NOTE TO USERS

STEAM-EXPLOSION PRETREATMENT OF MUNICIPAL SLUDGE TO ENHANCE ANAEROBIC DIGESTION

by

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B.Eng. (Environmental Engineering)

School of Engineering of Antioquia, 2002

A thesis submitted to

The Faculty of Graduate Studies and Research

In partial fulfillment of the requirements

For the degree of

Masters of Applied Science

Department of Civil and Environmental Engineering

Carleton University, Ottawa

The Master of Applied Science Program in Civil and Environmental Engineering is a joint program with the University of Ottawa, Administrated by the Ottawa-Carleton Institute for Civil and Environmental Engineering

Your file Votre référence
ISBN: 0-494-06789-6
Our file Notre référence
ISBN: 0-494-06789-6

ABSTRACT

This thesis presents results for the steam-explosion pretreatment of sludge, which is a promising alternative for enhancing anaerobic digestion by solubilizing organics before digestion. The steam-explosion process consists of the application of high-pressure steam (150-600 psi) at high temperature (180-260°C) in a reaction vessel. The sludge is release through a small orifice causing an explosion that further aids the disintegration of the organics.

In this study, samples containing a mixture of thickened waste activated sludge (TWAS) and anaerobically digested sludge cake (biosolids) and samples of biosolids from the City of Ottawa wastewater treatment facility were treated at different steam-explosion conditions and anaerobically digested in batch and semi-continuous flow reactors at mesophilic temperature. The effect of pretreatment on the TWAS was estimated from the digestion of the TWAS/Biosolids mixture and the biosolids alone.

Results of this study show that the steam-explosion solubilizes the organics present in the sludges, which concomitantly enhanced the subsequent anaerobic digestion. For example, pretreatment at 300 psi of TWAS/biosolids mixture and biosolids alone increased the degree of solubilization (SCOD/TCOD) from 7 to 41% and by 3 to 35%, respectively. Batch digestion of the TWAS/biosolids mixture after treatment at 300 psi resulted in a 43% increase of biogas yield over the control and the biosolids treated at the same pressure resulted in a 69% increase biogas yield over the control. Digestion in semi-continuous reactors was very stable even at the relatively low SRT of 8-days, which indicated that the organics solubilized during pretreatment at 300 psi were easily converted to biogas during the digestion without signs of inhibition. Additionally, biogas production of samples pretreated at 300 psi in the semi-continuous reactors also showed an improvement over the controls for both the TWAS/biosolids mixture and the biosolids.

ACKNOWLEDGEMENTS

I would like to express my most sincere gratitude to my supervisors Professors Wayne Parker and Kevin Kennedy for their generosity in sharing their knowledge with me and for their great insights and invaluable guidance through the course of this work.

I wish to thank Francisco Aposaga and Marie Jose Tudoret for the technical support in the laboratory. I also offer many thanks to my fellow students for providing help, encouragement and sharing which made my studies an enjoyable experience. Special thanks to my husband Nicolas for his constant support through the study.

Special thanks are owed to Bruce Holbein and Hua Wu Liu at the Super Blue Box Recycling Corporation (SUBBOR) for facilitating the steam-explosion apparatus and for providing the technical support.

The financial support provided by the City of Ottawa wastewater treatment facility, Robert O. Pickard Environmental Center (ROPEC), is gratefully acknowledged. Special thanks to Dave Robertson and Gary Robidoux from ROPEC for their kind assistance.

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LIST OF ACRONYMS

BOD_5: 5-day Chemical oxygen demand

CHP: Combined heat and power

CST: Capillary suction time

DR_o: Degree of disintegration

DS: Dry solids

GC: Gas chromatograph

HRT: Hydraulic retention time

ISTD: Internal standard solution

MLSS: Mixed liquor suspended solids

MLVSS: Mixed liquor volatile suspended solids

MSW: Municipal solid waste

ROPEC: Robert O Pickard Environmental Center

SCOD: Soluble chemical oxygen demand

SLR: Solids loading rate

SRT: Solids retention time

SS: Suspended solids

SUBBOR: Super Blue Box Recycling Corporation

TCD: Thermal conductivity detector

TCOD: Total chemical oxygen demand

TKN: Total Kjeldahl nitrogen

TOC: Total organic carbon

TS: Total solids

TVFA: Total volatile fatty acids

TWAS: Thickened waste activated sludge

VFA: Volatile fatty acids

VS: Volatile solids

VSS: Volatile suspended solids

WAS: Waste activated sludge

WWTP: Waste water treatment plant

CHAPTER 1
INTRODUCTION

1.1 GENERAL

Anaerobic biodegradation of sludges consists of the transformation of organic compounds in the absence of oxygen, primarily to methane and carbon dioxide as well as smaller amount of biosolids. The formation of methane is a unique and attractive characteristic of the anaerobic biotrasformation, because of the economic benefit of energy recovery. For decades, anaerobic digestion has been used for the stabilization of slurries and domestic sludges. Today, anaerobic digestion is the treatment of choice for the stabilization of sludge produced in many municipal wastewater treatment plants (MWTPs). These plants produce large amounts of sludge in the primary sedimentation and activated sludge processes. Owing to the high costs of transportation and disposal of sludge, its treatment has been a subject of special consideration in order to minimize its quantity and to produce a residual sludge with reduced pathogenic microorganisms, which allows for its use for purposes such as land application and landfill cover.

The anaerobic digestion process can be divided into three major phases: hydrolysis, acidogenesis and methanogenesis. Hydrolysis consists of the transformation of organics into compounds readily available for microbial metabolism; it is the first step in the anaerobic digestion process. For some substrates, the rate of hydrolysis determines the overall process performance. The sludge produced in the activated sludge process, wate activated sludge (WAS) for example is difficult to hydrolyze and therefore difficult to degrade anaerobically; it is known to be only half as degradable as the primary sludge from primary sedimentation (Parkin and Owen, 1986). This is because the main fraction of WAS consists of microbial solids in which cell walls act as barriers towards degradation. The degree of degradation of WAS, expressed as volatile solids (VS) or chemical oxygen demand (COD)

reduction is reported to be limited to 30-50% in mesophilic anaerobic treatment (Parkin and Owen, 1986). On the other hand, anaerobic digestion is well suited for the stabilization of primary sludge, because it contains large amounts of nonmicrobial organic matter. Parkin and Owen (1986) observed COD reductions of around 65% for this substrate. This result correlates well with typical values reported in the literature which indicate 40-60% COD reduction and 40-70% VS reduction (Metcalf and Eddy, 2003). From the three major components of primary sludge (protein, cellulose and lipids), lipids have been reported to have a slow degradation rate. Hence for a sludge with a high concentration of lipids, the hydrolysis and degradation of the lipid fraction controls the degree of stabilization and slows down the overall degradation process (Parkin and Owen, 1986).

When it comes to the treatment of sludge in wastewater treatment plants, the usual pattern is that both WAS and primary sludge require treatment before leaving the plant. Owing to this, anaerobic digestion is usually carried out with a mixture of these two sludges. For each treatment plant, the mixture will contain different proportions of the sludges, according to their relative production during wastewater treatment.

1.2 STATEMENT OF PROBLEM

Slow hydrolysis and slow bacteria metabolism during anaerobic digestion result in the requirement of long digester retention times. Generally, the residence time in conventional anaerobic digestion is about 20 days. To sustain long residence times, large reactors are required and therefore a high capital investment is needed. Therefore, there is an incentive to continue research on techniques to improve the anaerobic digestion process, to achieve a higher degree of waste stabilization and to minimize capital investment and operational cost.

Presently, several pretreatment approaches have been investigated to hydrolyze organics prior to anaerobic digestion to enhance the overall anaerobic degradation process. The most common techniques used are thermal disintegration, by autoclave treatment or by

thermal hydrolysis using Cambi technology; mechanical disintegration with stirred ball mill, high-speed cutter milling, by ultrasound, or with a high pressure homogenizer and chemical disintegration with ozone application, or alkaline hydrolysis.

In general, pretreatments attempt to cause the lysis of the cell membrane to accelerate hydrolysis. However, there are other benefits of pretreatment such as the break up of large organic molecules and the transformation of the particulate substrate. Stuckey and McCarty (1984) found an increase in particle surface area, led to more sites being available for reaction after thermal treatment. Müller *et al.* (1998) reported an increase in surface area of sludge due to floc structure destruction during mechanical disintegration. Tiehm *et al.* (2002) reported the use of ultrasound mechanical forces to cause aggregate degglomeration and Kopp *et al.* (1997) reported mechanical disintegration to destroy sludge floc structures and to increase the amount of colloidal particles. This destruction of particle structure was found to lead to an increased polymer demand and adversely affect the dewaterability of sludge (Müller *et al.*, 1998).

It is clear from the literature that disintegration pretreatments cause solubilization of organics present in sludge and can enhance its subsequent anaerobic digestion. On the other hand, in most cases (except with thermal pretreatment), pretreatment resulted in reduced dewaterability of the sludge (Müller *et al.*, 1998).

The steam-explosion pretreatment of sludge studied herein, is a complementary work to the ongoing investigations aiming to enhance anaerobic digestion. Steam-explosion as a pretreatment for sludge is an evolution of a technology recently developed by SUBBOR, which has demonstrated the use of steam-explosion to enhance the anaerobic digestion of municipal solid waste (MSW). The high temperatures and pressures of steam-explosion may provide solubilization of organics present in sludges and thus enhance its subsequent anaerobic digestion. In addition, the high temperatures attained during steam-explosion

treatment may improve dewaterability of sludge, as has been the case with other thermal pretreatments (Martin and Potts, year unknown; Haug, 1978; Pinnekamp, 1989).

1.3 RESEARCH OBJECTIVES

The main purpose of this experimental study was to assess the effect of steam-explosion technology on the solubilization of organics and ultimately on the degradability of municipal sludge, thickened waste activated sludge (TWAS) and biosolids, under mesophilic anaerobic conditions. The effect of the steam–explosion treatment on the dewaterability of the digested sludge was also evaluated.

The specific objectives of the investigation included:

- Characterization of TWAS/biosolids mixture and biosolids prior to steam-explosion treatment.
- Assessment of the degree of solubilization of TWAS/biosolids mixture and biosolids that could be achieved during steam-explosion treatment.
- Comparison of the anaerobic digestion performance of sludge treated under different steam-explosion conditions, using batch reactors at mesophilic temperature.
- Evaluation of the impact of HRT on the anaerobic digestion of the pretreated sludge using semi-continuous flow reactors.
- Estimation of the effect of pretreatment on TWAS based on the results obtained for the TWAS/biosolids mixture and the biosolids.
- Determination of the effect of steam-explosion pretreatment on the dewaterability of digested sludge.

1.4 SCOPE OF THE INVESTIGATION

The ability of a steam-explosion pretreatment to enhance the anaerobic digestion of TWAS/biosolids mixture and biosolids was evaluated using streams produced at ROPEC, which processes the wastewater of the city of Ottawa, ON. The effect of different steam-explosion conditions were evaluated and compared. The experiments were carried out in two main phases. In the first phase, exploded sludge was digested at mesophilic anaerobic conditions in batch reactors. Based on the results of phase one, the best treatment condition was selected. In phase 2, sludge that was generated under the best steam-explosion condition, as determined from phase 1, was digested in semi-continuous flow reactors where their performance at different retention times was evaluated.

1.5 THESIS OUTLINE

In *Chapter 2* a brief description of the anaerobic digestion process and some relevant parameters for the evaluation of digestion performance is presented. It also gives an overview of the relevant research findings encountered during the literature review for some of the sludge disintegration mechanisms recently investigated to improve anaerobic degradation. In *Chapter 3* the experimental design as well as the materials, apparatus and analytical methods used in this investigation are presented. *Chapter 4* contains the data analysis and the experimental results are discussesed. Finally, conclusions and recommendations, based on the experimental results are presented in *Chapter 5.*

CHAPTER 2
BACKGROUND THEORY AND LITERATURE REVIEW

2.1 BACKGROUND THEORY

2.1.1 ANAEROBIC BIODEGRADATION

During anaerobic stabilization, large amounts of nonmicrobial organic matter can be reduced substantially with minimal production of biomass. This is because anaerobic metabolism yields little energy for growth, thus, much of the energy in the original substrate is released as the product gases (methane and carbon dioxide) and only a small amount is converted to new cells (Parkin and Owen, 1986). Additionally a certain degree of inactivation of pathogenic microorganisms is achieved. Nevertheless, the remaining pathogen level, VS and possibly heavy metals that remain after sludge treatment, are still a concern when considering final sludge disposal alternatives such as land application (Metcalf and Eddy, 2003).

As shown in Figure 2.1 five different groups of bacteria are known to be involved in the anaerobic digestion of organics. Even though each group is responsible for a specific reaction, they all work simultaneously and depend on each other in a complex manner (Parkin and Owen, 1986). The interaction among bacterial species has been reported to significantly affect the anaerobic digestion performance (Parkin and Owen, 1996). However, to simplify the anaerobic digestion process it is usually described as a three-stage process, with each stage occurring independently. These three stages are hydrolysis, acidogenesis and methanogenesis. A summary of the various intermediate and final by-products of the anaerobic digestion of complex organics as well as the bacterial groups involved in the process.is shown in Figure 2.1.

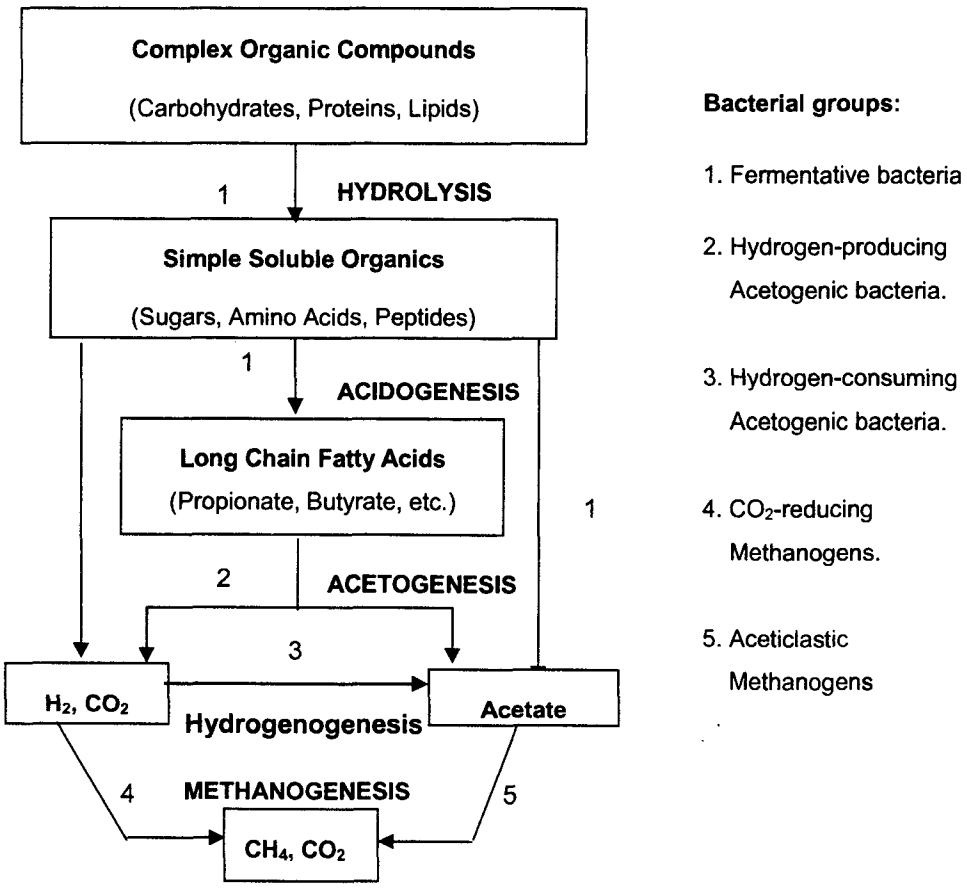

Figure 2.1 Anaerobic digestion process of complex organics

(Adapted from Parkin and Owen 1986, Duguay 2002)

Hydrolysis

Hydrolysis and liquefaction are the two processes involved in the first of the three stages of the anaerobic degradation. They consist of the solubilization of organics and the breakup of large soluble complex organic molecules, which facilitates transport across bacteria cell membranes for use as energy and nutrient sources. The solubilization of organics is a hydrolytic reaction, catalyzed by extracellular enzymes released to the medium by the bacteria (Parkin and Owen, 1996). During hydrolysis, complex organic compounds such as carbohydrates, proteins and lipids are converted to simple organic compounds such as sugars, amino acids and peptides. The hydrolysis phase is an important step in anaerobic digestion of complex organics because none of the subsequent processes required for

stabilization would succeed if this phase were not completed. In fact, the overall rate of stabilization and methane fermentation can be limited by the hydrolysis rate of complex organics (Parkin and Owen, 1986).

In particular, for the digestion of municipal sludge, the processes of hydrolysis and liquefaction are important because most of the sludge constituents are insoluble and therefore not readily available for bacterial assimilation. However, not all the organic compounds present in municipal sludge, can by hydrolyzed. Those that resist hydrolysis are referred to as nonbiodegradable or refractory components. Refractory compounds represent a major fraction of municipal sludge ranging from 35 to 40% up to as high as 70 to 80% of the VS (Parkin and Owen, 1986).

The two different sludges usually produced during wastewater treatment have different characteristics that make them more or less anaerobically degradable. Primary sludge contains mainly three VS components: carbohydrates, protein and lipids, with carbohydrates being the major component. Hydrolysis of protein and cellulose is relatively rapid, whereas lipid degradation is much slower. Lipid degradation is incomplete even when high VS degradation has been achieved, thus the hydrolysis of lipids generally controls the degree of primary sludge stabilization. In addition to the composition of the sludge, the particle size, i.e. surface area available for reaction, is also important in controlling the degradation rate of primary sludge (Parkin and Owen, 1996). WAS is particularly difficult to hydrolyze because its main fraction consists of microbial solids in which cell walls act as barriers towards hydrolysis of organics that lie inside the cell. The remaining fraction of WAS which contains mainly protein can be easily hydrolyzed to its constituent amino acids.

