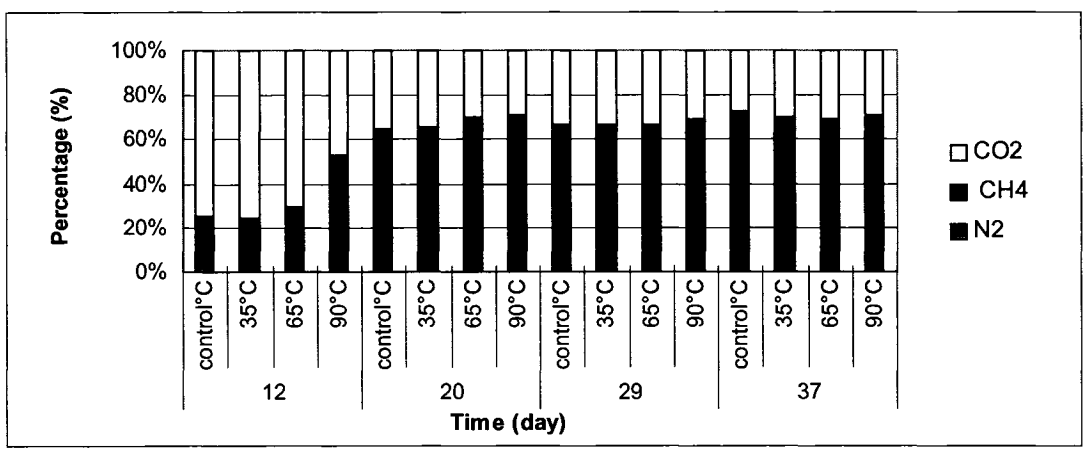
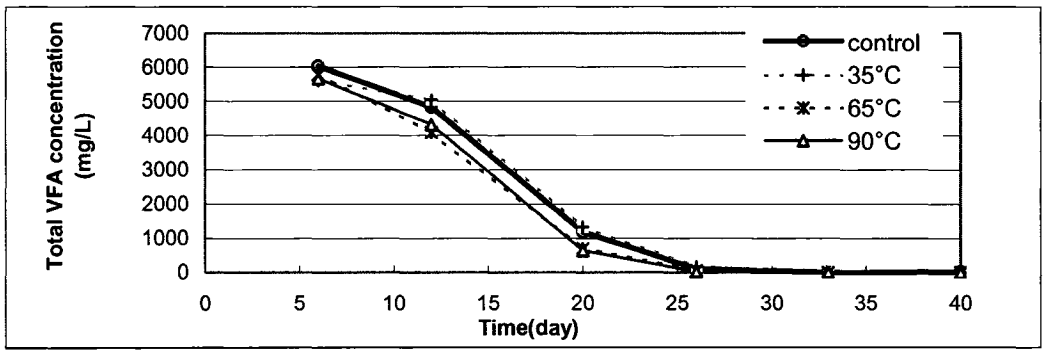


Biogas composition profile

Profile of VFA concentration, pH, and biogas composition in BMP assay for sludge at solid concentration 4% and pretreated at microwave intensity 80%, and MW energy input 19.47J/min.



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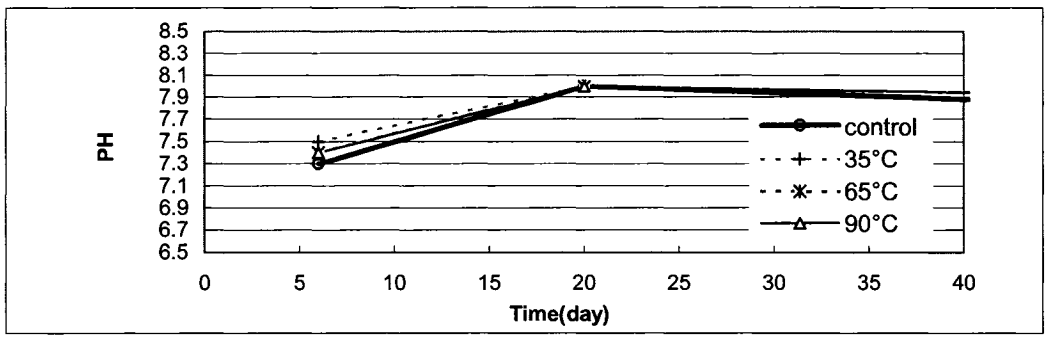