Hydrolysis reaction of organic molecules

The hydrolysis reaction consists of the substitution of water, or a form of water such as hydroxide ion, for another atom in an organic compound forming an alcohol derivative as one product. Water is added to the organic compound across a covalent bond, breaking the original bond. The hydrolysis reaction of an organic molecule is presented in Figure 2.2

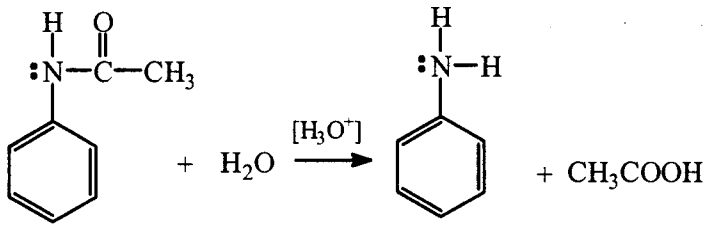

Figure 2.2 Hydrolysis reaction of an organic molecule

Source: www.organic/hydrolysis/hydrolysis.htm

Overall, hydrolysis is the degradation of an organic compound by inserting water, resulting in the formation of a new covalent bond with OH. The overall reaction may be summarized as:

$$RX + H_2O \rightarrow ROH + HX$$ **Equation 2-1**

Hydrolysis can be catalyzed by acids (activated by H_3O^+), by water molecules (neutral medium, or base catalyzed (activated by OH^-).

Acidogenesis

The second stage of anaerobic digestion is carried out by fermentative bacteria, which use the small molecules resulting from hydrolysis as a carbon source and in smaller proportion as an energy source. Similarly to the hydrolysis process, this phase involves transforming the organics into a different form, but no stabilization is achieved. Stabilization only occurs

when organics are transformed into energy but in this phase only an insignificant portion of the organics are used as an energy source. In this phase, organics are fermented to long chain organic acids, sugars, amino acids, and eventually to smaller organic acids such as propionic acid, butyric acid and valeric acid (Parkin and Owen, 1986). Because of the production of these acids, the name given to this phase is acidogenesis and the responsible microorganisms are called acid-producing bacteria.

Some of the acid-producing bacteria can oxidize organics without passing electrons to an organic acceptor in which case electrons are transferred to hydrogen ions, forming molecular H_2, which is released to the gaseous phase. If molecular hydrogen is not formed, reduced organic compounds such as butanol, ethanol, lactic acid and succintic acid are produced. Some of the hydrogen-producing bacteria also utilize volatile acids larger than acetic acid, as well as other reduced organic compounds released by other bacteria, to produce acetic acid, CO_2 and H_2. Therefore, when hydrogen-producing bacteria are active, the production of acetate is maximized while the production of reduced end products is minimized (Parkin and Owen, 1996). If the production of hydrogen ceases, the non-methanogenic phase results in insignificant reduction in COD because all electrons released in the oxidation of organics are passed to organic acceptors, which remain in the medium. On the other hand, when hydrogen is produced and passes from the liquid to the gaseous phase, the energy content of the liquid is reduced and therefore the COD is reduced (Parkin and Owen, 1996).

The collective activity of the hydrogen-producing bacteria is called hydrogenogenesis. The combined groups of hydrogen-producing bacteria and acid-producing bacteria are referred to as nonmethanogenic bacteria and their combined metabolism results in the formation of formic acid, acetic acid, CO_2 and H_2.

Methanogenesis

The third stage of the anaerobic degradation process consists mainly of the conversion of acetic acid into methane, which is insoluble in water and readily separates from the sludge in the biogas that leaves the system. Almost all the energy from the liquid is recovered in the methane (Parkin and Owen, 1996). Carbon dioxide is also produced and either escapes as gas or is converted to bicarbonate alkalinity. This phase is called the methanogenic phase and it is carried out strictly by anaerobic bacteria. This type of bacteria is very selective, and not any substrate can supply their energy. Only few a substrates including formic acid, acetic acid, and hydrogen are believed to serve as energy sources for methanogens (Parkin and Owen, 1986). Two distinct groups of bacteria have been recognized to produce methane. One group, known as the aceticlastic methanogens obtains its energy from the oxidation of acetate. The second group, known as the hydrogen utilizing methanogens, oxidize molecular hydrogen and obtain energy from this reaction (Parkin and Owen, 1996). However, aceticlastic methanogens are known to be the major precursors of methane. Approximately 72% of methane formed in anaerobic digestion of sludges comes from fermentation of acetate according to the following reaction (Parkin and Owen, 1986):

$$CH_3COOH \rightarrow CH_4 + CO_2$$ **Equation 2-2**

The remaining 28% of methane results from the reduction of carbon dioxide from organic acids by hydrogen utilizing methanogens or CO_2-reducing methanogens, using hydrogen as the energy source, as shown by the following reaction:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$ **Equation 2-3**

Formic acid has also been recognized to be utilized as substrate to produce methane. However, Parkin and Owen (1986) suggested this may be because it breaks down easily to produce hydrogen and carbon dioxide.

Requirements for optimal anaerobic digestion

Generally, the relationship among the microbial consortia that carries out the anaerobic digestion process is unstable. Therefore, in order to operate an anaerobic digester in optimum conditions, the operational parameters that interfere with the microbial environment must be kept under strict supervision and control. In effect, poor results of anaerobic digestion are usually a consequence of the lack of knowledge of the process fundamentals by plant operators. The fact that a broad knowledge regarding digestion microbiology is required has caused a loss of credibility in anaerobic digestion systems. However, as the microbiology is now better understood, anaerobic digesters have been more easily operated and hence widely used for many municipal and industrial applications (Parkin and Owen, 1986).

The parameters most commonly used for conventional anaerobic digestion monitoring are biogas production, gas composition and the sludge solids content in the influent and effluent of the reactor. These parameters are usually monitored daily to evaluate the digestion performance. The methane content of the reactor biogas can also be used as indicator of inhibition, although when methane production decrease significantly it may be already too late to bring the reactor back to normal operational conditions. Typical values of some monitoring parameters for digestion of primary and secondary sludge are presented in Table 2-1. Additionally other parameters such as pH, volatile fatty acids and ammonia concentrations are measured regularly to assess the possibility of inhibition in the reactor. The optimum and extreme operational conditions for conventional anaerobic digestion of sludges are presented in Table 2-2.

Table 2-1 Typical values for mesophilic anaerobic digestion of WAS and primary sludge[a].

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

a. Source: Adapted from (Parkin and Owen, 1986 and Malina and Pohland, 1992)

Table 2-2 Environmental factors affecting anaerobic digestion.[a]

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

a. Source: Adapted from Metcalf and Eddy, 2003 and Parkin and Owen, 1986)

2.1.2 DEWATERING

Dewatering is used to reduce moisture content of sludge and biosolids. Conventional mechanical dewatering removes free water from the sludge, which is defined as the water that escapes when the sludge particles settle under their own weight and floc water, which is the water trapped inside the flocs. Capillary water, the water that is attached to the particle lattice by capillary forces, cannot be removed by mechanical means unless extreme pressure is applied. Water chemically attached to the particles is the type of water which is

the most difficult to remove and its removal can only be achieved with chemical or thermal treatments (Metcalf and Eddy, 2003).

Table 2-3 presents typical dewatering performances for various types of sludge using two of the most commonly used dewatering techniques.

Table 2-3 Typical dewatering performances for various types of sludge using two different dewatering mechanisms.[a]

	Cake dry solids (%)	
Type of sludge	**Belt-filter press**	**Solid-bowl centrifuge**
Primary and trickling filter	23-30	20-25
Primary and WAS	20-28	12-20
WAS	5-15	12-20
Anaerobically digested		
Primary	24-30	25-35
WAS	12-20	____
Primary and WAS	20-25	15-20

a. Adapted from Metcalf and Eddy (2003).

As can be observed in

Table 2-3 WAS is very difficult to dewater using traditional dewatering mechanisms. This is due to the large fraction of bound water generally present in this sludge. Good dewatering results for WAS have been reported only after thermal treatment. Pinnekamp (1989), for example, reported a thermal treatment to break down the cell structures of WAS which released internal cell water, as well as interstitial and capillary water resulting in improved dewaterability.

2.2 LITERATURE REVIEW

In the search for more efficient anaerobic digestion of sludges many techniques have been developed which focus on improving the hydrolysis process by destroying microbial cells to make intracellular organics available for degradation. Different methods including thermal, mechanical, chemical and biological treatments have been studied and have generally proved to increase the solubilization and hence the biodegradability of sludge.

This literature review contains a brief description of some of the most common sludge disintegration techniques, developed for enhancing the anaerobic digestion process (Table 2-4). The second part of this section presents a summary of the findings of some specific pretreatment techniques. The studies are classified according to the disintegration mechanism. The findings of these studies were summarized with attention to solubilization, anaerobic digestion performance and dewaterability of the sludge after pretreatment. The literature review is concluded with a brief discussion of some research findings. A summary of the most relevant results of each of the studies is given in Table A.1.

Hydrolysis is the process that causes the organics molecules to break down, as explained in the previous section. Molecular disintegration can also occur by applying mechanical forces that physically break molecular bonds. Both mechanisms of molecular disintegration achieve similar results. Therefore, in the following section the different pretreatment processes are all considered disintegration mechanisms whether the disintegration is performed by mechanical forces or by a hydrolysis reaction.

Table 2-4 Description of various disintegration techniques.

Disintegration method	Description
MECHANICAL	
Stirred ball mill	Consists of a cylindrical grinding chamber that is partially filled with grinding beads. The beads are forced to rotate by a mechanical rotor. The microorganisms are disintegrated between the beads by shear and pressure forces[a].
Lysis-thickening-centrifuge	The technique is designed to be adapted to the centrifuge at the discharge of the thickened sludge and consists of a rotor which stresses the sludge by shear forces. The extra energy required to operate this disintegration method is relatively little. However the degree of treatment improvement is very low[a].
Ultrasound	The driving force for ultrasonic disintegration is cavitation. This force is created by overpressure and underpressure generated by sound waves.[a]
CHEMICAL	
Oxidation with ozone	Disintegration of cell walls with ozone occurs by simply mixing the sludge with ozone in a reactor. In addition to cell disruption ozone reacts with refractory organic compounds to oxidize them to smaller bioavailable compounds.[a]
THERMAL	
Autoclave	Heating in autoclave at temperatures from 120 to 170°C usually for around 30 minutes.
Thermal disintegration	Rapid thermal conditioning for 20 seconds at high pressure and at temperatures of around 180 to 200°C.[b] Thermal treatment under 8 to 12 bar vapor pressure and temperatures of 130 to 170°C for 30 to 45 minutes (Cambi technology).
BIOLOGICAL	
Enzymatic treatment	Consists of the addition of specific enzymes that catalyze the degradation of organic substances.[c]

a. From Winter *et al.* (2002)

b. From Dohanyos *et al.* (1997)

c. From Barjenbruch *et al.* (2003)

2.2.1 THERMAL DISINTEGRATION

Thermal disintegration has been extensively used to improve the dewaterability of raw or digested sludge. The dry solids (DS) content of digested sludge after conventional dewatering ranges from 12 to 35% depending on the type of sludge digested and on the dewatering mechanism. For raw sludge, DS after dewatering range from 5 to 30% (Metcalf and Eddy, 2003). A significant improvement on dewatering results has been achieved with thermal pretreatment. Hirst (1972) obtained 50% DS in sludge cake after thermal hydrolysis of domestic sludge. Sheerwood and Philips (1970) observed an increase from 20 to 25% in a dewatered mixture of primary, trickling filter and digested sludge to 40 to 50% in dewatered cake from a thermally hydrolyzed mixture.

The use of thermal treatment to improve dewaterability has been traditionally performed after the anaerobic digestion process. This arrangement has had some disadvantages, including the generation of odours, and the production of a liquor that is high in organics. This liquor often had to be treated before being recycled to the treatment plant. Haug (1978) reported that if not treated, the soluble organics in the recycled liquor may increase the COD loading to the secondary facilities by up to 30%. Additionally, the requirement of energy for the thermal treatment was considered a disadvantage (Haug, 1978). Owing to these downsides, and despite the evident improvement in sludge dewaterability that was achieved with thermal treatment, almost all thermal plants built from 1938 to the 1970s were closed due to technical and odor problems as well as for economical reasons (Kepp *et al.*,1999).

To overcome some of the difficulties previously faced with thermal treatment Haug (1977) proposed the use of thermal treatment prior to anaerobic digestion. This introduced the possibility of combined treatment of solids and liquor in the anaerobic digestion process thus eliminating the problem of treating the liquor. It was also believed that odours would be reduced during anaerobic digestion. Additionally, the fact that the residual heat in the sludge

following thermal pretreatment can be used for mesophilic or thermophilic digestion and save energy used in digester heating. Furthermore, heat treatment was observed to improve biodegradability of sludge resulting in increased energy production during the anaerobic digestion.

Haug (1978) reported the effect of thermal pretreatment on the biodegradability and dewaterability of primary sludge, WAS and a 1:1 by weight mixture of these two sludges. Initially thermal treatment was performed in a 150 ml pressure reactor at 175°C. The reactor required 90 minutes to reach the operational temperature, and after that, the temperature was held for 30 more minutes. In the latter part of the study a larger reactor that was constantly mixed, and could reach the ideal temperature in only 20 minutes was used. Treatment temperatures from 100 to 225°C with 25°C intervals were considered.

Solubilization during thermal treatment was assessed by measuring soluble COD (SCOD) and ammonia concentrations after treatment, and comparing these values with those of the untreated sludges. Solubilization was found to increase with treatment temperature up to 175°C. At 225°C solubilization was found to be less than would be predicted by extrapolating data from the lower temperature treatments. A possible explanation for this was the formation of insoluble humic substances, or the presence of a fixed percentage of organics that could not be solubilized under the heat treatment. Table 2-5 presents the degree of solubilization expressed as the SCOD fraction of the total COD (TCOD) for samples after treatment at temperatures of 175 and 200°C and for untreated sludge (control), as well as the ammonia concentration of the centrate for the same samples.

Table 2-5 Degree of solubilization and ammonia concentration for control and samples treated at 175 and 200°C.

Sample	SCOD/TCOD (%)	Ammonia mg/l as N
Control	5.1	470
175°C	42.7	770
200°C	53.9	1170

To study anaerobic biodegradability, eight continuously-stirred 2-liter digesters, were maintained at 35°C and batch-fed daily to maintain a 15 day HRT. The reactors were inoculated with digested sludge from a WWTP and were fed with samples that were treated at temperatures from 100 to 225°C. Control reactors were fed with untreated sludges. The monitoring of the anaerobic digestion was conducted by daily measurements of biogas production. Alkalinity, pH, volatile acids, total and VS, and the COD in the digester effluents were also measured regularly. In most cases the results were presented as average values over a 10 day period when the digesters had reached steady-state operation, which was determined by stable COD measurements. Additionally, COD, total solids (TS) and VS of the feed sludges were measured a number of times during the experiments.

The results of the primary sludge digestion showed that thermal treatment at 175°C had no significant impact on either total biogas production or methane production for primary sludge. The performance of both the control and thermally treated fed digesters were similar, with both attaining VS and COD destruction greater than 60%, which were expected values for this type of sludge. The production of methane was reported to be close to the theoretical value of 395 ml per gram of COD destroyed at 35 °C.

On the other hand, thermal treatment at 175°C was found to have a significant impact on the digestion of WAS. For this sample, biogas production in the thermally treated digester increased 88% above the control in the first day of digestion. The increased biogas production continued for 8 days during which time the digesters with pretreated sludge were reported to be stable. During this time the pH increased 0.2 units above controls, and the effluent COD decreased by 10%. However, after 8 days, a decrease in biogas production was observed. From day 8 to 23 biogas production with pretreated sludge was only 26% greater than the control and after day 23 the biogas production was only 18% greater than the control.

From the other parameters measured during the digestion of WAS, an increase of volatile acids from nearly zero to 1000 mg/l with a corresponding decrease in pH was observed after eight days. The volatile acids concentration continued to rise and was 1500 mg/l at 23 days of digestion. After the first 15 days, the ammonia concentrations were 900 mg/l and 1450 mg/l for the control and the thermal pretreated digesters respectively. In the following days, the ammonia concentration for the controls remained almost stable, whereas for the thermally treated digester ammonia rose to 1700 mg/l after 23 days of digestion. The decreased gas production observed was not attributed to inhibition due to VFA concentrations or ammonia but to other toxic substances produced during pretreatment.

The initial inhibitory period was observed to be only temporary, with acclimation occurring after feeding about two reactor volumes. At this point the reactors started to acclimate to the feed and the biogas production again rose rapidly to reach a value that was 70% higher than the control. During the digestion of WAS treated at 135°C only a slight inhibition was noticed while no inhibition was observed after treatment at 100°C.

The digestion of pretreated WAS showed that increases in pretreatment temperature up to 175°C resulted in increased biogas production and VS destruction (after acclimation of reactors). Compared to control digesters, methane production increased by 60-70% with the 175°C pretreatment. On the other hand, pretreatment at 200 and 225°C resulted in the production of inhibitory materials that adversely affected digestion. For digesters fed with samples treated at the higher temperatures, no acclimation was observed and biogas production was only 15% of the control. The volatile acids concentrations for these digesters were reported to be as high as 4500 mg/l.

For the mixture of primary sludge and WAS pretreated at 175°C an increase of 14% in methane production over the control was observed during the 27 day run. This result was reported to be close to the value predicted by the independent studies carried out for primary and WAS which was 18%. No inhibitory effects were observed during the digestion of the primary sludge and WAS mixture.

In this study, a semi-quantitative method, known as the time-to-filter-test was used to measured dewaterability. These measurements were obtained by plotting the filtrate volume (v) against the vacuum time (t) applied divided by the volume, giving a slope (b) as follows:

$$b = \frac{v}{t/v}, \text{ therefore, } \quad b = \frac{v^2}{t} \qquad \textbf{Equation 2-4}$$

Higher values of *b* (i.e., less time required for removing a certain volume of filtrate) were indicative of better dewaterability.

The results of those dewaterability tests showed that for all samples studied, thermally pretreated sludge exhibited much improved dewaterability over the controls. Dewaterability of primary sludge was reported to improve significantly by heat treatment. The b values for

this sample increased from 0.36 before pretreatment to 0.90 after treatment at 175°C. For WAS, dewaterability was found to increase with increasing treatment temperature with 225°C being significantly better than the lower temperatures. The values of b increased from 0.05 - 0.16 to 1.26 - 7.3 after treatment at 175°C and up to 106 after treatment at 225°C. For the WAS and primary mixture dewaterability was found to be best enhanced by heat treatment at 175°C with a b value increase from 0.10 in the untreated sample to 95 with treatment. A very important observation was that subsequent digestion of pretreated sludge did not significantly alter the dewaterability.

Energy balances were performed assuming a 70% increase in biogas production for WAS treated at 175°C. It was reported that for a conventional system, with anaerobic digestion before thermal treatment, about 4.25 x 10^6 Btu/ton of sludge would be produced by anaerobic digestion. An energy input of about 1.50 x 10^6 Btu/ton of sludge was required for digester heating and another 4.50 x 10^6 Btu/ton of sludge was required for operation of the thermal treatment system. Therefore, for this system a net input of 1.76 x 10^6 Btu/ton of sludge would be required. If thermal treatment preceded digestion, improvements in degradability would increase biogas production to 7.25 x 10^6 Btu/ton of sludge. The same 4.51 x 10^6 Btu/ton of sludge would still be required for the thermal reactor and hence a net energy production of 2.75 x 10^6 Btu/ton of sludge could be achieved. For a mix of primary and WAS, assuming no increase in biogas production for the treated primary sludge, thermal pretreatment prior to anaerobic digestion was reported to result in considerably more net energy production than the conventional thermal conditioning system.

Stuckey and McCarty (1984) investigated the effect of thermal pretreatment on anaerobic digestibility and toxicity of WAS from a WWTP containing a solids concentration of 4.3% TS. Thermal pretreatment was performed in a 634 ml reactor that required 45 minutes to reach

the desired temperature, after which the temperature was maintained for one hour. The treatment was carried out at temperatures from 150-275°C with intervals of 25°C.

The thermal pretreatment was found to increase solubilization of the WAS substantially up to 175°C. However, even at low temperatures (150°C) pretreatment was reported to attain substantial solubilization of the organics present in bacterial cells, and was observed to increase biodegradation.

Anaerobic digestion experiments were conducted in serum bottles of 250 ml capacity, which were initially inoculated, buffered and kept at mesophilic or thermophilic temperature over periods of 24 and 81 days. Biogas volume and composition were monitored. Previous research by the same authors with pretreatment of WAS at similar temperatures, was reported to promote hydrolysis and split complex nitrogen polymers in to simpler more biodegradable constituents. However, at pretreatment temperatures higher than 200°C nitrogenous organic materials were found to become less biodegradable and to likely form compounds toxic to anaerobic digestion.

WAS biodegradability increased with increasing pretreatment temperature up to a maximum at 175°C. The increase in biodegradability was thought to be attributable to improved accessibility of biologically active sites after pretreatment. An increase in methane production of up to 27% over the control was observed with the pretreatment. It was noted that small changes in the solid particles structure due to pretreatment can have a significant effect on both toxicity and biodegradability.

Pinnekamp (1989) also investigated the effect of thermal treatment at temperatures from 120 to 220°C on digestibility and dewaterability of WAS from different treatment plants (with solids loading rates (SLR) variations from 0.03 to 2.0 kg of 5-day biochemical oxygen demand (BOD_5) per kg MLSS*d), primary sludge and digested sludge. The performance of

digested sludge was evaluated to assess the viability of recycling biosolids cake back to the digester to obtain extra energy production from sludge.

Thermal treatment was conducted in an autoclave at an operating pressure of around 28 bars (392 psi). The preheating time for all tests was approximately 45 minutes. Longer preheating times were found to be impractical, as only a slight increase in stabilization performance was achieved, while shorter preheating times were not feasible with the autoclave used in the tests.

It was observed that the thermal pretreatment caused solubilization of sludge constituents, especially proteins present in large quantities in the sludge were observed to solubilize. Pretreatment was also reported to notably decrease the VS content of sludge. Table 2-6 presents the volatile solids reduction of various sludge samples during pretreatment at different temperatures.

As can be observed in Table 2-6, with the exception of the excess sludge from the high loading rate activated sludge process, VS reductions during thermal treatment were significant. It can also be observed that this reduction rose significantly with increasing pretreatment temperature.

Table 2-6 Volatile solids reduction during thermal pretreatment at various temperatures.

Sample	VS reduction (%)		
	Pretreatment temperature 150°C	Pretreatment temperature 170°C	Pretreatment temperature 220°C
WAS			
SLR[a] 0.15	22	32	54
SLR 0.60	2	1	23
Primary sludge	10	13	34
Digested sludge	32	34	___

a. SLR units: kg BOD_5/kg MLSS*d

Semi-continuous digestion of WAS was performed in four 25-liter reactors that were operated at successively reduced digestion times. One reactor was set to operate with untreated sludge and the other three with sludges that were treated at different pretreatment conditions. Biogas volume was constantly monitored and VS was measured in both the feed sludge and in the digester effluents. Biogas yield was estimated using the influent VS.

The effect of pretreatment temperature on the anaerobic digestion performance, expressed as biogas yield and increase in biogas yield with respect to the controls is summarized in Table 2-7.

Table 2-7 Maximum increase in biogas yield from anaerobic digestion of different sludges when pretreated at the optimum temperature.[b]

Sludge type	Biogas yield ($l/kgVS_{infl}$)		Increased biogas yield over control (%)	Optimum pretreatment temperature (°C)
	Without pretreatment	With pretreatment		
Digested sludge	60.4	223.0	269.2	180
Primary sludge	259.0	326.6	26	170
Excess sludge:				
SLR[a] 0.03	124.7	278.1	123.0	135
SLR 0.015	314.7	546.7	73.7	170
SLR 0.60	596.8	600.0	0.5	135
SLR 2.0	234.7	334.2	42.4	135

a. SLR units: kg BOD_5/kg MLSS*d

b.From Pinnekamp (1989)

Digestion of anaerobically pre-stabilized sludge revealed that the controls had a relatively low biogas yield as was anticipated. However, the biogas yield for this sample increased significantly after pretreatment at 180°C, rising to 223 $l/kgVS_{infl}$. This was about 270% greater than the control. Therefore, it was concluded that it is possible to increase the biogas yield of anaerobically stabilized sludge by pretreatment at 180°C and obtain biogas yields as high as those achieved with pretreated raw sludges.

When investigating the effect of digestion retention time, a 20 day digestion time, corresponding to a volumetric load of 0.45 kg VS/m^3d, produced a biogas yield of approximately 360 l/kg VS_{infl}. At 10-day digestion time, the biogas yield decreased to approximately 335 l/kg and at 7.5 days (equivalent to a load of 1.5 kg VS/m^3*d) it was significantly reduced to about 278 l/kg. It was also observed that the optimum pretreatment temperature was reduced from 170 to 135°C when the retention time increased from 10 to 20 days.

It was concluded that for sludges with lower VS concentrations a higher increase in biogas yield is attainable by thermal pretreatment. Therefore, for sludges with a high VS concentration, which in any case have a high biogas yield, thermal pretreatment is not as valuable. With respect to pretreatment temperature, it was found that for raw sludges the biogas yields for pretreatment temperatures between 120 and 180°C were similar. Thus, for most of the sludges pretreatment at 120°C may be sufficient.

Solubilization was increased at pretreatment temperatures over 180°C, however, a sharp decrease in biogas production during digestion was observed. This was attributed to a possible reaction of sugars contained in the sludge with amino acids, forming compounds with similar structure to humic acids that were difficult to degrade or inhibitory.

It was concluded that, in general, thermal pretreatment increases biogas production that when combusted in a gas engine would increase electricity generation by about 40% and excess heat by some 70%. This indicated a clear economic advantage for thermal pretreatment. The excess heat for an overall system composed of thermal pretreatment, anaerobic stabilization and digester with biogas electricity generation was significantly higher than that for a system without pretreatment. Another economic benefit of thermal pretreatment was sludge pasteurization, which allows for land application of sludge thereby reducing disposal cost.

Li and Noike (1992) continued to investigate the impact of thermal hydrolysis of sludge on anaerobic digestion. In this study the effect of digestion retention time was studied. Thermal pretreatment was performed at temperatures from 62 to 175°C at durations ranging from 15 to 90 minutes on samples of WAS. The study was intended to find optimum conditions for thermal pretreatment and also for the operation of the subsequent anaerobic digestion.

In this study, the WAS was diluted before the thermal treatment to maintain a COD concentration from 13000 to 16000 mg/l. Treatment at temperatures below 100°C, was conducted in a 500 ml reactor set in a temperature controlled water bath. For this reactor the test temperature was reached in 30 minutes. Treatments at temperatures higher than 100°C were conducted in an autoclave and the temperature was held for 30 minutes. This reaction time was established after observing that at durations higher than 30 minutes, thermal treatment did not significantly increase solubilization.

It was observed that the untreated WAS was mainly composed of particulates and during pretreatment the WAS was solubilized to soluble carbohydrates, protein and lipids and to lower molecular weight compounds such as VFAs, as shown by an increase in the soluble fraction of the total concentration of each compound (solubilization ratio). The solubilization ratio was observed to generally increase as the treatment temperature was increased up to 175°C when the best solubilization results were observed. COD material balances were conducted on these components. For pretreatment at 170°C the percentage of particulates was reported to decrease from 92.1 to 50.3% of the COD and the percentages of soluble organics and VFA increased from 5 to 29% and 1.11 to 12.9% of the SCOD respectively. Table 2-8 presents the solubilization ratios for COD and the various classes of organic compounds with treatment at 175°C for 30 minutes.

Table 2-8 Characteristics of WAS pretreated at 175°C.[b]

Parameter	Control		Sample treated at 175°C for 30 min	
	Total concentration (mg/l)	Solubilization ratio (%)	Total concentration (mg/l)	Solubilization ratio (%)
COD	15090	7.9	15930	55.2
Carbohydrate	713	6.0	823	50.8
Protein	5880	4.8	5520	48.0
Lipid	738	16.6	1492	30.1
VFA[a]	166	-----	1912	-----

a. In mg/l as COD

b. Adapted from Li and Noike (1992)

As can be observed in Table 2-8 the increase in solubilization for the major classes of organic compounds in the WAS was better for carbohydrates followed by proteins and the least effect was observed for lipids. About 50% of carbohydrates, 48% of the proteins and only 30% of the lipids were found to be solubilized by pretreatment.

To asses the biodegradability of the sludge, four continuous flow reactors with a working volume of 2 liters were operated at 35°C. Before the test the innoculum was acclimated to the treated sludge for 3 months. The reactors were then operated at retention times ranging from 1.5 to 10 days. The reactors were routinely monitored for pH, volatile fatty acids (VFA), biogas production and composition, COD, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). These parameters where used to establish a

steady–state condition At each experimental retention time steady-state conditions were defined to occur when the variation of the measured parameters was smaller than 10% for a three weeks period. COD removal during digestion was greatly increased by the pretreatment. Good removal efficiencies were achieved with retention times as low as 5 day. COD removals for reactors operating at 5 day retention time with samples treated at different temperatures are presented in Table 2-9.

Table 2-9 COD removals during anaerobic digestion of thermally pretreated samples.

Pretreatment temperature (°C)	COD removal (%)
No pretreatment	28.3
120	49.7
150	54.9
170	64.3
175	59.0

From Table 2-9 it can be observed that the best COD removal efficiency (64.3%) was achieved with thermal pretreatment at 170°C. This COD removal was superior to removals normally achieved during conventional anaerobic digestion of WAS, which are reported to be a maximum of 50% (Parkin and Owen, 1986). It is also important to notice that these values were obtained at a short retention time of 5 days.

VSS degradation efficiency during digestion was observed to be better at 170°C pretreatment temperature. This was interpreted as an indication that the VSS remaining

after treatment at 170°C were easier to hydrolyze in anaerobic digestion than those remaining after treatment at the other temperatures.

The SCOD concentration in digester effluents was observed to decrease as the retention time was increased. However, for retention times higher than 5 days, no further reduction of SCOD was observed. For a 5 day retention time the SCOD concentration was reduced from 6000-9000 mg/l to 1430-1740 mg/l with higher concentrations for higher treatment temperatures. Effluent SCOD values for the control reactors were lower. However, for these reactors the influent concentration was similarly low with almost no change during treatment. The SCOD results were interpreted as an indication that almost all the soluble organic compounds produced by thermal pretreatment were anaerobically degradable and only a very small part of those were refractory organics.

At all pretreatment temperatures, the biogas yield during digestion was reported to increase as compared to the control and the methane content for all the samples was close to 70%. At a retention time of 5 days, biogas yields were reported to increase with temperature up to 170°C then slightly decrease at 175°C as shown in Table 2-10. Pretreatment at 170°C was reported to be the optimum for increasing both the anaerobic digestibility and the methane production from WAS.

Table 2-10 Biogas yields at different pretreatment temperatures at 5 days retention time.

Pretreatment temperature (°C)	Biogas yield (ml/g COD)	Biogas yield increase over control (%)
Control	108	____
120	159	47.2
150	208	92.6
170	223	106.5
175	216	100

Corresponding to the solubilization results, anaerobic digestion of the major organic compounds in the WAS, was better for carbohydrates followed by proteins and the least effect was observed for lipids. Degradation efficiencies of carbohydrate and protein were observed to increase under all pretreatment conditions. However the degradation efficiency of lipids did not significantly change with treatment at 120 and 150°C. For the untreated WAS, again degradation efficiency was better for carbohydrates, followed by proteins and the poorest result was observed for lipids. It was suggested that the carbohydrates in the control were difficult to degrade because of the composition of cells walls, which resisted degradation.

Of the 50% of carbohydrates solubilized by pretreatment almost all were completely degraded in the anaerobic digestion, which indicates that the degradability of carbohydrates was significantly improved with pretreatment. On the other hand, despite the high solubilization ratio obtained by pretreatment of proteins, a large fraction of these compounds

were found in the digester effluent. This was considered an indication that part of the soluble proteins produced during pretreatment were refractory compounds.

In general it was observed that particulates remaining after treatment were easier to hydrolyze during digestion since a higher reduction of VSS occurred with treated samples as compared to the control at all the operating SRTs, even at the shorter SRT of 1.5 days. The yield of soluble organic matter was reported to decrease with increase of retention time, while the yields of methane were observed to increase with the increase of retention time. It was also observed that the degradation efficiencies of the various classes of organic matters as well as the biogas production increased as the retention time increased at all pretreatment temperatures. However, no significant increase was observed when the retention time was longer than 5 days. Table 2-11 presents the effect of various pretreatment temperatures on the degradation of the three major organic components of WAS at different retention times.

Table 2-11 Effect of thermal pretreatment temperature on the anaerobic degradation of WAS components at different retention times.

Retention time (days)	1.5	3.0	5.0	10.0
Carbohydrates degradation rate (%)				
Control	14	18	22	26
170°C	48	62	64	60
Proteins degradation rate (%)				
Control	17	25	28	34
170°C	50	58	63	60
Lipids degradation rate (%)				
Control	19	30	35	38
170°C	62	64	65	46

From these results and from the biogas production measurements, it was concluded that the degradable organic matter in the thermally treated WAS was almost completely converted into methane at the retention time of 5 days. Another observation was that, at this retention time, COD removal efficiency was the highest and the population of methanogenic bacteria reached a maximum. Therefore, it was concluded that with pretreatment temperatures from 150 to 175°C, digestion retention time may be reduced to 5 day and still achieve high COD removal efficiencies of around 60% and obtain biogas production over 200 ml/g COD, which was about 2 times the value of the controls.

In 1995 a new process was developed by the Norwegian company Cambi to disintegrate sludge and enhance anaerobic digestion. The main purpose of the Cambi process was to minimize the amount of residual sludge and maximize biogas production during anaerobic

digestion (Kepp *et al.*,1999). Cambi is a thermal disintegration process, which utilizes high temperature and pressure to disrupt and hydrolyze sludge, producing a pasteurized, more homogeneous sludge that is more amendable to anaerobic digestion (Abraham *et al.*, 2003). Cambi technology has been used in several WWTPs in Norway, Denmark, and the United Kingdom. Additionally the stabilized sludge is claimed to be virtually free of pathogens (Kepp *et al.*, 1999).

In the Cambi process sludge passes through three pulpers before entering the hydrolysis reactors. In the pulpers the sludge is preheated to 95°C and then in the reactor the sludge is kept for a maximum of 45 minutes under 12 bar of vapor pressure and a temperature of 160 to 170°C. The steam is then released until the pressure drops to 3 bar. This sudden reduction in pressure is believed to cause cell wall disruption, due to fluctuations of the fluid contained within the cell. The released steam is use to heat the sludge in the pulpers and the remaining pressure is used to transfer the hydrolyzed sludge to a flash tank. The hydrolyzed sludge is passed through heat exchanges to reduce its temperature to approximately 38-41°C before anaerobic digestion. Hot water recovered from the heat exchangers is use as feed water to the boilers, and to preheat the sludge going into the pulpers. A diagram of the Cambi process is presented in Figure 2.3.

Abraham *et al.* (2003) carried out commissioning and re-design of a thermal Cambi hydrolysis facility in the Dublin WWTP. The hydrolysis process was preceded by sludge dewatering to reduce sludge volume and thus the capital cost of the hydrolysis reactors. The process was expected to operate at 13.5 to 15% dry solids. However, only 6 to 8% sludge solids concentration was initially attained. To overcome this problem, the sludge solids concentration was increased by mixing the hydrolyzed sludge with digested sludge. The best blend obtained was 67% digested sludge and 33% hydrolyzed sludge, by volume.