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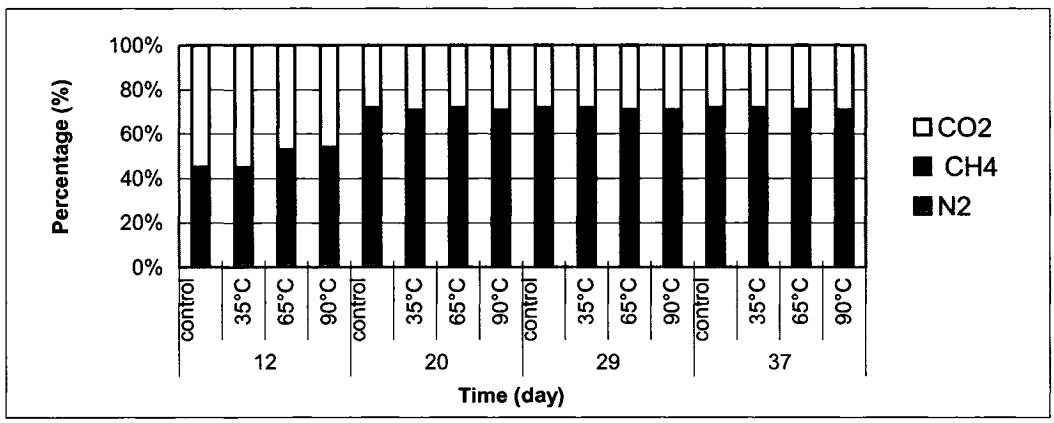
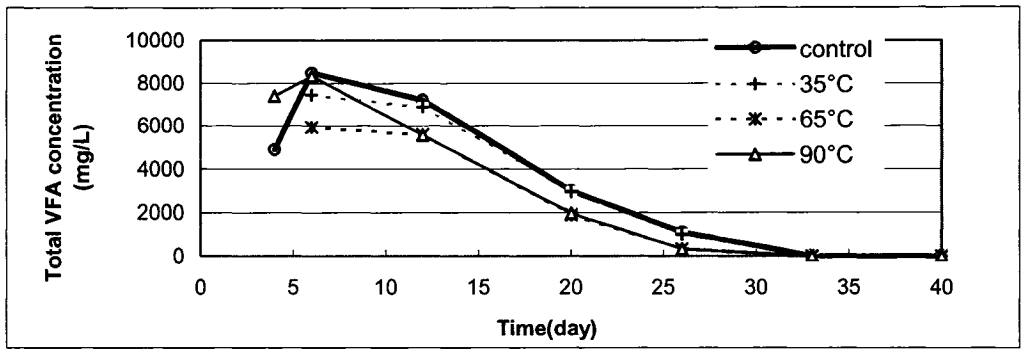
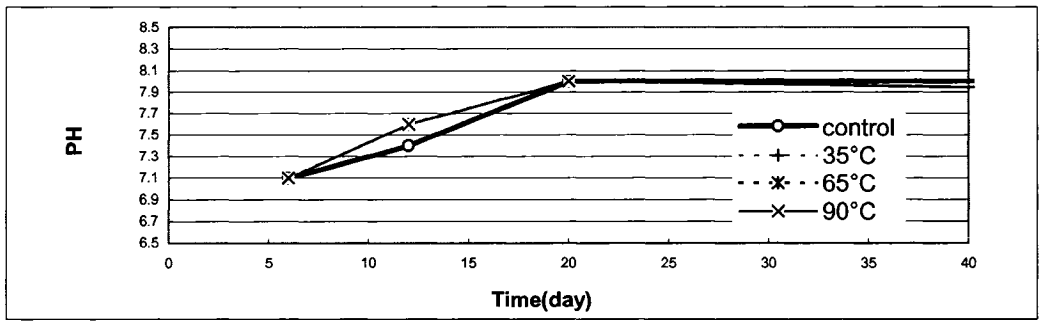


Biogas composition profile

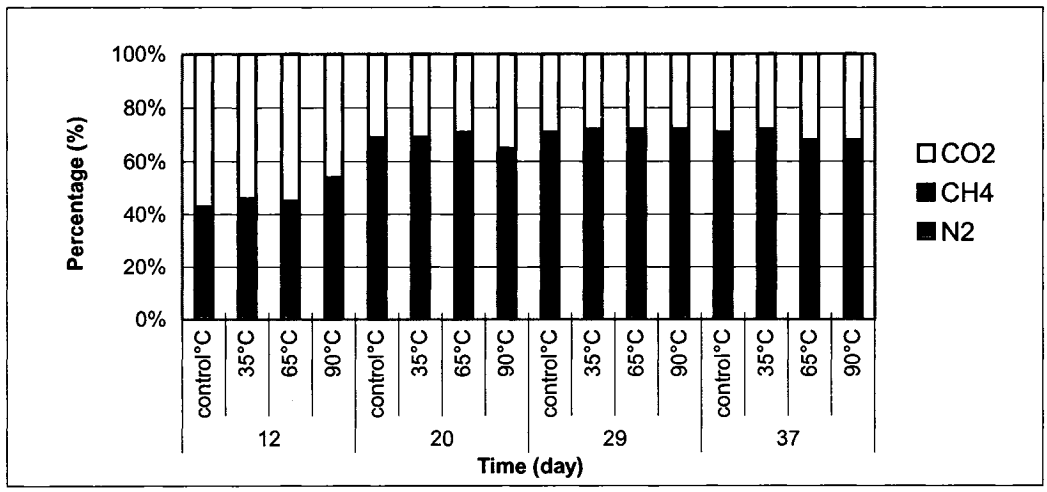
Profile of VFA concentration, pH, and biogas composition in BMP assay for sludge at solid concentration 2% and pretreated at microwave intensity 40%, and MW energy input 9.73J/min.