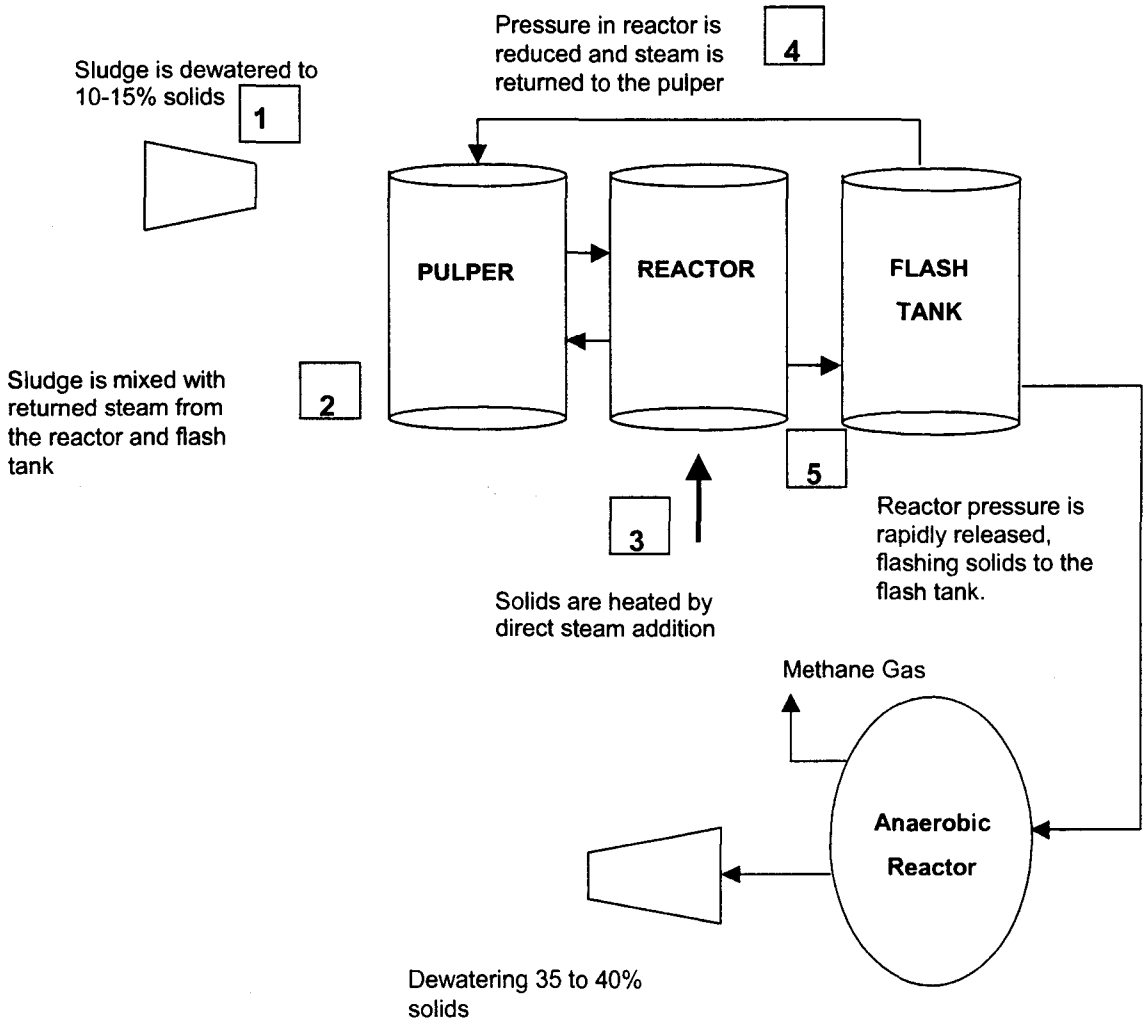

Figure 2.3 CAMBI process diagram

The sludge fed to the digesters was a mixture of primary, WAS and recycled digested sludge. Recycling digested sludge was considered advantageous because it increased the pH of the hydrolyzed sludge before digestion. The pH of the digested sludge was close to eight, with ammonia concentrations of around 2500 mg/L. The recycling of sludges also permitted a more concentrated sludge be fed to the digester, resulting in a higher solids

concentration and a more stable process. At these operational conditions of the anaerobic digester after thermal hydrolysis, a VS destruction 50% greater than conventional mesophilic digestion was observed.

Martin and Potts (year unkown) evaluated the effect of thermal hydrolysis with the Cambi technology on the anaerobic digestion process of an existing full-scale facility. Thermal hydrolysis was performed in batch reactors with preheated sludge at a concentration of 14% dry solids. Steam was applied to increase the pressure to 10 bar and the temperature to 165°C for 30 minutes. After 30 minutes the pressure was reduced to 3 bar, which consequently decreased the temperature to 135°C. The remaining pressure was used to flush the sludge to a flash tank. The released steam was recycled to preheat the incoming sludge.

Sludge from the flash tank was fed to anaerobic digesters operating at a mesophilic temperature with a retention time of 18 days at average sludge production. Before entering the digesters, the sludge was cooled in heat exchangers to around 39°C. Following the heat exchangers, dilution water was added to adjust the solids content to between 10-12% solids. Digestion performance was evaluated by daily measurements of VFA, alkalinity, ammonia, total DS and biogas composition.

In Table 2-12 various operational parameters of the digester fed with hydrolyzed sludge at 12% DS and a VS loading rate of 4.5 kg VS/m^3/d are compared with conventional sludge digestion, which generally occurs at 6% DS and 15 days retention time and thus has a lower VS loading rate of 2.8 kg VS/m^3/d. Higher loading rates resulted in higher total nitrogen yields from protein material entering the digester. Therefore more ammonia was produced and more alkalinity in the form of ammonium bicarbonate was expected.

Table 2-12 Anaerobic digestion operating ranges for digesters fed with hydrolyzed sludge and untreated sludge.[a]

Parameter	Thermally hydrolyzed sludge digestion		Conventional sludge digestion	
	Low	High	Low	High
pH	7.4	8.4	6.5	7.6
VFA (mg/l)	2,000	6,000	200	500
VFA/ total alkalinity	n/a[b]	0.3	n/a	0.2
Methane (%)	60	n/a	55	n/a
Total ammonia (mg/l)	n/a	2,500	n/a	800
Feed solids concentration (%)	8	12	5	8
Temperature (°C)	36	39	32	38

a.From Martin and Potts (year unkown)

b.Not available

After thermal hydrolysis anaerobic digestion achieved 53% VS destruction. This value can be considered high if the sludge treated was 100% WAS and low for primary sludge. Unfortunately the type of sludge treated was not mentioned in the study. Biogas generation was improved compared to conventional anaerobic digestion, with a 20% increase in available energy.

Table 2-13 presents the biogas, the energy and the volume of the cake produced in the anaerobic digestion of thermally hydrolyzed sludge and in conventional anaerobic digestion.

Table 2-13 Available energy and daily cake volume produced in the digestion of untreated sludge and thermally hydrolyzed sludge.[a]

	Thermally hydrolyzed sludge digestion	Conventional sludge digestion	Difference between hydrolyzed and conventional sludge digestion (%)
Daily biogas generation	15,800 m^3/d	13,167 m^3/d	20 (increase)
Total available energy from daily sludge load	4,206 kW	3,505 kW	20 (increase)
Daily cake volume	75 m^3/d	110 m^3/d	32 (reduction)

a.From Martin and Potts (year unkown)

For hydrolyzed sludge a 33% solids concentration after dewatering was observed, which is compable to the maximum of 30% reported in the literature for best conditions of dewatering (Metcalf and Eddy, 2003). Additionally, the residual sludge after digestion was reported to be used for land application, which may indicate that some sterilization was achieved during pretreatment.

With regards to energy consumption it was reported that the heat required for mesophilic anaerobic digestion is provided by the residual heat from the hydrolysis process, while the steam at 11 bar required, is generated primarily by a combined heat and power (CHP) system supplemented by a dual fuel boiler that uses the biogas generated in the digestion.

Kepp *et al.* (1999) reported on the performance of the first Cambi plant, which was started in Norway in 1995. In this Cambi plant, sludge was dewatered to 15-20% DS prior to hydrolysis, and was then heated at 130-180°C for about 30 minutes at about 8 to 12 bar vapor pressure. Once the hydrolyzed sludge was transferred to the anaerobic digester, the solids concentration of digester feed was between 10-12%. The sludge viscosity was thought to change during hydrolysis, when the cell water was released. Therefore, it was reported that sludge with a 12% solids concentration handled similarly to sludge with just 5-6% solids, which allowed for higher loading rates to the digester.

The best solubilization effects for WAS were observed at treatment with temperatures between 165 and 180°C and a holding time of 10 minutes which was observed to achieved the same results as a 30 minutes holding time. Kepp *et al.* (1999) reported the solubilization results were similar to those observed by Brooks (1970). Brooks (1970) investigated thermal treatment of samples of WAS and a mixture of primary sludge and WAS, and found that at a treatment temperature of 170°C yielded 30-50% and 28-35% increases in dissolved solids for the two samples respectively. For temperatures between 175 and 200°C, only a 14 to 34% increase in dissolved solids was observed.

Compared to conventional digestion, the digestion of hydrolyzed sludge was observed to save over 50% of the digester volume because sludge with higher concentration was fed to the digester. Also the solids reduction during digestion was increased by 23%. The residual mass reduction was observed to be 50% due to improved dewaterability of the sludge.

2.2.2 MECHANICAL DISINTEGRATION

Mechanical disintegration has been reported by many authors to achieve a high degree of solubilization of sludges by physical disruption of cellular material. Also, improved anaerobic degradation of disintegrated sludges has been observed. Baier and Schmidheiny (1997) investigated the effect of ball milling and high-speed cutter milling of several types of

sludges. Both techniques were found to be effective in the solubilization of most sludges. However, ball milling showed better results than cutter milling. For aerobic and anaerobic sludges, the soluble fraction of COD (SCOD/TCOD) changed from 1- 5% in the original sludges to 47% after milling. For other residues such as distillery slops and brewery wastes however, no increase in SCOD was observed.

Ball milling had the best impact on the solubilization of WAS, with a SCOD/TCOD ratio of 20% after treatment. Aerobically digested WAS and activated sludge from extended aeration however, had SCOD/COD values of only 4 to 7% after ball milling. The lowest percentage of SCOD was obtained with anaerobically digested sludge with a SCOD/TCOD ratio of only 1 to 3% after treatment.

The high shear forces of the cutting mill were used in combination with high temperature (60 to 100°C) to generate a sludge with low viscosity. The cutting milling increased the SCOD/TCOD ratio of brewery and distillery slops by only 4%. On the other hand, the SCOD/TCOD ratio for WAS that was aged five days, rose from 8% in the original sludge up to 16% in the milled sludge. However, the solubilization effect of the cutting mill was believed to be more attributable to the high temperature rather than to the milling effect.

Anaerobic digestion experiments with ball milled sludges and control (untreated) sludges were conducted in batch reactors operated at mesophilic conditions. The digestion period was 20 days. It was observed from the experiments that pretreatment enhanced anaerobic degradation of the sludge All disintegrated samples showed identical or higher degradation of organic material measured as VS and COD destruction, compared to the controls. For most samples, COD degradation increased by a factor 1.2 to 1.5 and the net biogas production was enhanced by the same order of magnitude. Also, for the WAS, the biogas production rate during the initial 50 hours was improved by 11% after disintegration as compared to the control.

Milling was found to have a better impact on the anaerobic digestion of digested sludges than raw excess sludge. After 25 days digestion of the control samples of anaerobically digested sludge and extended aeration sludge only 4.2 and 8.2% destruction of influent VS were observed, respectively. After ball milling, the percentage of VS destroyed was doubled for both sludges and COD elimination was increased by a factor of 1.3 to 1.5 compared to the control sludges. Consequently, biogas production rose by 62% for anaerobically digested sludge and 24% for extended aeration sludge compared to controls.

An improvement in the digestion performance of WAS was also observed. VS destruction was enhanced from 38% in the control sample to 57% in the treated sludge. However, the COD elimination changed only from 51 to 53%, biogas production was enhanced only by 10% and initial rate of biogas production rose only by 11% with respect to the original sludge. A possible explanation for these results was thought to be the low rate of anaerobic digestion of cell disruption products, which was not completed within the 20 days of the experiment. Although mechanical disintegration of already stabilized sludges showed the highest beneficial degradation effect, it was stated that milling of WAS represented the highest potential for overall sludge minimization.

The energy requirements for the milling treatment were estimated from laboratory experiments. Consumption was found to be in the range of 1 to 1.25 kW per m^3 of sludge treated per day, which was considered indicative of a commercial potential, however the need for further verification prior to full scale operation was acknowledged.

Tiehm *et al.* (2001) used low ultrasound with frequencies ranging from 20 and 40 kHz to cause strong mechanical forces by cavitation. The effect of these mechanical forces on the disintegration and biodegradation of sludge were investigated. Ultrasound was applied to a sludge mixture containing 53% primary sludge and 47% WAS by weight. After 96 seconds of ultrasound treatment, a solubilization increase of more than 30% of the maximum sludge

solubilization (determined by incubation in 0.5 mol/l sodium hydroxide for 22 hours at 20°C) was achieved. On average, ultrasound treatment resulted in an increase of SCOD from 630 mg/l in the untreated sludge to 2270 mg/l after ultrasound disintegration (260% SCOD increase). SCOD increases were attributed to microbial cell disruption, whereas particle size distribution was measured to evaluate changes in particle structure. Based on a reduction in the latter parameter it was concluded that ultrasound mechanical forces, collectively with cell destruction, also caused aggregate degglomeration.

To evaluate anaerobic digestibility of the pretreated sludges, five semi-continuous flow digesters with volumes of 150 liters were operated simultaneously at mesophilic temperature. Experiments with pretreated samples were conducted at 22,16,12 and 8 day residence times and a control digester was operated at a 22 day residence time. VS destruction for the reactors operated at 22 days were 50.3 and 45.8% for the disintegrated and control sludges, respectively. Biogas production was 2.2 time higher than the control at the 22 days residence time. Biodegradation of the disintegrated sludge was observed to be stable even at the shortest residence time of 8 days.

VS destruction for reactors fed with disintegrated sludge was found to be constant at reduced retention times, even at the shortest time of 8 days. However, despite better VS destruction for the reactor fed with disintegrated sludge as compared to the control, biogas production was observed to be higher for the control at the 22 day residence time.

Müller *et al.* (1998) evaluated the effects of several mechanical disintegration technologies including ball mill, high-pressure homogenizer, ultrasound homogenizer and shear gap homogenizer on the solubilization and anaerobic digestion of WAS that contained 1-4% suspended solids (SS) and 70% VSS. Measurements of particle size distribution were carried out to describe changes in structure, while SCOD was measured to estimate cell disruption caused by the mechanical treatment. SCOD was measured after concluding that

particle size distribution analysis was not effective for determining cell disruption. The degree of disintegration (DR_o) was assesses using the specific oxygen consumption using the following equation:

$$DR_o = 1 - (OC_m / OC_u) \qquad \textbf{Equation 2-5}$$

OC_m: Specific oxygen consumption of treated sludge

OC_u: Specific oxygen consumption of untreated treated sludge

Among the disintegration technologies investigated, high degrees of cell disruption were found with the stirred ball mill, high-pressure homogenizer (400 bar) and ultrasonic homogenizer. The degree of disintegration (DR_o) for the hi-pressure homogenizer at 200 bar, the hi-pressure homogenizer at 400 bar and the stirred ball mill were 26, 40 and 43% respectively. Meanwhile, with the shear-gap homogenizer a poor solubilization performance was observed.

Anaerobic mesophilic digestion of the disintegrated sludge was carried out in 20-liter continuous flow reactors. Digestion was performed in two stages. In the first stage, sludge was digested for 2 to 7 days in fixed bed reactors. After the first digestion, the sludge was disintegrated again in a high-pressure homogenizer or was partially oxidized by ozonation and subsequently digested for 10 days in conventional digesters using suspended microorganisms. In the first phase, the specific biogas production and degradation of organic substances were observed to increase by 10 to 20% for sludge treated with the high-pressure homogenizer, compared to the untreated sludge. In the second digestion a correlation between the degree of disintegration, achieved with both the high-pressure homogenizer and ozone treatment, and the degree of degradation was observed. The performance of disintegrated sludge in subsequent anaerobic digestion showed no significant differences between sludge treated with chemical or mechanical disintegration.

As a result of a better anaerobic digestion, especially protein degradation, the concentration of ammonia was observed to increase as compared to the control and the mean value of the return flow of total Kjeldahl nitrogen (TKN) was reported to be about 20 to 30% higher than the control.

The higher degree of disintegration led to poorer dewatering results and polymer demand increased as a result of disintegration, which was considered a drawback of the technology. Dewatering experiments were conducted in a lab-scale centrifuge at 3000 rpm for 5 minutes. The SS concentration of the sludge cake were determined to evaluate dewatering performance. Table 2-14 presents the results of SS after dewatering for untreated sludge and sludge treated with different disintegration mechanisms before and during anaerobic digestion.

Table 2-14 Percentage of SS after dewatering of treated and untreated sludge before and during anaerobic digestion.

Pretreatment	SS content after dewatering (%)				
	Before digestion	After 2 days digestion	After 7 days digestion	After 12 days digestion	After 17 days digestion
Untreated sludge	7.6	7.7	7.4	7.1	6.4
Hi-pressure homogenizer (200 bar)	6.8	7.3	6.9	6.5	6.4
Hi-pressure homogenizer (400 bar)	6.8	7.1	6.5	6.5	6.4
Stirred ball mill	6.4	6.8	6.2	6.5	6.4

As for the energy consumption, the comparison of the mechanical methods was based on the specific energy required, which was calculated as the amount of mechanical energy that produced a given stress on a certain mass of sludge and thus a certain degree of disintegration. Table 2-15 presents specific energy required to achieve a certain degree of disintegration (DR_o) for three disintegration technologies.

Table 2-15 Specific energy required to achieve different disintegration degrees (DR_o) for different technologies.

Pretreatment	Energy requirement (kJ/kg)		
	DR_o= 30%	DR_o= 60%	DR_o= 90%
Hi-pressure homogenizer	800	1250	6250
Ultrasound homogenizer	1250	10000	85000
Stirred ball mill	Less than 1000	2500	60000

As can be seen from Table 2-15 the high-pressure homogenizer and the stirred ball mill were the most cost effective disintegration methods. Ultrasonic treatment required a higher amount of energy, although this method was not operated in a continuous process.

The energy yield from the improved anaerobic digestion was found to be of the same order of magnitude as the energy required for mechanical disintegration. Also, the investment for disintegration technology was considered to be compensated for by reduced digester volume and reduced cost of sludge disposal, leading to a practical use of the technology.

2.2.3 CHEMICAL DISINTEGRATION

Chemical disintegration has been widely used mostly to achieve complete stabilization of sludge and it was not traditionally considered as an alternative for upgrading existing sludge

digestion plants (Baier and Schmidheiny, 1997). However some authors have proposed the use of chemical treatment before conventional anaerobic digestion to enhance the degradation process (Mukherjee and Levine, 1992; Goel *et al.*, 2003).