Total VFA profile

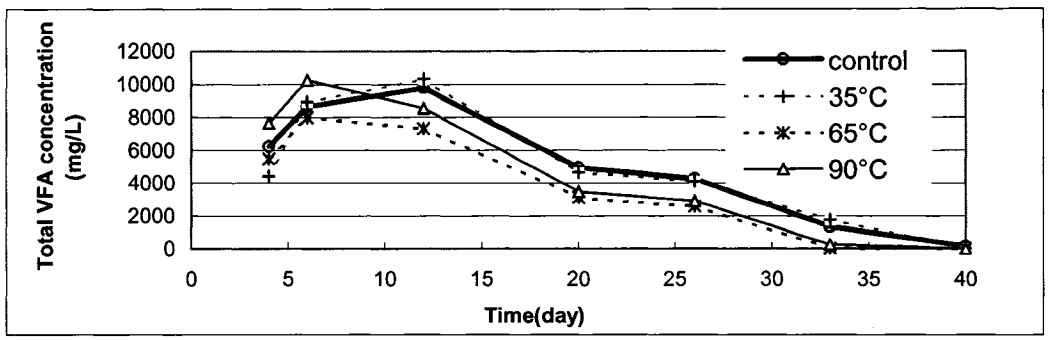


pH profile

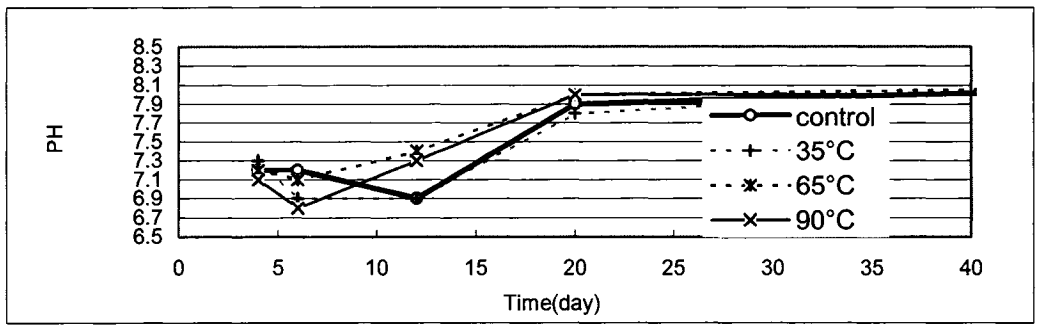


Biogas composition profile

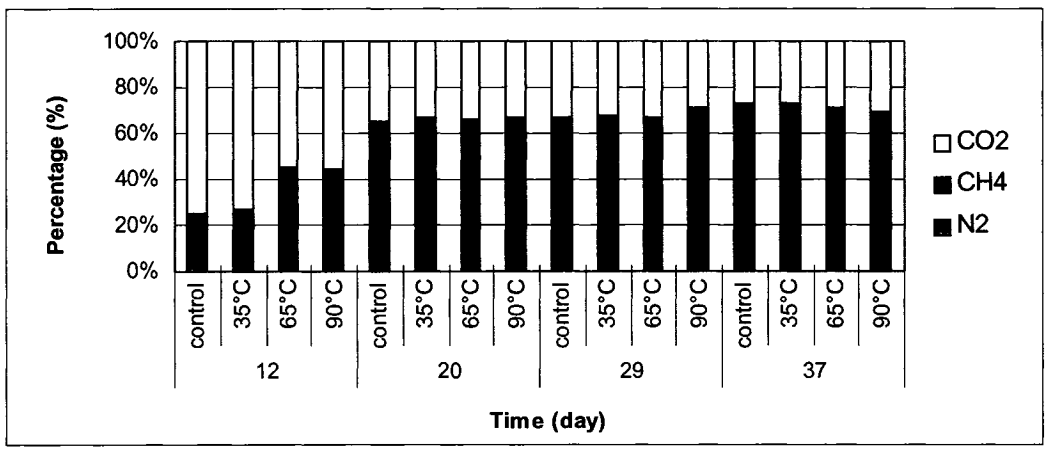
Profile of VFA concentration, pH, and biogas composition in BMP assay for sludge at solid concentration 3% and pretreated at microwave intensity 40%, and MW energy input 9.73J/min.



Total VFA profile



pH profile



Biogas composition profile

Profile of VFA concentration, pH, and biogas composition in BMP assay for sludge at solid concentration 4% and pretreated at microwave intensity 40%, and MW energy input 9.73J/min.

Appendix C TCOD and VS Removal Efficiency in Duplicated BMP Reactors

TCOD Removal Efficiency in Duplicated BMP Reactors

Intensity 80%					Intensity 40%				
Sample			TCOD removal (%)		Sample			TCOD removal (%)	
TS 1%	Control	#1	64.8	64.3					
		#2	63.7						
	35°C	#1	68.7	69.3					
		#2	69.9						
	65°C	#1	65.9	66.2					
		#2	66.4						
	90°C	#1	66.9	66.9					
		#2	66.9						
TS 2%	Control	#1	67.5	66.4	TS 2%	Control	#1	72.0	70.0
		#2	65.3				#2	68.0	
	35°C	#1	63.5	62.1		35°C	#1	69.2	70.2
		#2	60.7				#2	71.1	
	65°C	#1	60.7	59.3		65°C	#1	73.3	73.3
		#2	57.8				#2	73.3	
	90°C	#1	61.3	62.3		90°C	#1	70.0	69.5
		#2	63.2				#2	68.9	
TS 3%	Control	#1	66.9	65.8	TS 3%	Control	#1	68.1	70.2
		#2	64.6				#2	72.2	
	35°C	#1	65.5	66.0		35°C	#1	72.4	71.8
		#2	66.6				#2	71.1	
	65°C	#1	62.0	63.5		65°C	#1	67.0	69.2
		#2	64.9				#2	69.3	
	90°C	#1	65.4	65.5		90°C	#1	69.6	68.7
		#2	65.5				#2	67.8	
TS 4%	Control	#1	69.2	69.0	TS 4%	Control	#1	69.2	69.0
		#2	68.7				#2	68.7	
	35°C	#1	70.1	69.5		35°C	#1	69.1	68.6
		#2	68.9				#2	68.0	
	65°C	#1	70.7	71.6		65°C	#1	70.8	69.1
		#2	72.4				#2	67.4	
	90°C	#1	71.8	71.5		90°C	#1	70.0	70.0
		#2	71.1				#2	69.9	

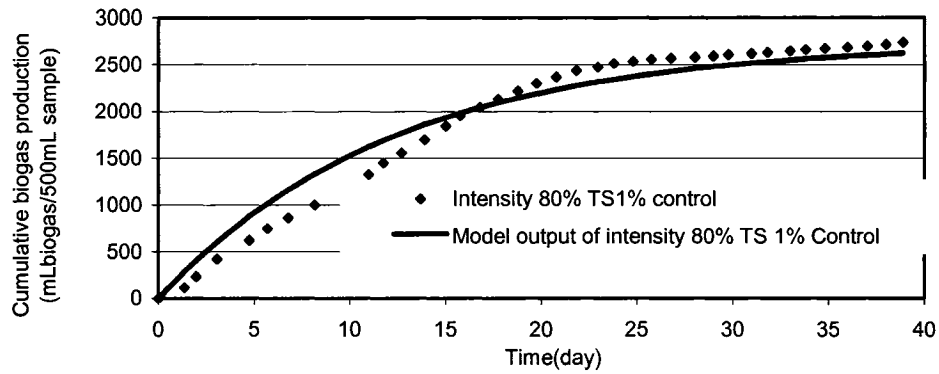
* MW intensities 80 and 40% represent MW energy input 19.47 and 9.73 J/min.