Goel *et al.* (2003) investigated solubilization and mineralization of a WAS with a solids content of 2-3% at low ozone doses of 0.015-0.05 g O_3/ g TS. The effect of ozone dose and SRT, on solid degradation efficiencies during anaerobic digestion and the behavior of VFA, ammonia and inorganic solids were also investigated in continuous experiments that ran for six months. These long-term experiments allowed for the study of biomass acclimation to the ozone pretreatment. Activated sludge was prepared in the laboratory using a batch reactor of 160 liter capacity. The MLSS in this reactor was around 5000-6000 mg/l. Part of the WAS produced was treated with ozone and then fed to one digester, while the other portion was directly digested without ozone treatment.

To assess the extent of solubilization during pretreatment, VSS were measured before and after ozonation. It was estimated that ozone pretreatment solubilized around 19-37% of the solids (measured as VSS reduction) at a dose of 0.015-0.05 g O_3/ g TS. Solubilization did not vary for sludge solids concentrations ranging from 1.8 to 2.6%.

Anaerobic digestion was conducted in two reactors of 2-liter capacity which were mixed and temperature controlled at 35°C. One reactor was operated with ozone pretreated WAS and the other with untreated WAS. Initially both reactors were inoculated with sludge from a WWTP and then they were batch-fed daily after removing an equivalent volume of mixed liquor. Reactors were operated at retention times from 7 to 28 days.

VS reduction efficiencies in the digester for untreated WAS at a 28 SRT ranged from 25-35% during the six months of reactor operation. A 0.015 g O_3/g TS ozone dose achieved VS reduction efficiencies that were 10 and 30% higher than the control, at SRTs of 28 and 14 days, respectively. With an ozone dose of 0.05 g O_3/g TS the VS reduction efficiencies

improved to 59% (SRT 28 d) and 50% (SRT 14 d) with improvements over the controls of 85 and 90%, respectively. However, it was observed that 2 months were necessary before the difference between the control and ozonated samples became significant, suggesting that acclimation was necessary. At a reduced SRT of 7 days, the VS reduction efficiency for un-ozonated sludge dropped significantly from 27 to 17% whereas for ozonated sludge it was only reduced from 50 to 46%. In general, VS removal efficiencies during anaerobic digestion increased by 35-90% depending on ozone dose and the improvement of VS degradation correlated well with degree of solubilization. The observed methane production was slightly lower (10-15%) than expected based on VS removals. This was attributed to a possible loss in CH_4 recovery due to organic mineralization and change in the oxidation state of organics during ozonation.

From the other parameters measured it was observed that the total organic carbon (TOC) and VFA (expressed in terms of COD) followed almost similar trends, suggesting that most of the soluble organic matter was present as organic acids. Very high VFA concentrations in all reactors suggested inhibition of methanogens, while higher ammonia levels observed in the reactors fed with ozonated sludge correlated well with their higher degradation efficiencies.

2.2.4 DISCUSSION

The findings of the different disintegration technologies presented in the literature review are encouraging for this study. The main promising results were the good solubilization and digestion results obtained with all the thermal treatments. It is also encouraging that all the thermal treatments had a positive effect on the dewaterability of the sludge. Additionally, the energy requirements for the thermal reactors were reported to be compensated for by the additional biogas production from the enhanced digestion and the saving on the reactor heating. One more advantage of the thermal treatment observed in the literature review was

the sterilization of the sludge due to the high temperatures, which can possibly allow for its use in land application.

Mechanical and chemical pretreatments generally achieved poorer results in the anaerobic digestion of the sludge than the thermal treatments. In addition, the mechanical treatments also had a negative effect on the dewaterability of the sludge, thus additional energy was required for dewatering. Also some of the mechanical treatments require a high-energy input to achieve good solubilization.

CHAPTER 3
MATERIALS AND METHODS OF ANALYSIS

The experimental approach of this thesis was divided into four main stages: the first one included sample selection, sample preparation and sample characterization. In the second stage the samples were treated with steam-explosion with subsequent characterization to assess the effect of the pretreatment on the sludge. The third stage was the anaerobic digestion of all the pretreated samples as well as control samples in batch reactors. The fourth and final stage consisted of anaerobic digestion of the most promising pretreated sludges from stage 3 and control samples in semi-continuous flow reactors. Figure 3.1 presents a flow diagram of the experimental approach.

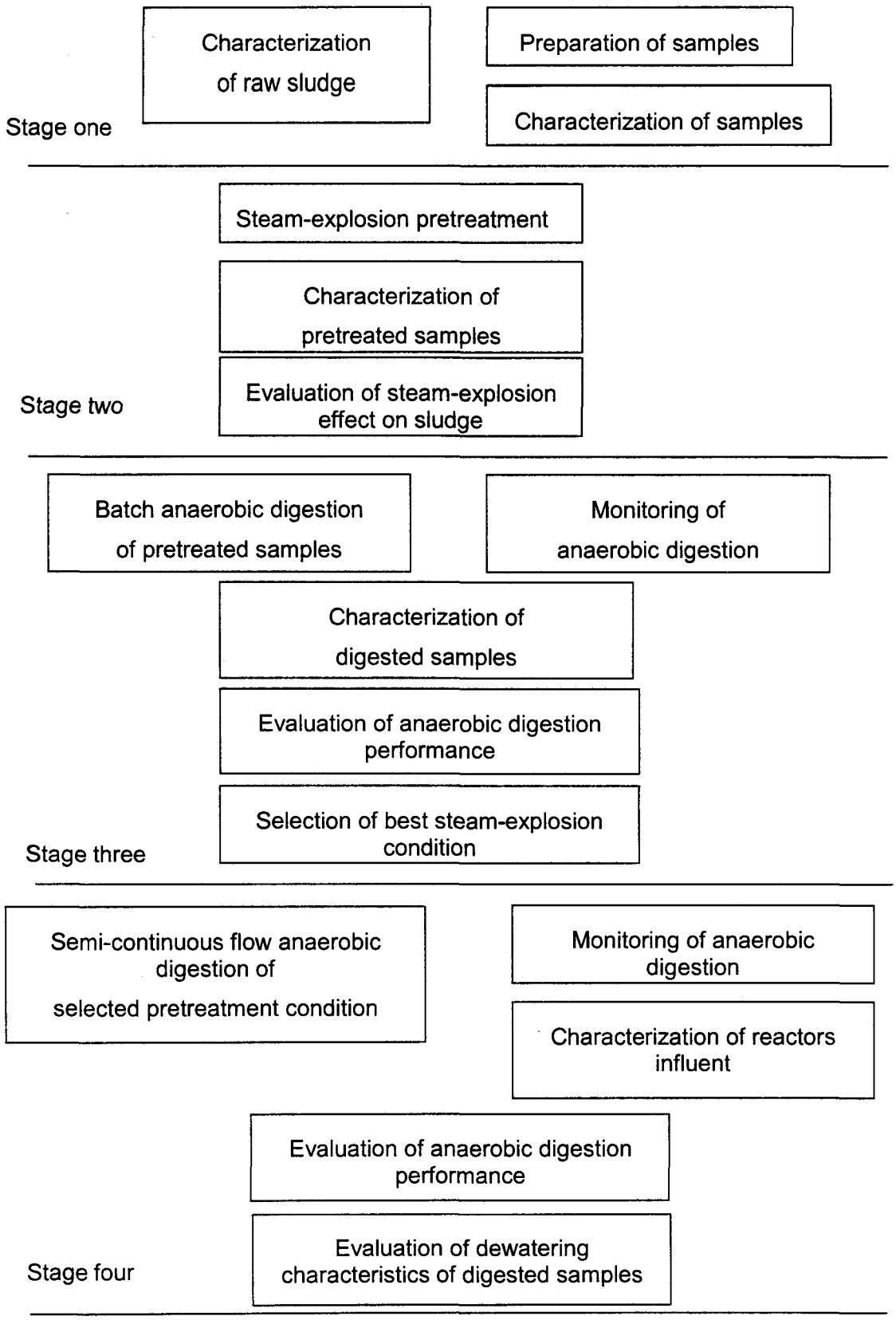

Figure 3.1 Experimental approach

3.1 SAMPLES

3.1.1 SELECTION OF SAMPLES FOR STEAM-EXPLOSION

Because WAS is typically more difficult to degrade than primary sludge and other sludges, it was of particular interest in this study to evaluate the effect of pretreatment on the WAS. The WAS was collected from ROPEC after the thickening process and had a solids concentration of 6%. However, because a minimum solids concentration of 15% was recommended for the steam-explosion pretreatment, based on the experience at the SUBBOR plant, the percentage of solids of the TWAS had to be increased before the steam-explosion treatment. To increase the solids concentration of the TWAS it was mixed with biosolids that were collected after dewatering of the anaerobic digestion effluent from ROPEC and had a solids concentration of 30%. The quantities of TWAS and biosolids to be mixed were calculated based on the total mass of solids required to prepare a given volume of mixture at 15% solids, and the solids concentration of each sample. The result was a mixture with approximately 30% TWAS and 70% biosolids by weight. The detailed calculations for mixture preparation are presented in Appendix B.

It was also of interest to estimate the improvements in anaerobic digestion of digested biosolids due to steam-explosion pretreatment. Therefore, the steam-explosion pretreatment was also carried out on samples of biosolids alone. With the results of the pretreatment effect on the biosolids, it was possible to determine the relative contribution of the biosolids to the TWAS-biosolids mixture and with that estimate the effect of pretreatment on the TWAS alone.

3.1.2 SAMPLES FOR ANAEROBIC DIGESTION

The steam applied during steam-explosion pretreatment added water to the sludge in different quantities according to the pretreatment intensity. To pressurize the sludge at 600 psi more steam was required. Therefore, more water was added to the samples of TWAS/biosolids mixture and to the biosolids when treated at this condition. Similarly the pretreatment at 150 psi required less steam and therefore the least dilution was observed in samples treated at this pressure. The dilutions observed with pretreatment at 300 psi were in between those of the other two treatment intensities as expected. The largest dilution observed after pretreatment led to a reduced solids concentration of 3%. Therefore, this solids concentration was selected to start the anaerobic digestion, since it was also appropriate for the digestion in batch reactors. Preliminary experiments with primary sludge and TWAS from ROPEC showed that at concentrations of around 6% the mixing of the reactor contents was difficult and digestion was not completed in a reasonable time. The concentration of 3% was also maintained for the anaerobic digestion in semi-continuous flow reactors. Samples with higher solids concentrations were diluted to the 3% solid concentration by adding tap water. For batch rectors the dilution was done once before adding the samples into the serum bottles. For the semi-continuous flow operation sludge was diluted regularly and stored in the refrigerator for the daily feeding of the reactors. Generally, enough sample for a two to three weeks period was prepared every time.

3.2 EXPERIMENTAL DESIGN, APPARATUS AND OPERATION

3.2.1 STEAM-EXPLOSION PRETREATMENT

The steam-explosion of the sludge samples was conducted at the SUBBOR plant using a pilot-scale reaction vessel of approximately 40 liters capacity. The steam-explosion reactor was manipulated to vary the quantity of steam applied so as to control pretreatment pressure and temperature. As shown in Figure 3.2 sludge is fed through an opening (2)

located at one side of the cooker. Once the sludge is inside the cooker (1), steam is applied through three different input-ports of the steam pipe (3) to allow for a uniform distribution of heat. Solids are heated and pressurized to the desired pressure and the conditions are maintained for 5 minutes before the pressure and solids are released through a restricted orifice (5). Pressure and temperature are monitored by several gauges located around the cooker. The release of the sludge at high pressure through the small orifice causes an explosion effect, which further disintegrates the sludge. Following the explosion, steam is released through an exhaust pipe (7) and the sludge is removed from the sludge collector (8).

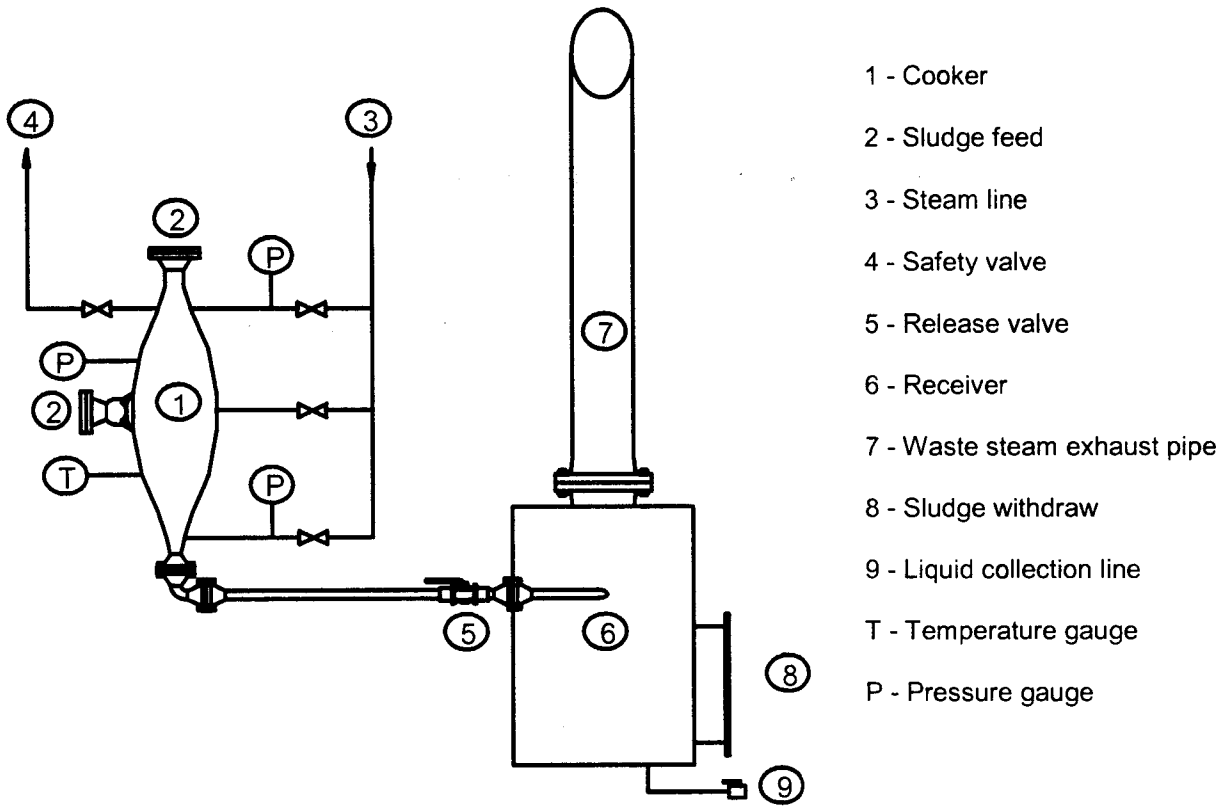

Figure 3.2 Steam-explosion apparatus

Courtesy of SUBBOR Corporation

The steam-explosion was carried out on the TWAS-biosolid mixture and also on the biosolids alone at three different intensities. Three samples of 20 liters of TWAS/biosolids mixture were exploded. Each time the steam-explosion pressure was doubled. The first explosion was done at 150 psi, the second at 300 psi and the third at 600 psi. The temperature consistently increased by 40°C as a result of each pressure increase. Hence, the temperature at 150 psi was 180°C, at 300 psi, 220°C and at 600 psi, 260°C. Three samples of 10 kg of biosolids were exploded using the same steam pressures and temperatures.

3.2.2 ANAEROBIC DIGESTION IN BATCH REACTORS

Batch anaerobic digestion was completed in Wheaton® graduated media bottles of one-liter capacity. The bottles were closed with rubber-lined septa and secured with plastic screw caps. The screw caps had an opening at the top that allowed for the sampling of biogas by inserting a needle through the rubber cap. Figure 3.3 shows the batch anaerobic reactors.

Reactors were prepared with samples of TWAS/biosolids mixture and biosolids pretreated with steam-explosion at 150, 300 and 600 psi and with corresponding samples without treatment as controls. All samples were digested in duplicate reactors. Additionally, a reactor with TWAS without pretreatment was prepared. A total of 17 reactors were prepared and digested until biogas production ceased. Table 3-1 summarizes the different samples digested in the batch anaerobic digestion. Samples used in the batch test were characterized both prior to digestion and after the digestion was completed. The reactors were not opened during digestion, only biogas measurements were performed regularly by inserting a needle through the rubber caps.

Before adding the samples to the reactors they where purged with nitrogen gas. Each bottle was kept up-side down for 5 minutes while nitrogen was being applied, after the 5 minutes the bottle was rapidly turned and the sample was added. While adding the sample nitrogen

was constantly injected to the bottle. The bottles were started with 500 ml of sample and 100 ml of primary digester effluent from ROPEC that was used as the innoculum. 1.4 g of $KHCO_3$ and 1.4 g of $NaHCO_3$ were added to each bottle to obtain a total alkalinity concentration of 4000 mg/l, as $CaCO_3$, and ensure enough buffer capacity during the digestion. The buffer capacity was intended to neutralize the acids produced during digestion to avoid acidification of the reactors. After filling the bottles they were immediately capped.

The reactors were kept in a temperature controlled environmental shaker to mix the contents and to maintain the temperature at 35°C. The reactors were only outside the shaker for small periods of time during the biogas measurements. The anaerobic digestion performance in the batch reactors was evaluated based on the biogas production and the percentage of methane in the biogas during digestion, as well as the volatile solids destruction and COD removals achieved during digestion.

Table 3-1 Samples used in the anaerobic batch reactors.

Sample	Sample conditions			
TWAS/Biosolids mixture	150 psi 180°C	300 psi 220°C	600 psi 260°C	No treatment
Biosolids	150 psi 180°C	300 psi 220°C	600 psi 260°C	No treatment
TWAS				No treatment

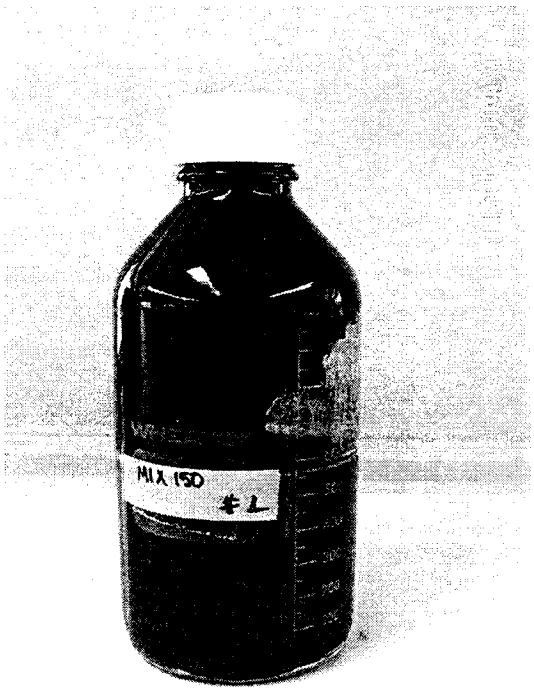

Figure 3.3 Batch anaerobic digestion reactors

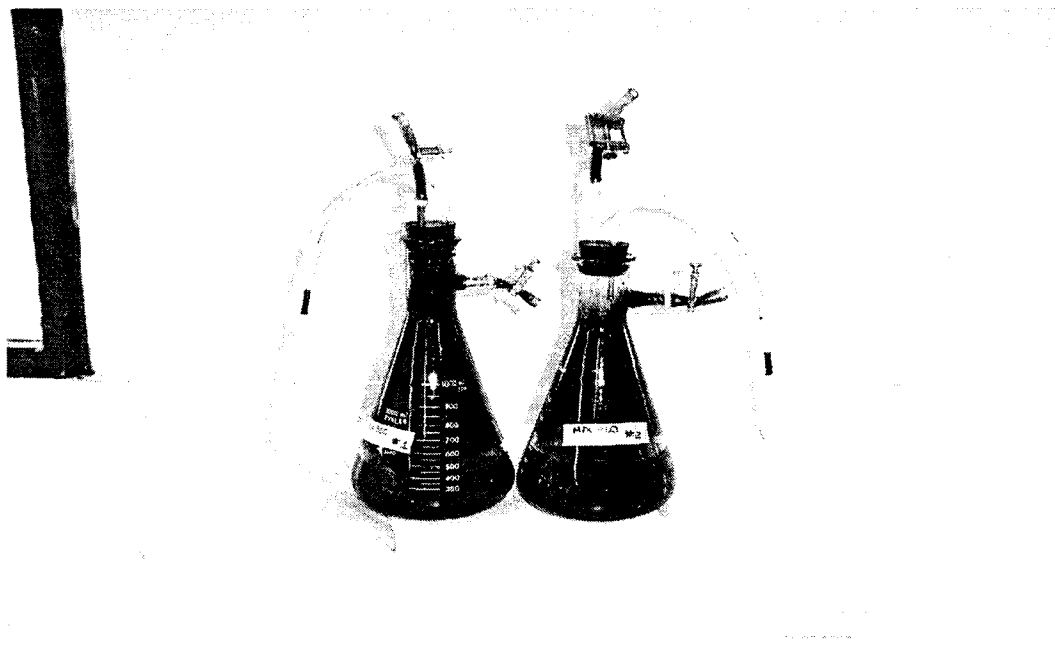

Figure 3.4 Semi-continuous flow anaerobic digestion reactors

3.2.3 ANAEROBIC DIGESTION IN SEMI-CONTINUOUS FLOW OPERATION

Side-armed 1-liter volumetric flasks were used as semi-continuous flow reactors. The upper opening of the volumetric flasks was tightly closed with a rubber stopper. Three sampling ports were built into the reactors. The side-arm was adapted as the feeding port by attaching a 5 cm long piece of tubing to it. The tubing was closed at the end with a Castaloy screw compressor clamp. The rubber stoppers were perforated to fit two tubes to make two additional ports. The openings in the rubber stoppers were made slightly smaller than the diameter of the tubes to ensure gas-tightness of the reactors. One of these ports was used to withdraw sludge from the reactors. A 5 cm long piece of tubing was attached to the end of the effluent tube and was closed with a Castaloy screw compressor clamp. The other port was connected with tubing to a SKC 231 series 1-liter tedlar bag for collection of the biogas. The tedlar bags where equipped with an inlet valve for filling and flushing and a septum fitting that was used for sample collection for biogas composition analysis. The tedlar bags were emptied daily to measure biogas production. Figure 3.4 shows a picture of the semi-continuous reactors.

Before starting the reactors they where tested for air-tightness by pressurizing the reactors with nitrogen gas and immersing them in water. A Leak-Tec® leak detector liquid was also used to test the air-tightness of the reactors but it was found to not be as effective.

Based on the results of the batch tests, the semi-continuous flow reactors were used to treat samples of the mixture (TWAS-biosolid) and biosolids that were treated at 300 psi, which was found to be the best pretreatment condition. Reactors with samples without pretreatment were used as controls and all reactors were run in duplicates. In total eight semi-continuous reactors were used.

Initially reactors were started with 140 ml of innoculum and 560 ml of sample. The reactors were initially fed only twice a week a volume of 50 ml to allow for acclimation to the feed. However, after 20 days of acclimation, biogas production was still low. Therefore the reactors where started again, adding more innoculum. 420 ml of innoculum were used and 180 ml of sample. 1.4 g of $KHCO_3$ and 1.4 g of $NaHCO_3$ were added to each bottle to obtain a total alkalinity concentration of 4000 mg/l as $CaCO_3$, and ensure enough buffer capacity during the digestion. Before adding the contents to the reactors they were purged with nitrogen gas following the same procedure as with the batch reactors. The reactors were maintained in a temperature controlled environmental shaker at 35°C. After the acclimation period, which lasted for about 30 days, the reactors were fed everyday with samples at 3% solids concentration.

The SRT, which was equal to the HRT, was maintained by removing a constant volume from the reactor and adding the same volume of feed. The sludge was extracted with a 50 ml syringe that fit tightly into the sampling port. The syringe was connected to the sampling port before opening the screw compressor clamp that kept the tubing closed, samples were withdrawn or added to the reactor as needed, and then the compressor clamp was closed before removing the syringe. The feed was kept in the refrigerator and was brought to a temperature of around 25°C on a warm water bath. Feed temperature was measured with a mercury-filled thermometer. The sample of sludge removed from the reactors was used for analysis of the various digestion monitoring parameters. The biogas produced in the digestion was collected in the tedlar bags that were permanently attached to the reactors. Every day the volume of the biogas collected in the tedlar bag was measured using a manometer.

Operation was started at a 14-day HRT, achieved by daily removing and feeding a volume of 50 ml. This retention time was considered appropriate because it is in the lower range of the typical retention times used in anaerobic digestion. Reactors were considered to be at steady-state when stabilization of the daily biogas production occurred. The reactors were kept at steady-state condition for a minimum of three times HRTs. After completing acclimation and data collection for the SRT 14 day the SRT was reduced to 8 days by increasing the volume of sludge fed and removed to a volume of 75 ml per day. The reduced SRT allowed a better assessment of pretreatment improvements because the treated sludge was expected to be more readily digested. Feeding the reactors with sludge at 3% solids concentration led to solids loading rates of 1.2 kg VS/m^3 per day at the 14-day SRT and 1.8 kg VS/m^3 per day at he 8-day SRT. These loading rates are somewhat lower than the typical loading rates generally used for full-scale operations, which range from 1.5-6.2 kg VS/m^3. However, they were appropriate for the bench-scale operation of this study.

3.2.4 EXPERIMENTAL ANALYSIS

Sludge was characterized at five different stages, before steam-explosion treatment, after the steam-explosion pretreatment, after the batch anaerobic digestion and during the semi-continuous flow digestion, where the influent and effluents of the reactors were characterized. The parameters measured to characterize the sludge before and after the steam-explosion were measured on a single occasion in duplicate analyses. To evaluate the anaerobic digestion in batch reactors, the characterization results after steam-explosion were used as the influent values and after the completion of digestion the same parameters were measured to assess the extent of the digestion. During digestion, biogas production was measured daily and biogas composition was monitored regularly. The feed sludge for the semi-continuous flow operation was analyzed several times during the digestion process to ensure a constant feed was used. The effluent of these digesters was used daily for

alternate measurements of the various monitoring parameters, while biogas production was monitored daily and biogas composition regularly. Table 3-2 presents the parameters evaluated at each stage. The parameters that were measured only once are indicated with a circle and for the other parameters the measurement frequency is indicated.

Table 3-2 Testing protocol for sample characterization and anaerobic digestion monitoring.

Parameter	Before steam-explosion	After steam-explosion	Influent batch anaerobic digestion	Effluent batch anaerobic reactors	Influent Semi-continuous flow reactors	Effluent Semi-continuous flow reactors
pH	○	○	○	○	○	2 times/week
TS	○	○	○	○	○	Once/week
VS	○	○	○	○	○	Once/week
Ammonia	○	○	○	○	○	Once/week
VFA	○	○	○	○	○	2 times/week
Alkalinity	○	○	○	○	○	2 times/week
TCOD	○	○	○	○	Once/ month	2 times/week
SCOD	○	○	○	○	Once/ month	2 times/week
Biogas production	n.a.	n.a.	n.a.	Daily	n.a.	Daily
Biogas composition	n.a.	n.a.	n.a.	3 times/week	n.a.	2 times/week
Temperature	n.d	n.d	n.d	n.d	Daily	n.d
CST	n.d	n.d	n.d	n.d	n.d	5 times

n.a. not applicable

n.d. no data

° measured once

3.2.5 ANALYTICAL TECHNIQUES PERFOMED TO CHARACTERIZE SAMPLES

Table 3-3 presents a summary of the methods and the apparatus used to measure the various parameters analyzed during the study.

Table 3-3 Analytical methods and apparatus.

Parameter	Method	Apparatus	Other equipment used
pH	Potentiometric	Fisher Accumet® pH/ion meter model 750	Kimwipes® EX-L wipes
TS		105°C Fisher Isoterm drying oven	Ceramic crucibles, graduated cylinder, Sartorius 2001MP2 analytical scale (Δ=0.1mg), desiccators
VS		550°C Thermolyne F62700 furnace	Ceramic crucibles, Sartorius 2001MP2 analytical scale (Δ=0.1mg), desiccators
Ammonia	Selective electrode	ORION model 95-12 ammonia electrode, Fisher Accumet model 750 pH/Ion meter	Magnetic stirrer, pH meter
VFA	Titration and gas chromatography.	pH meter, HP 5840A Capillary column GC,5840 terminal, 7672A autosampler	Magnetic stirrer, 50 ml burette.Brinkman model 5415 mini-centrifuge
Alkalinity	Titration	pH meter	Magnetic stirrer, 50 ml burette
TCOD		Spectrophotometer, 150°C GCA mechanical connection oven	COD digestion tubes,vortex,bottle top calibrated dispensers
SCOD		Spectrophotometer, 150°C GCA mechanical connection oven	Centrifuge, 0.45μm membrane filters, PALL science Gelman magnetic funnel, Gelman instruments 60 psi pressure/vacuum pump model 13154
Biogas production	Volumetric	Manometer built at Carleton University's environmental laboratory 350 ml capacity	1- litre Tedlar bags with rubber septum port
Biogas composition	Gas chromatography		1 ml disposable syringe
Temperature		Mercury-filled Celsius thermometer	
CST		CST apparatus	CST paper, thermometer, 10 ml plastic syringe

Sample preservation

For the characterization of the raw sludge and the samples after steam-explosion, the measurement protocol was designed so that analyses of the most unstable parameters were done first. The sample storage before each analysis was done in accordance with Standard Methods Table 1060:I (APHA, 1995). For COD analysis preservation with sulfuric acid was done when the samples had to be stored for extended periods. For the COD analysis of the anaerobic digestion effluents of the semi-continuous reactors, which were kept in the refrigerator only for one night, this procedure was not followed. The raw sludge, the sludge after steam-explosion and the prepared feed for the anaerobic semi-continuous flow digesters were kept in a refrigerator at 4°C.

Total and volatile solids

TS and VS determinations were based on Standard Methods procedure 2540G (APHA, 1995). Sludge samples were considered semi-solids samples and therefore were analyzed according to procedure 2540G.2a. Samples of biosolids were considered solid samples and were analyzed according to procedure 2540G.2b. The samples were dried over night in a drying oven pre-heated at 103 -105°C. The residue remaining after drying was cooled down for 1 hour in desiccators, weighed and then placed in a Thermolyne F62700 furnace at 550°C for 1 hour to measure VS. After ignition in the furnace crucibles were cooled down in the drying oven for half an hour and transferred to the desiccators were they where kept for an additional half hour before weighing.

The crucibles were prepared the day before analysis according to procedure 2540G.1a. and were kept in the desiccators until the time of the analysis.

For the semi-solid samples, 30 ml of sample that were measured with a graduated cylinder were used for analysis. Sludge remaining in the graduated cylinder was rinsed-off with distilled water and added to the crucibles. For the biosolids samples, 30 g were placed in the crucible for analysis. Samples were always analyzed in duplicate. The calculation of TS and VS for both the solid (Eq 3.1,3.2) and semi-solid (Eq 3.3, 3.4) samples were calculated according to the following equations, respectively.

$$mgtotalsolids/L = \frac{(A-B)\times 1000}{samplevolume, ml} \qquad \textbf{Equation 3-1}$$

A= weight of dried residue + crucible, mg

B= weight of crucible, mg

$$mgvolatilesolids/l = \frac{(A-B)\times 1000}{samplevolume, ml} \qquad \textbf{Equation 3-2}$$

A= weight of residue + crucible before ignition, mg

B= weight of residue + crucible after ignition, mg

$$\%totalsolids = \frac{(A-B)\times 100}{C-B} \qquad \textbf{Equation 3-3}$$

A= weight of dried residue + crucible, mg

B= weight of crucible, mg

C= weight of wet sample + crucible, mg

$$\%volatilesolids = \frac{(A-D)\times 100}{A-B} \qquad \textbf{Equation 3-4}$$

D= weight of residue + crucible after ignition, mg

The fixed solids fraction of the sample was calculated as the difference between the TS and the VS.

pH

The pH was measured using a glass electrode that was connected to a Fisher Accumet® pH/ion meter model 750. Before analysis, the pH meter was calibrated with VWR Scientific pH 7 solution. When samples had been stored in the refrigerator they were brought to room temperature before measurements. Samples collected from the anaerobic rectors were analyzed immediately after collection to minimize contact of the sample with the air. The electrode was rinsed between measurements with distilled water and dried with Kimwipes® EX-L wipes.

Alkalinity and VFA

A two-stage sequential titration method was used to determine bicarbonate alkalinity and total volatile acids concentration. This method developed by Anderson and Yang (1992) was proved to have a recovery of 96% from standard solutions. It allows the direct measurement of bicarbonate alkalinity, which is the most significant portion of alkalinity found in anaerobic digesters and the quantification of TVFA. The test was performed on the supernatant of the sludge, that was obtained by centrifuging the samples for 20 minutes at 10,000 rpm in a Dupont Instruments Sorvall® SS-3 Automatic centrifuge. The sludge samples were usually centrifuged the day before analysis and the supernatants were stored in the refrigerator at 4°C. Before analysis, samples were brought to room temperature, which was approximately 21-25°C. To begin the test the supernatant was placed in a small beaker and pH was measured and recorded, the sample was titrated with 0.1N sulfuric acid, prepared in accordance to the Standard Methods (APHA, 1995), to two end points, first to pH 5.1 and then from 5.1 to 3.5. During titration the sample was constantly mixed with a magnetic stirrer. The pH probe was rinsed with distilled water and dried with Kimwipes® EX-L wipes

before every measurement. The bicarbonate and TVFA concentration were derived from the dissociation equilibrium equations of bicarbonate and VFA as described by Anderson and Yang (1992).

For samples containing low VFA concentrations this titration method was found to not be accurate. Generally the readings for these samples resulted in negative values of TVFAs. Therefore, analysis of VFA were also performed using a Hewlett-Packard 5840A gas chromatograph (GC) equipped with a flame ionization detector. The GC was equipped with an injection port with a temperature of 250°C, a Chromosorb 101 packed column held at 180°C, an automatic sampler and a model 5840 integrator. Helium gas saturated with formic acid was the carrier gas running at a flow rate of 15 ml/min.

The analysis was performed on the sludge supernatant, which was prepared and stored in the refrigerator at 4°C since the previous day. Before testing, samples were brought to room temperature and centrifuged again in a Fisher micro centrifuge model 235A at 5000 rpm for 5 min, using VWR Scientific 1.7 ml plastic disposable microcentrifuge tubes. This centrifugation was performed to avoid any clogging of the GC column with solids remaining in the sample. However, only a very small pellet was generally separated from the liquid at this point. Each sample was prepared by adding 0.5 ml of supernatant from the microcentrifuging tubes and 0.5 ml of Internal Standard solution (ISTD), with a 500 μL model 4700 Eppendorf ejector pipetter, to a clean glass vial.

The GC was calibrated every time before analysis, with a standard containing 0.5 mL ISTD and 0.5 ml VFA standard mixture. The ISTD contained 2000 mg/l isobutyric acid and the VFA standard mixture contained 2000 mg/l of each acetic, propionic, and butyric acids. It was expected that the standard should read 2000 mg/L ± 50. If this concentration was not read, the standard would be run several times, usually just two times, until a value within this range was read. If too many attempts were necessary two achieve a good reading, the

laboratory technician would change the formic acid solutions of the GC. The changing of the formic acid was necessary only a few times during the 8 month period of the experiments.

Ammonia

Dissolved ammonia concentrations were determined from the supernatant of the sludge, which was obtained by centrifuging the sludge samples for 20 minutes at 10,000 rpm in a Dupont instruments Sorvall® SS-3 automatic centrifuge. Ammonia measurements were carried out using an ORION Model 95-12 ammonia gas sensing membrane electrode, connected to a Fisher Accumet® pH meter model 750 with a direct millivolt readout. The analysis was conducted according to Standard Methods 4500D procedure (APHA, 1995) and according to the instruction manual of the ammonia electrode.

Before reading the ammonia concentration, the pH of the samples was adjusted to 11-12 by adding 1 ml of NaOH to a 50 ml sample. The NaOH was prepared as directed in Standard Methods (APHA, 1995). The ammonia electrode was placed in the sample as soon as the NaOH was added and the pH was measured, to avoid the loss of ammonia to the air. During the measurements the sample was constantly mixed with a magnetic stirrer. The measurement was taken after a stable reading was obtained. After each measurement the electrode was thoroughly rinsed with distilled water.

A slope check with standard concentrations of 10, 100 and 1000 ppm was used prior to every measurement to verify proper electrode operation. A ten-fold change in concentration of a 0.1 M NH_4CL standard should represent a change in the electrode reading of –54 to –60 mV. If the reading of the standard concentration curve was correct the readings of the sample would proceed. The calibration curve was used to read the ammonia concentration of the samples by inputting the mV reading of each sample.