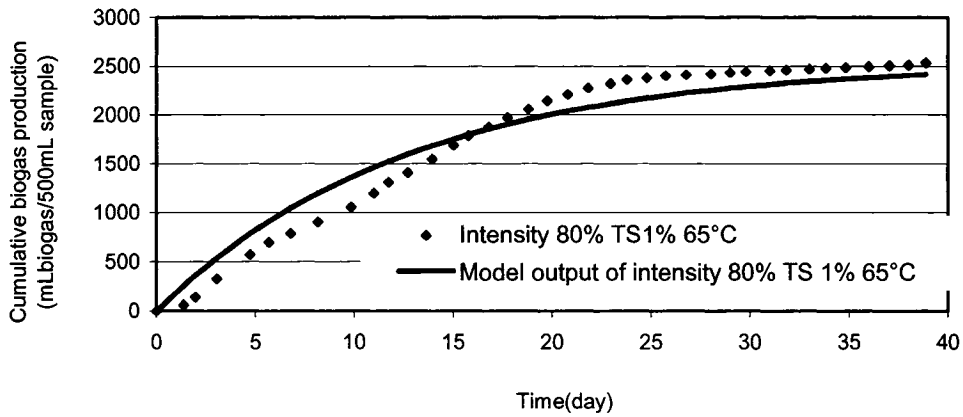
VS Removal Efficiency in Duplicated BMP Reactors

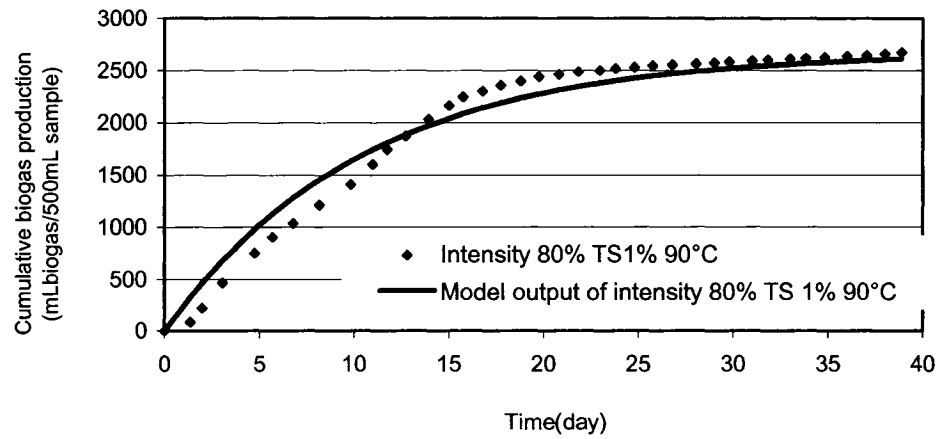
Intensity 80%					Intensity 40%				
Sample			VS removal (%)		Sample			VS removal (%)	
TS 1%	Control	#1	60.3	58.1					
		#2	55.9						
	35°C	#1	60.3	59.9					
		#2	59.4						
	65°C	#1	60.2	60.0					
		#2	59.7						
	90°C	#1	59.2	60.2					
		#2	60.5						
TS 2%	Control	#1	65.8	65.2	TS 2%	Control	#1	67.4	68.3
		#2	65.5				#2	69.1	
	35°C	#1	63.6	63.5		35°C	#1	71.4	70.4
		#2	63.3				#2	69.3	
	65°C	#1	63.0	64.2		65°C	#1	68.8	68.7
		#2	65.3				#2	68.5	
	90°C	#1	65.5	65.1		90°C	#1	66.2	66.0
		#2	64.7				#2	65.7	
TS 3%	Control	#1	68.1	67.9	TS 3%	Control	#1	67.7	68.0
		#2	67.7				#2	68.3	
	35°C	#1	66.3	66.6		35°C	#1	66.9	66.9
		#2	66.9				#2	66.9	
	65°C	#1	64.3	65.7		65°C	#1	68.2	68.8
		#2	67.0				#2	69.3	
	90°C	#1	65.6	66.9		90°C	#1	68.5	68.2
		#2	68.1				#2	67.9	
TS 4%	Control	#1	69.5	69.8	TS 4%	Control	#1	69.5	69.8
		#2	70.1				#2	70.1	
	35°C	#1	68.7	68.4		35°C	#1	67.2	65.9
		#2	68.1				#2	64.5	
	65°C	#1	68.3	67.9		65°C	#1	68.5	68.0
		#2	67.5				#2	67.4	
	90°C	#1	69.3	69.9		90°C	#1	68.9	68.9
		#2	70.5				#2	68.8	

* MW intensities 80 and 40% represent MW energy input 19.47 and 9.73 J/min.