The electrode was kept immersed in 0.1 M NH_4CL standard solution overnight. The membrane and ammonia electrode filling solution of the electrode were changed regularly when a ten-fold change in the standard solution concentration was not giving a change in the electric potential within the expected range of –54 to –60 mV.

Total and soluble COD

A colorimetric technique was used to calculate COD concentrations, based on Standard Methods procedure 5250D of (APHA, 1995). A Coleman Perkin-Elmer spectrophotometer model 295 set at 600 nm light absorbance was used. The standard digestion solution and reagents were prepared according Standard Methods (APHA, 1995). Kimax and Pirex culture tubes (25 x 150mm) with Teflon-lined bakelite screw caps tubes were used for digestion. A volume of 10 ml of sample were combined with 6 ml of digestion solution and 14 ml of the catalyst. The sample was pipetted first into the tubes followed by the addition of the reagents using bottle top calibrated dispensers with fixed volumes. Predilution of samples was always necessary. Usually a dilution factor of 40 was used because of the high COD concentration of the sludge ranging from 20,000 to 60,000 mg/l. For SCOD determinations, dilutions of 3 to 20 times were generally used, with concentrations in the range of 300 to 2000 mg/l.

After adding the reagent to the COD tubes they were closed and the contents were mixed three times using a Fisher Genie 2 vortex. The tubes were placed in a 150°C oven for three hours, cooled in the fumehood for several hours and left in a dark cabinet overnight before reading the concentration with the spectrophotometer. The spectrophotometer was turned on one hour before readings to allow the warm-up of the apparatus. Before the readings of the samples were taken, the spectrophotometer was calibrated. Standards for the calibration curve was prepared monthly and stored in a dark cabinet.

Before reading the COD concentration, the tubes were cleaned with distilled water and dried with Kimwipes® EX-L wipes to avoid any disturbance of the reading due to dirt. Attention was also put into the selection of the tubes, all scratched tubes were discarded as well as any deteriorated caps.

For SCOD analysis the sludge samples were centrifuged for 20 minutes at 10,000 rpm in a Dupont instruments Sorvall® SS-3 Automatic centrifuge. The supernatant was filtered through GN-6 Metricel® S-Pack membrane Disc Filters with 0.45 μm pore size and used for the SCOD determinations. The same procedure used for the TCOD determinations was used for the supernatant samples. TCOD and SCOD analyses were performed in duplicates when characterizing the raw sludge and the sludge after the steam-explosion pretreatment. In the other phases of the study (batch and semi-continuous digestion), when a more intensive measuring routine had to be followed, the analysis was not duplicated.

The COD tubes were washed with a solution of sulphuric acid at 20% concentration before using them for the first time. After each analysis the tubes where left overnight in a soap solution. In the morning the tubes were washed two times in a washer machine. The first time Crystal dishwasher detergent was used and the machine rinsed the tubes two times, once with tap water and the second time with distilled water. For the second wash the machine was operated without soap followed by a rinse with tap water and a final rinse with distilled water.

The COD concentration was calculated by inputting the absorbance values of the samples in a calibration curve prepared with standards at different concentrations. The calibration curve is presented in Appendix C.

Biogas production and composition analysis

(a) Batch reactors

A customized U-tube manometer capable of measuring up to 350 ml was used for the biogas measurements of the batch digestion. A needle connected to one leg of the manometer was inserted through the rubber stopper of the batch reactor to allow the biogas to flow into the manometer. The biogas volume was calculated by measuring the height of the water column displaced by the biogas and multiplying by the transverse area of the manometer tubing. The manometer was calibrated by adding volumes from 50 to 500 ml with a syringe. It was found that the readings of the manometer needed correction by a factor of 1.2. The daily measurement of biogas were corrected using this factor. Figure 3.5 shows the manometer used for the biogas measurement with the attached needle that was used to sample the biogas from the batch reactors.

(b) Semi-continuous reactors

Biogas produced in the semi-continuous flow reactors was collected in SKC 231 series 1-liter tedlar bags. Daily biogas production was measured by pumping the contents of the tedlar bags into a manometer using a Cole Palmer easy-load pump model 75553-02 with a Masterflex speed controller. Figure 3.6 shows the biogas pumping from the tedlar bag to the manometer for biogas measurements.

Biogas composition was measured with a HP gas chromatograph model 5710A equipped with a thermal conductivity detector (TCD) using helium as the carrier gas. The GC terminal was a PC with Labview software, which received the GC signal, calculated the concentration of carbon dioxide, nitrogen and methane gas and the percentage of each gas in the sample. For the batch tests the sample for biogas composition analysis was collected before measurements of biogas production. The sample was collected directly from the media bottles with a 1-ml syringe by inserting the syringe needle through the bottle's rubber

stopper. 1 ml of sample was collected, the syringe was filled and emptied back into the bottle twice before the final sampling to obtain a more representative sample. After sampling, the needle was immediately closed with a rubber stopper and transported to the GC. Before injecting the sample to the GC, 0.5 ml of sample were wasted and the remaining 0.5 ml were injected. The analysis duration was 8 minutes per each sample. After each sample was analyzed the concentration results from the PC were recorded before proceeding with the injection of another sample.

For the semi-continuous flow reactors the samples for biogas composition analysis were collected from septum ports located in the tedlar bags that collected the biogas. The same procedure used in the batch test was followed for analysis.

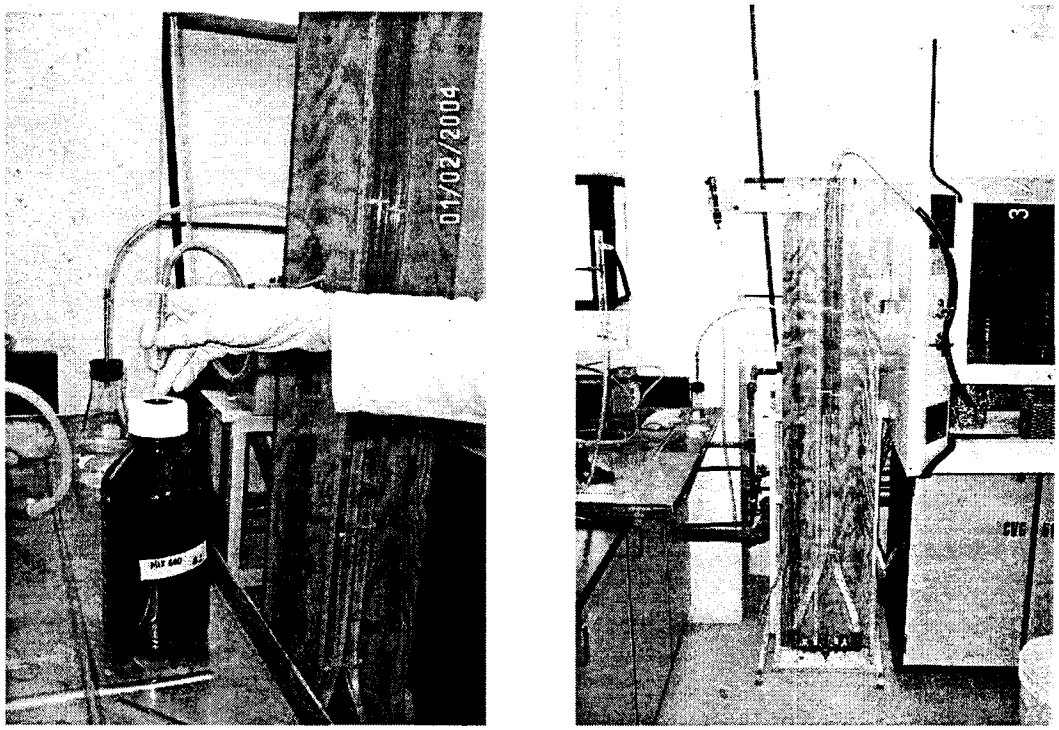

Figure 3.5 Batch reactors biogas measurements

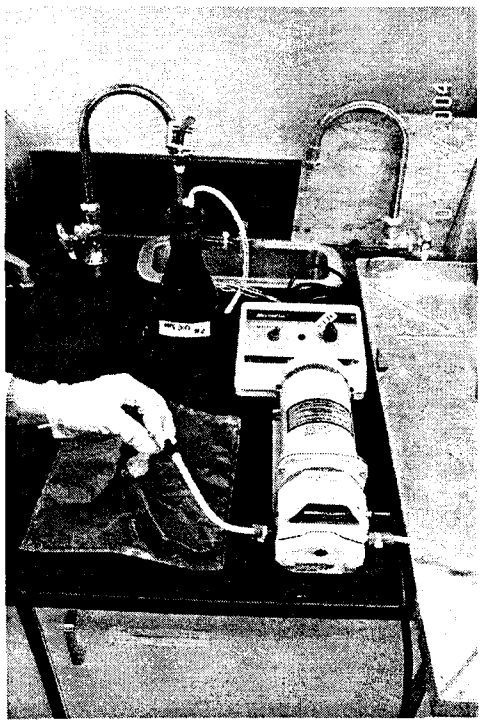

Figure 3.6 Biogas measurements from tedlar bags

Capillary suction time

The capillary suction time (CST) test was performed to assess the dewaterability of the sludge after the semi-continuous digestion based on the rate of water released from the sludge. The test was performed according to procedure 2710G of Standard Methods (APHA, 1995).

The CST test was carried out with digested sludge collected from the effluent of the semi-continuous flow reactors. Sludge was collected and stored in the refrigerator the day before the test. Before testing, samples were warmed on a warm-water bath until a temperature of 23 to 25°C was reached. Temperature was measured with a mercury-filled thermometer. Immediately after the temperature reading, 7 ml of sample were placed into the CST apparatus sludge reservoir for analysis. A digital detector connected to two electrical contacts would sense the water flow as it moved from one contact to the other. When the second contact was reached the digital detector would stop and the time, in seconds, was recorded. The apparatus was calibrated with distilled water samples and with samples of TWAS from the ROPEC treatment plant. Due to a significant variability in the test results, 5 replicates of each sample were tested each time.

CHAPTER 4
RESULTS, DATA ANALYSIS AND DISCUSSION

4.1 CHARACTERIZATION OF RAW SLUDGE AND SAMPLES AFTER STEAM-EXPLOSION

Before and after the steam-explosion treatment, all samples were analyzed for TCOD, SCOD, ammonia, pH, VFA, TS and VS. Figure 4.1 presents the solids concentrations for samples of the TWAS/biosolids mixture and the biosolids before and after steam-explosion at 150, 300 and 600 psi. It also presents solids concentrations of the TWAS and innoculum without pretreatment. The TWAS without pretreatment was analyzed for all the parameters and was used as a reference value to compare with the values that were calculated for untreated TWAS from the digestion of the biosolids and the mixture. It can be observed from Figure 4.1 that pretreatment at the different pressures added different quantities of water to the samples. Both samples, the TWAS/biosolids mixture and biosolids were significantly diluted during pretreatment. As the pretreatment intensity increased, samples were more dilute, because more steam was required to pressurize the sludge to a higher pressure.

The analyses performed after steam-explosion were carried-out immediately after the pretreatment, at which point all the samples had different solid concentrations. Due to the direct relation between solids concentration and other parameters such as TCOD, SCOD, the measurements of these parameters were normalized by dividing the values by the solids concentration of the sample. This procedure was also applied to the ammonia and VFA results. This normalization of the results allows for a more meaningful comparison between the different samples.

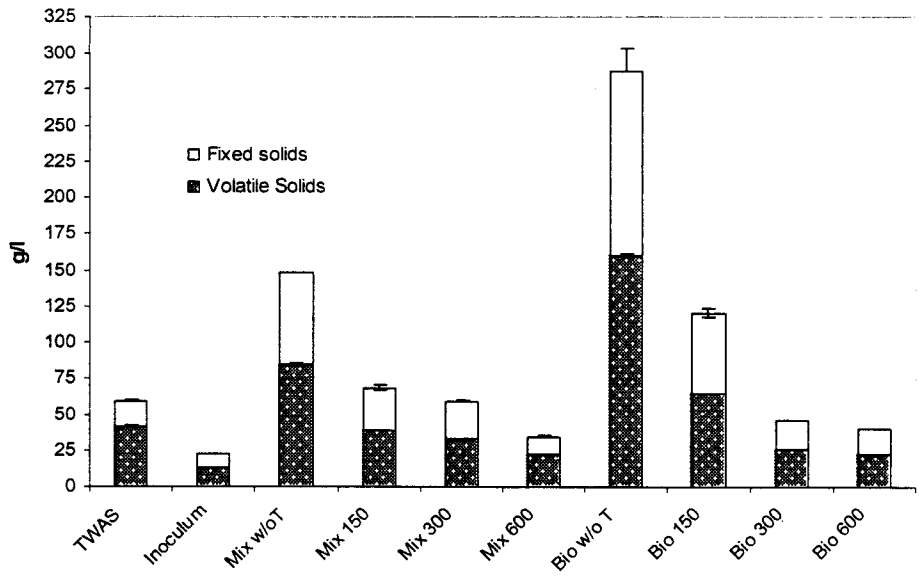

Figure 4.1 Solids concentration for untreated sludge and sludge after steam-explosion treatment.

Figure 4.2 presents the concentrations of TCOD per gram of TS for samples of TWAS/biosolids mixture, biosolids without pretreatment and after steam-explosion at 150, 300 and 600 psi. It also presents the estimated values for the TWAS calculated by removing the expected contribution of the biosolids in the TWAS/biosolids mixture. Figure 4.2 also shows the measured TCOD/TS concentration of TWAS without treatment. The error bars represent the combined error from the difference between duplicate analysis for the TCOD and the TS tests. The combined error was calculated using the following equation (Taylor, 1997).

$$\%CE = \sqrt{(\%E_{TCOD})^2 + (\%E_{TS})^2} \qquad \textbf{Equation 4-1}$$

where,

CE is the combined percentage error

E_{TCOD} and E_{TS} is the percentage error of the TCOD and TS tests, respectively.

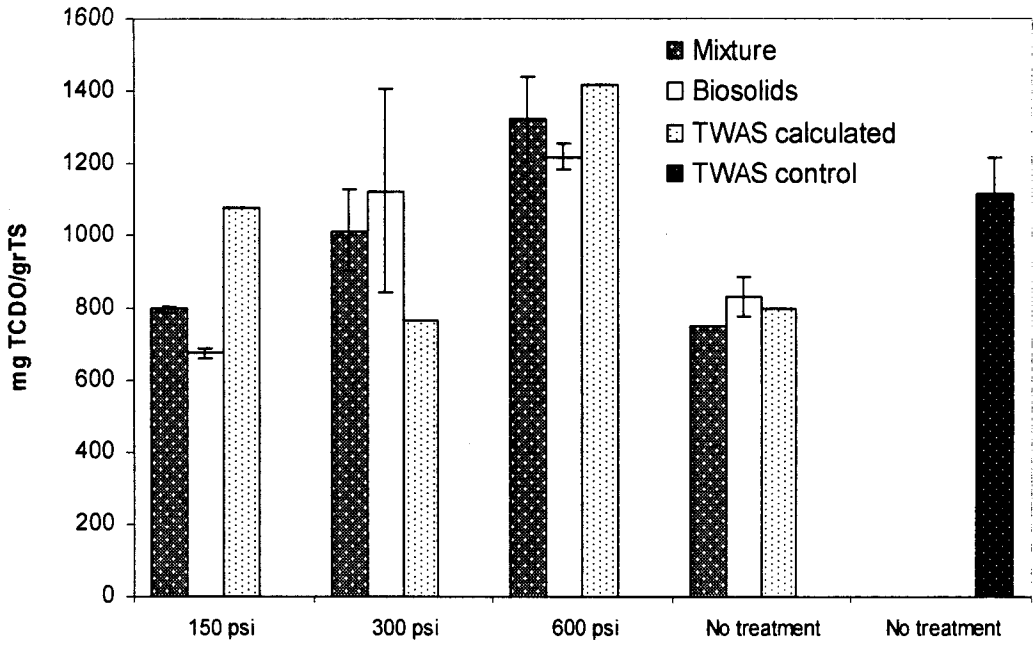

Figure 4.2 TCOD per gram TS in control samples and pretreated samples.

It can be observed from Figure 4.2 that there was some variability in the TCOD/TS ratio for both for the TWAS/biosolids mixture and the biosolids as well as in the estimated values for the TWAS. This ratio was not expected to be modified by the pretreatment and hence the ratio for all the samples should have been similar to the ratio observed for the untreated sludges. The ratio observed for the TWAS control agrees with the average TCOD and TS values reported by ROPEC for this type of sludge.[1] The average TCOD/TS ratio was around 1000±250 mg TCOD/g TS.

The relatively high ratios observed for the samples pretreated at 600 psi were attributed to a error in the preparation of the samples for the TS test. After steam-explosion the samples pretreated at 600 psi had significantly higher water content and the solids were finer, thus

[1] Personal communication from Mr. G. Robidoux, ROPEC, 2003.

the solids settled more in the buckets where they were stored. The fine solids on the bottom were not fully stirred before the collection of the samples leading to a lower measurement of solids concentration in these samples. This problem only occurred for the TS analysis and not for any other parameter. Before measurement of the other parameters, the samples were fully mixed by transferring the contents of the bucket to an empty bucket to ensure that no solids were left at the bottom of the first bucket. The TCOD analysis were performed on well mixed samples, therefore higher TCOD concentrations than would be expected from the TS measured in the samples pretreated at 600 psi were observed.

The discrepancy between the value calculated for the untreated TWAS and the TWAS control may have been partly due to the inaccuracy of the assumption involved in the calculation. The assumption was that the biosolids alone would behave similar to the biosolids in the mixture, which may not necessarily be true.