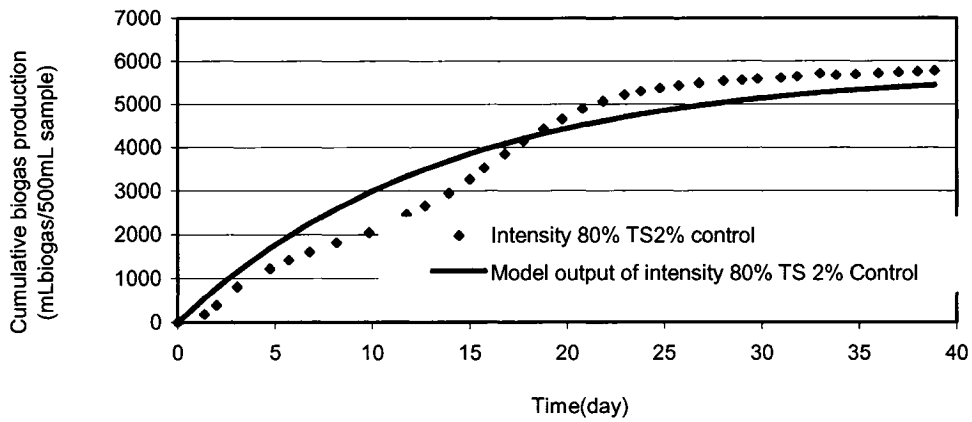
Appendix D Comparison of experimental biogas production and model output

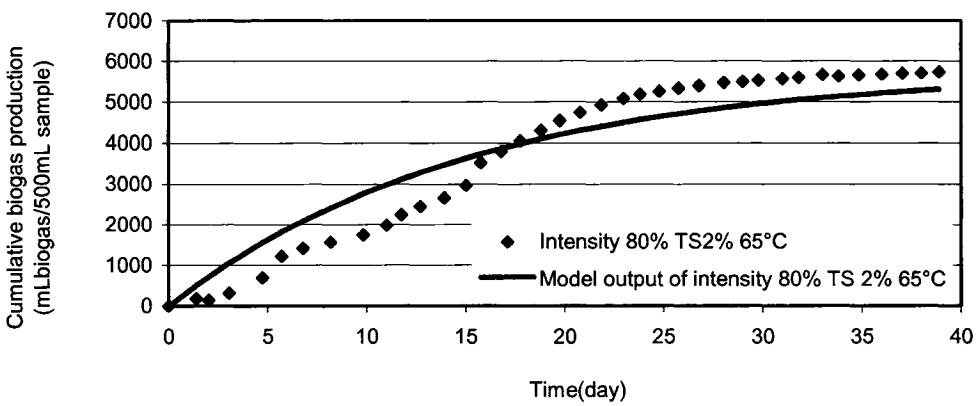


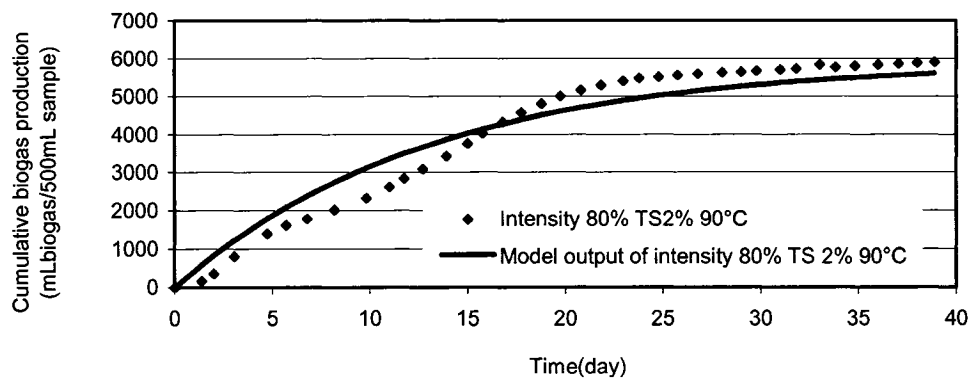




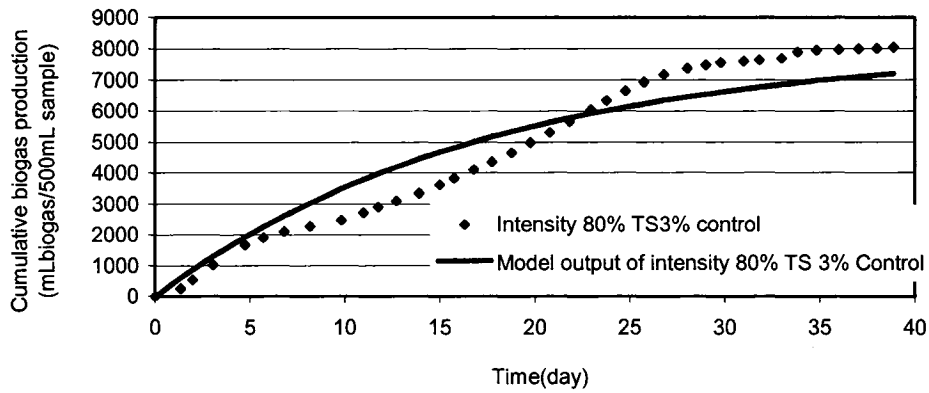
Comparison of experimental biogas production and model output for sludge at sludge concentration 1% and microwave intensity 80% (energy input 19.47J/min)

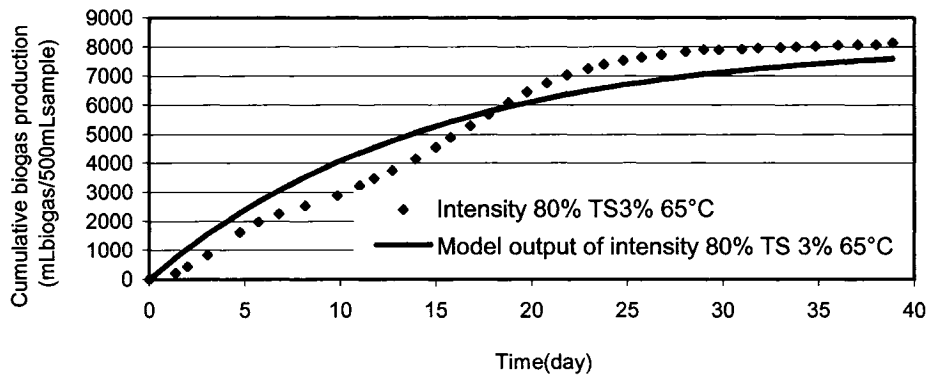


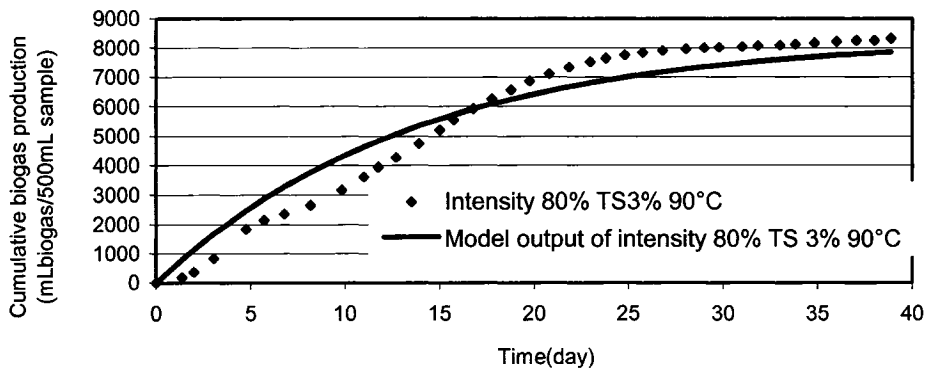




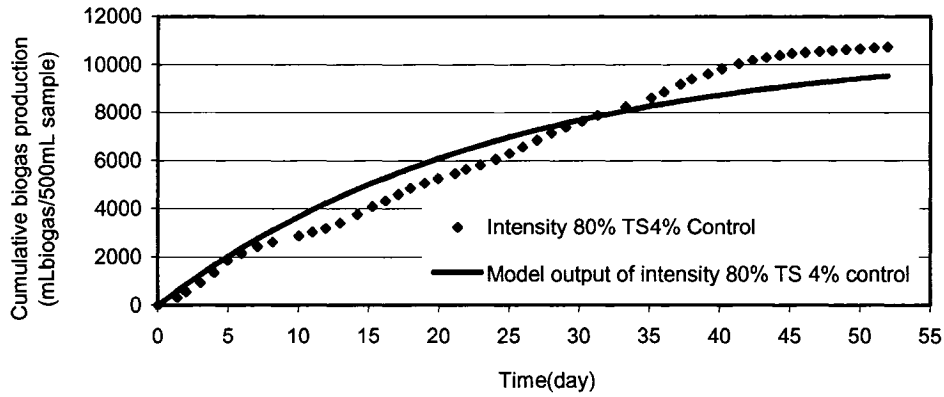
Comparison of experimental biogas production and model output for sludge at sludge concentration 2% and microwave intensity 80% (energy input 19.47J/min)

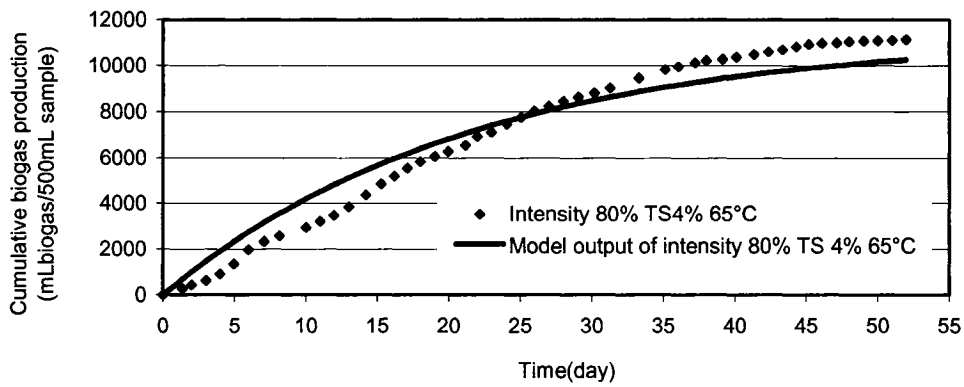


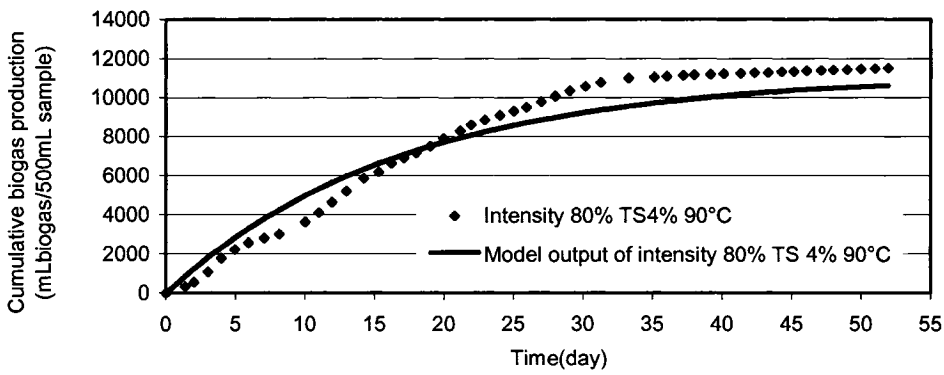




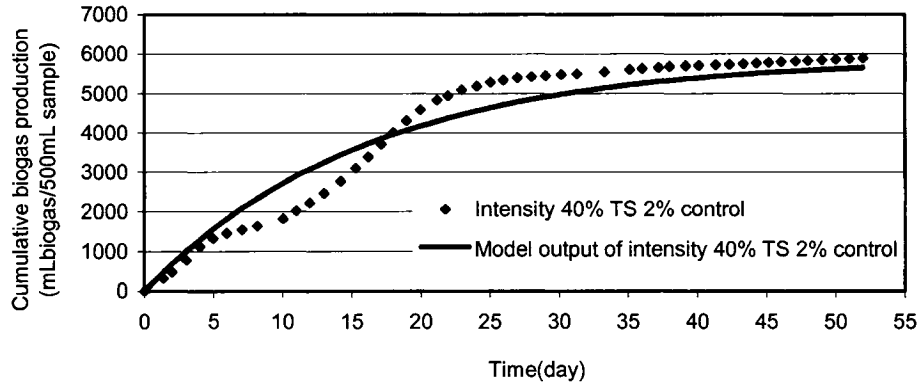
Comparison of experimental biogas production and model output for sludge at sludge concentration 3% and microwave intensity 80% (energy input 19.47J/min)

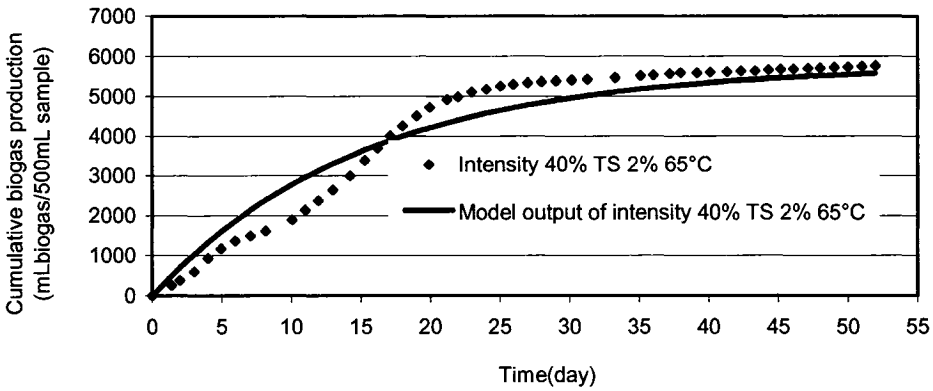


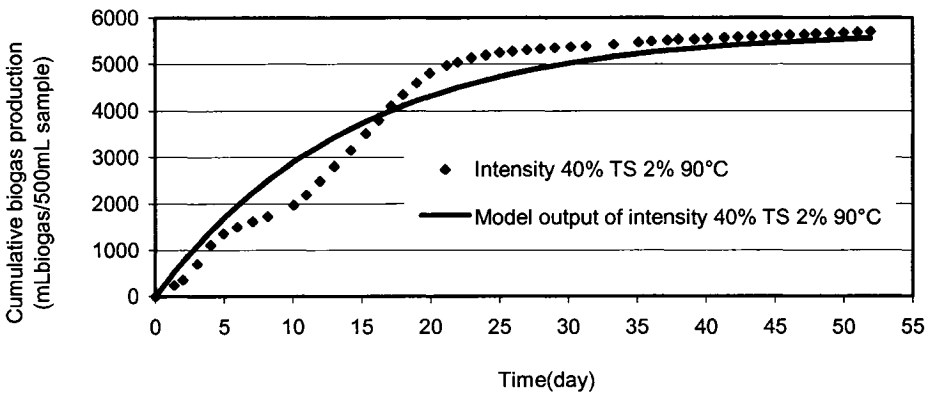




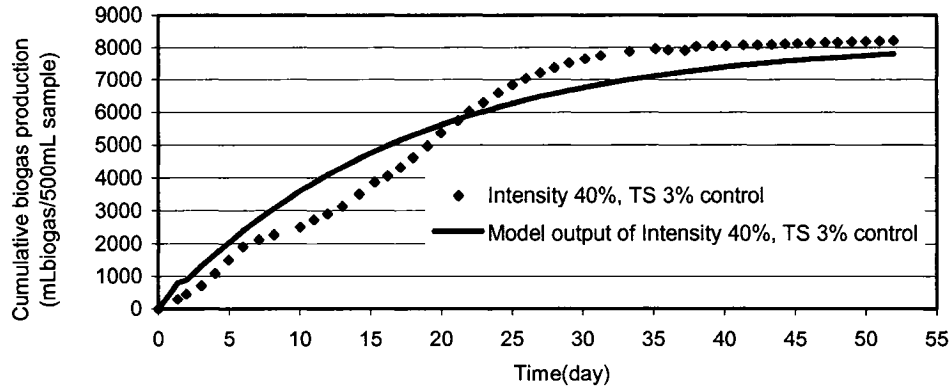
Comparison of experimental biogas production and model output for sludge at sludge concentration 4% and microwave intensity 80% (energy input 19.47J/min)

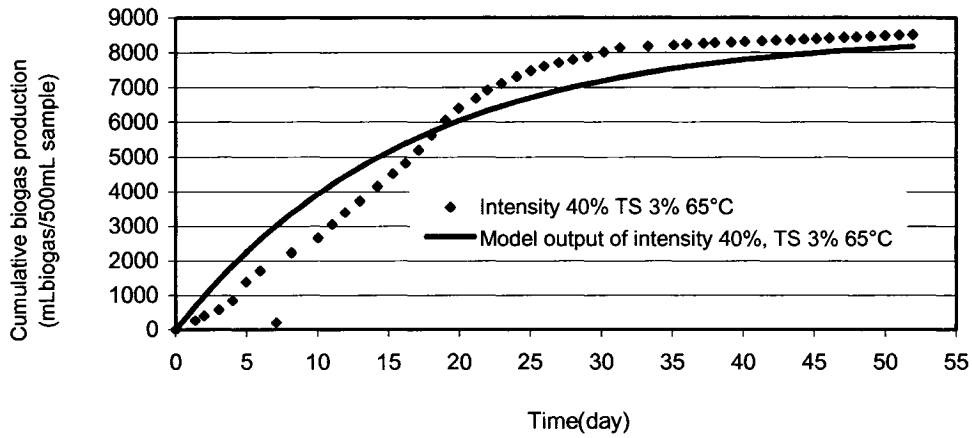


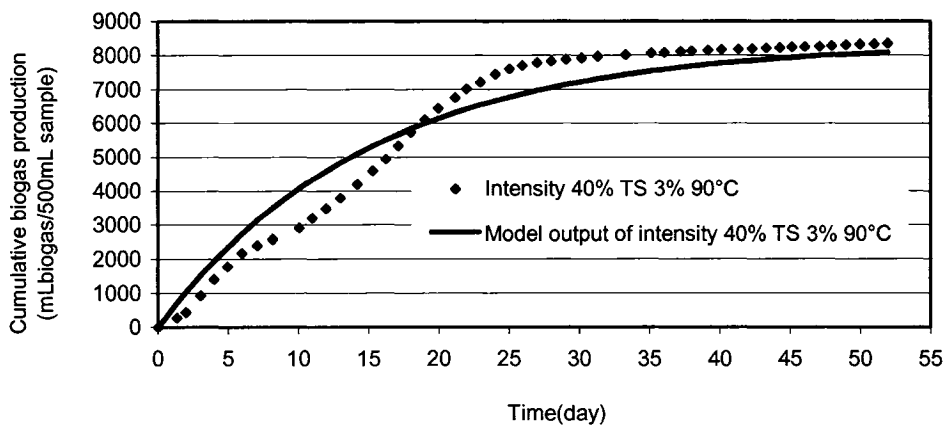




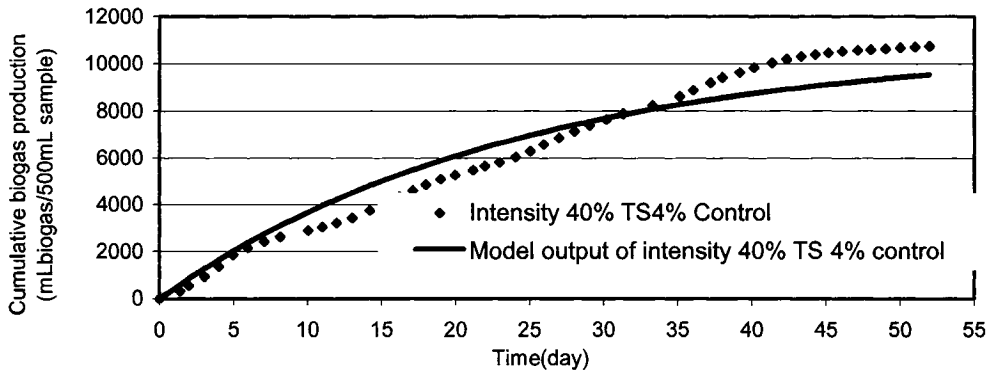
Comparison of experimental biogas production and model output for sludge at sludge concentration 2% and microwave intensity 40% (energy input 9.73J/min)

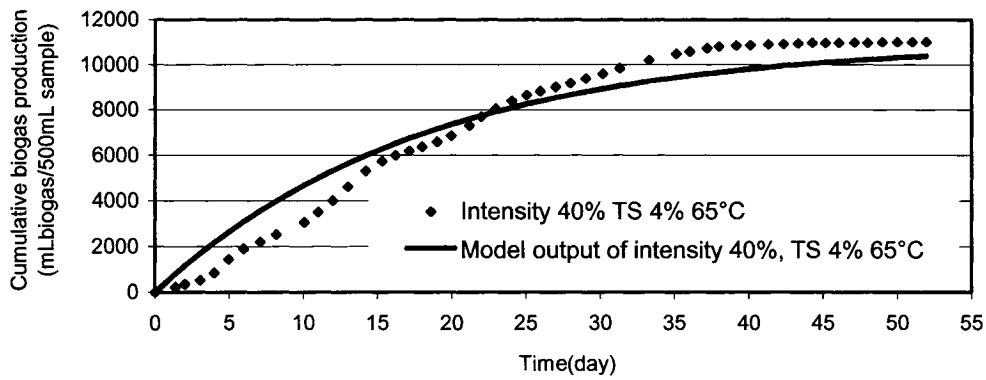


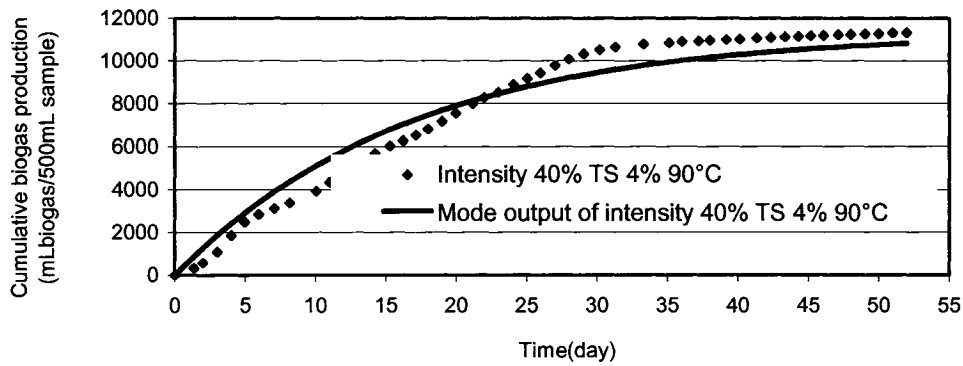




Comparison of experimental biogas production and model output for sludge at sludge concentration 3% and microwave intensity 40% (energy input 9.73J/min)







Comparison of experimental biogas production and model output for sludge at sludge concentration 4% and microwave intensity 40% (energy input 9.73J/min)