The calculations of TCOD per gram of TS of TWAS are presented in Table D.1. The following equation was used:

$$\frac{TCOD_{TWAS}}{TS_{TWAS}} = \frac{(TCOD_{mix} - R_{bio} \times TS_{bio\_in\_mix})}{TS_{TWAS\_in\_mix}} \qquad \textbf{Equation 4-2}$$

where,

$TCOD_{TWAS}$:TCOD of TWAS, mg/l

$TCOD_{mix}$: TCOD of TWAS/biosolids mixture, mg/l

$TS_{TWAS\_in\_mix} = TS_{mix} \times 0.3$ (mixture had 30% solids from TWAS, % by weight), g/l

$TS_{bio\_in\_mix} = TS_{mix} \times 0.7$ (mixture had 70% solids from biosolids, % by weight), g/l

TS_{TWAS} : TS of TWAS, g/l

$$R_{bio} = \frac{TCOD_{bio}}{TS_{bio}}$$

$TCOD_{bio}$: TCOD of biosolids, mg/l

TS_{bio}: TS of biosolids, g

It is often assumed that the SCOD represents the portion of the organics that are more readily available for digestion. Therefore it was of interest to determine if the pretreatment increased the soluble fraction of the TCOD. Figure 4.3 presents the SCOD as a fraction of the TS. The error bars represent the combined error of the difference between duplicate analysis for the SCOD and the TS tests. The changes in SCOD concentration observed after pretreatment were substantial. As can be seen in Figure 4.3, pretreatment at 150 psi caused 2 and 4 fold increases in the SCOD for the TWAS/biosolids mixture and for the biosolids, respectively, compared to the controls. The SCOD concentration calculated for the TWAS with pretreatment at 150 psi shows an increase over the control of 41% at this pretreatment intensity.

Pretreatment at 300 and 600 psi significantly increased the SCOD of the sludge. However for the samples pretreated at 600 psi the actual ratio would be slightly lower than the value shown due to the aforementioned error of the TS measurements. The SCOD after pretreatment at 300 psi increased by 8 and 18 fold for the TWAS/biosolids and biosolids, respectively. The SCOD concentration calculated for the TWAS increased by 4 fold over the control. Pretreatment at 600 psi did not produce any further significant increase in the SCOD concentration with respect to the 300 psi treatment for the mixture or the biosolids. Nonetheless, the SCOD concentration calculated for the TWAS was slightly higher than the concentration calculated for the pretreatment at 300 psi. The experimental SCOD value obtained for the TWAS control, was considerably lower than the SCOD value calculated for

the untreated TWAS. This discrepancy was likely attributable to the inaccuracy of the assumption implicit in the calculation.

In general, the high solubilization achieved during the pretreatment especially at 300 psi and 600 psi, suggests that treated sludge would be more easily degradable in the anaerobic digestion.

The calculation of SCOD for the TWAS is presented in Table D.2. The following equation is used:

$$\frac{SCOD_{TWAS}}{TS_{TWAS}} = \frac{(SCOD_{mix} - R_{bio} \times TS_{bio\_in\_mix})}{TS_{TWAS\_in\_mix}} \qquad \textbf{Equation 4-3}$$

Where

$SCOD_{TWAS}$: SCOD of TWAS, mg/l

$SCOD_{mix}$: SCOD of TWAS/biosolids mixture, mg/l

$$R_{bio} = \frac{SCOD_{bio}}{TS_{bio}}$$

$SCOD_{bio}$: SCOD of biosolids mixture, mg/l

TS_{bio}: TS of biosolids, g

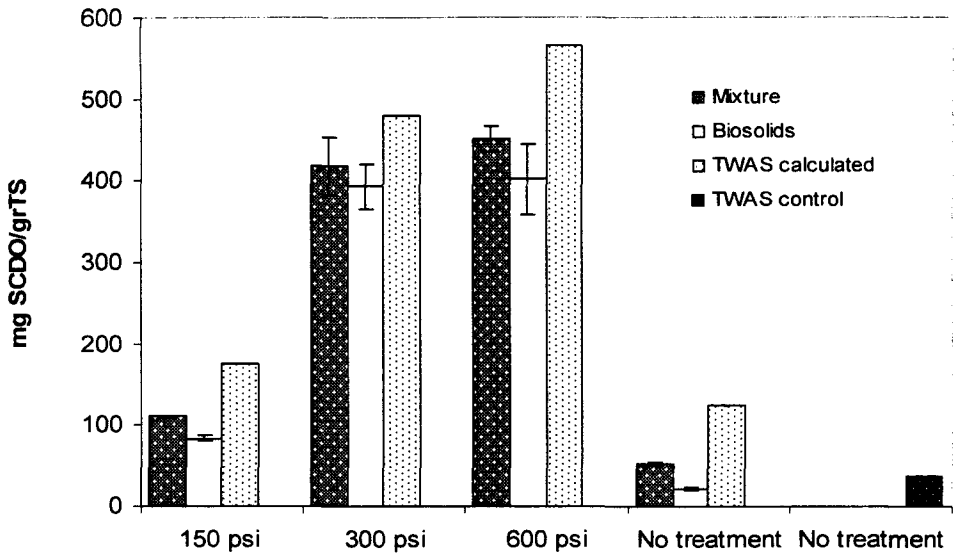

Figure 4.3 SCOD per gram of TS in control samples and pretreated samples.

The degree of solubilization, which was calculated as the SCOD divided by the TCOD, is presented in Figure 4.4. This parameter represents the portion of the TCOD that is soluble and has been used in many studies to assess the performance of anaerobic digestion enhancing pretreatments (Haug, 1978; Li and Noike, 1992; Baier and Schmidheiny, 1997).

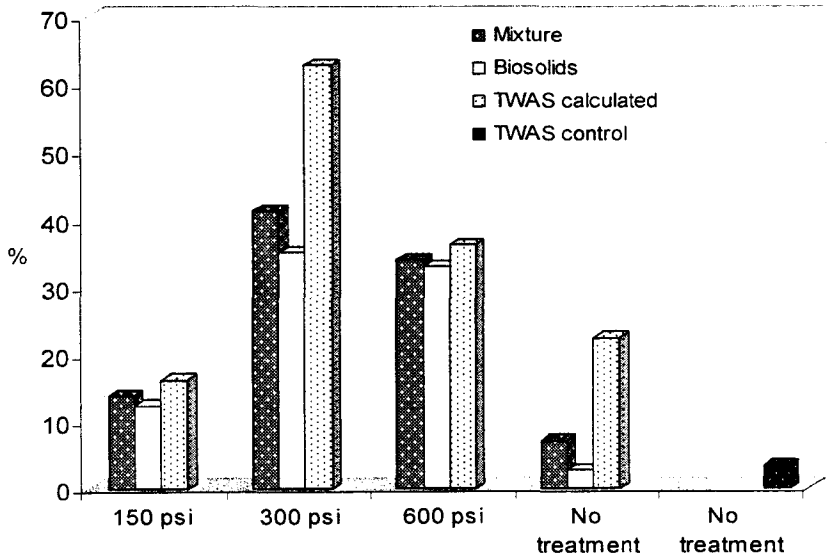

Figure 4.4 Degree of solubilization based on COD

The data presented in Figure 4.4 indicate that for the pretreatment at 300 and 600 psi around 30 to 40% of the organics in both the TWAS/biosolids mixture and the biosolids were soluble after pretreatment. The value calculated for TWAS at 300 psi was high, because the calculated TCOD for TWAS was low at this pretreatment intensity. After pretreatment at 150 psi, a degree of solubilization of around 15% was observed for the TWAS/biosolids mixture, the biosolids and the TWAS.

The samples of mixture and biosolids without pretreatment had a significantly lower soluble portion of the organics as expected. The biosolids coming from a digestion process were expected to have low concentration of soluble organics, because soluble organics are removed efficiently during digestion. TWAS was also expected to have low soluble organics because most of the organics in the TWAS are contained inside microbial cells. The degree of solubilization found for the TWAS control was only around 4%. This degree of solubilization is close to the value of 5.1% obtained by Haug (1978) for untreated sludge. Again there was a discrepancy between the calculated values for TWAS without pretreatment and the TWAS control. This was likely due to the aforementioned assumptions that the calculation involves.

To avoid problems due to sample to sample heterogeneity all samples for a given treatment were combined, properly mixed together, and a new TS value was obtained. Therefore, the normalization of all of the subsequent parameters was carried out with the new TS values.

The ammonia concentration was expected to increase during pretreatment due to the solubilization of the organic nitrogen present in the sludge. Figure 4.5 presents the ammonia concentration normalized by the solids concentration for control samples and samples after pretreatment. The error bars are the combined error between the differences in the duplicate analysis of ammonia and TS.

As can be observed in Figure 4.5 pretreatment at 150 psi of the TWAS/biosolids mixture and the biosolids had higher increases of ammonia than pretreatments at 300 and 600 psi. For both samples at 150 psi, a 2 fold increase was observed after this pretreatment. However this is contrary to what the results of solubilization had suggested, i.e., that more ammonia would be released during pretreatment at 300 and 600 psi. It is suspected that some ammonia may have escaped with the exhausted steam during pretreatment. The fact that more steam was applied for pretreatment at the higher intensities may explain the higher losses of ammonia and hence the lower concentrations observed after pretreatment at 300 and 600 psi.

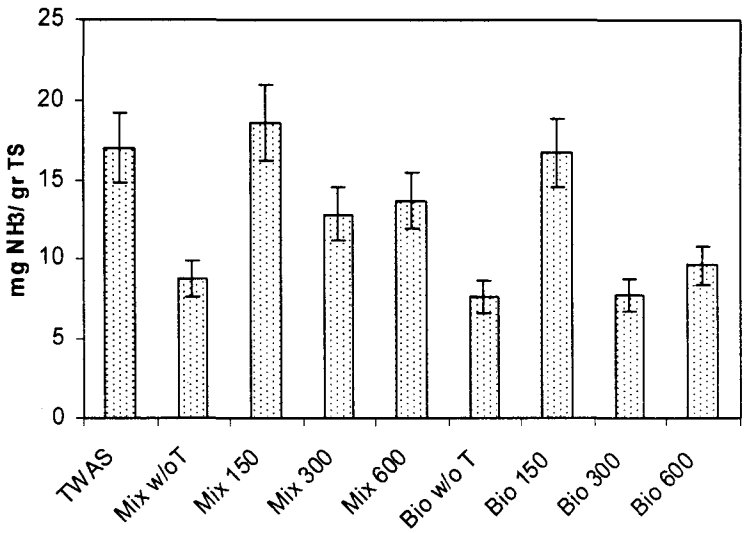

Figure 4.5 Ammonia per gram TS before and after steam-explosion

The VFA concentrations were also expected to increase with steam-explosion pretreatment due to solubilization of organics present in the sludge. Figure 4.6 presents the VFA values, reported as mg of acetic acid, normalized by the solids concentration of the sample for control samples and samples after steam-explosion. It shows that pretreatment increased the VFA of both the TWAS/biosolids mixture and the biosolids. For the mixture, the highest

increase was observed for the pretreatment at 300 psi followed by the pretreatment at 600 psi, with increases of 4 and 3 fold, respectively, over the control. Pretreatment of the mixture at 150 psi caused a VFA increase of 90% over the control. For the biosolids higher increases of VFA were found at higher pretreatment intensities. The highest increase was observed for the pretreatment at 600 psi with a 6 fold increase over the control while a 3 fold increase over the control was observed for pretreatment at 150 psi.

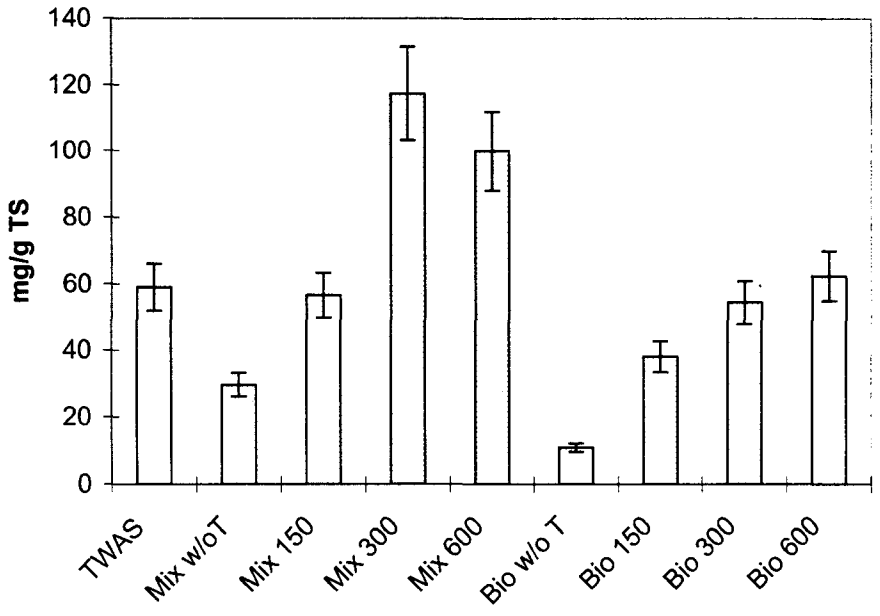

Figure 4.6 Total volatile fatty acids per gram TS before and after steam explosion

Figure 4.7 presents the alkalinity concentration and pH of the control samples and samples after steam-explosion. The error bars represent the difference in duplicate analysis. As can be observed in Figure 4.7 alkalinity decreased significantly during pretreatment. The water added to the sludge by the steam-explosion process likely contained low concentrations of alkalinity as it was steam condensate. This likely reduced the alkalinity of the samples. Clearly, at higher pretreatment intensity higher reductions of alkalinity were observed.

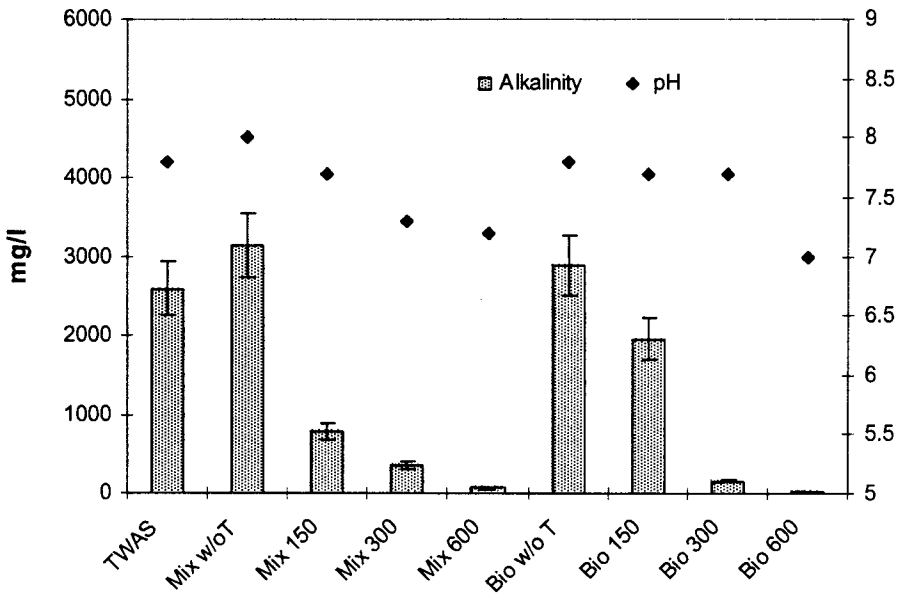

Figure 4.7 Bicarbonate alkalinity before and after steam explosion

The alkalinity concentrations observed after pretreatment were low for conducting the anaerobic digestion. The anaerobic digesters were prepared with samples at 3% TS concentration. At this solids concentration, the mixture without pretreatment for example would have an alkalinity concentration of 600 mg/l which is below 2000 mg/l, the minimum alkalinity concentration for optimum anaerobic digestion operation (Table 2-2). Therefore sodium and potasium bicarbonate alkalinity was added to the reactors before digestion for both the batch and the semi-continuous operation as discussed in the methods section.

As can be observed in Figure 4.7 the pH values for the samples did not change significantly during pretreatment. However a slight drop was observed which is most likely due to the addition of water during the steam-explosion which would have a slightly lower pH than the samples.

4.2 PERFORMANCE OF ANAEROBIC BATCH REACTORS

4.2.1 BIOGAS PRODUCTION DURING BATCH DIGESTION

The cumulative biogas volume and the cumulative methane volume produced during the anaerobic digestion in the batch reactors are presented in Figure 4.8 to Figure 4.11. The daily values presented are the average values of duplicate reactors. The difference between cumulative biogas productions from duplicate reactors ranged from 3 to 8%. Figure 4.8 shows the cumulative biogas volumes generated by the samples of the TWAS/biosolid mixture, treated at 150, 300 and 600 psi, as well as the biogas production for the TWAS/biosolid mixture and TWAS without treatment. Figure 4.9 presents the cumulative methane volumes for the same samples of the TWAS/biosolid mixture and TWAS. Figure 4.10 presents the cumulative biogas volumes for samples of biosolids pretreated at 150, 300 and 600 psi and for the biosolids without treatment. Figure 4.11 presents the cumulative methane volumes for the same biosolids samples.

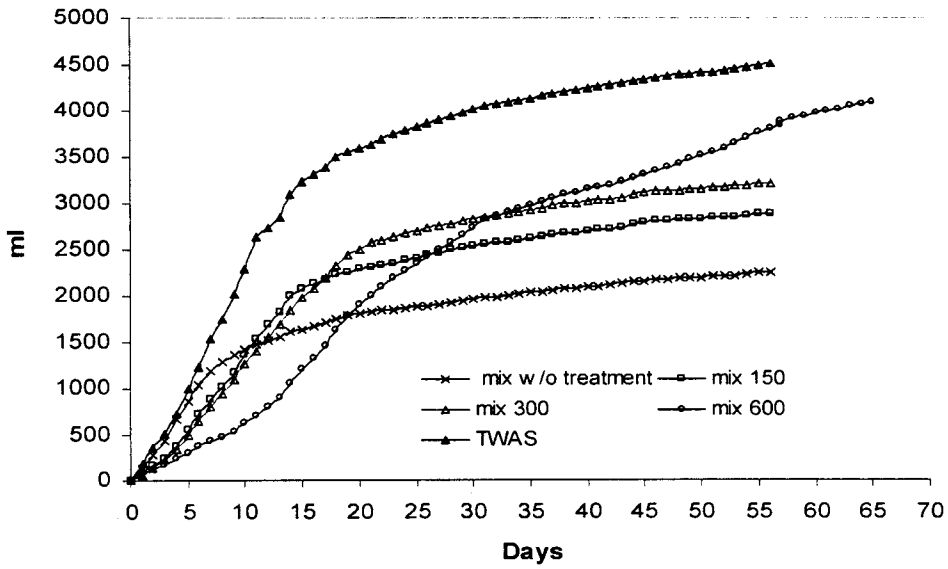

Figure 4.8 Cumulative biogas volume TWAS/ biosolids mixtures and TWAS

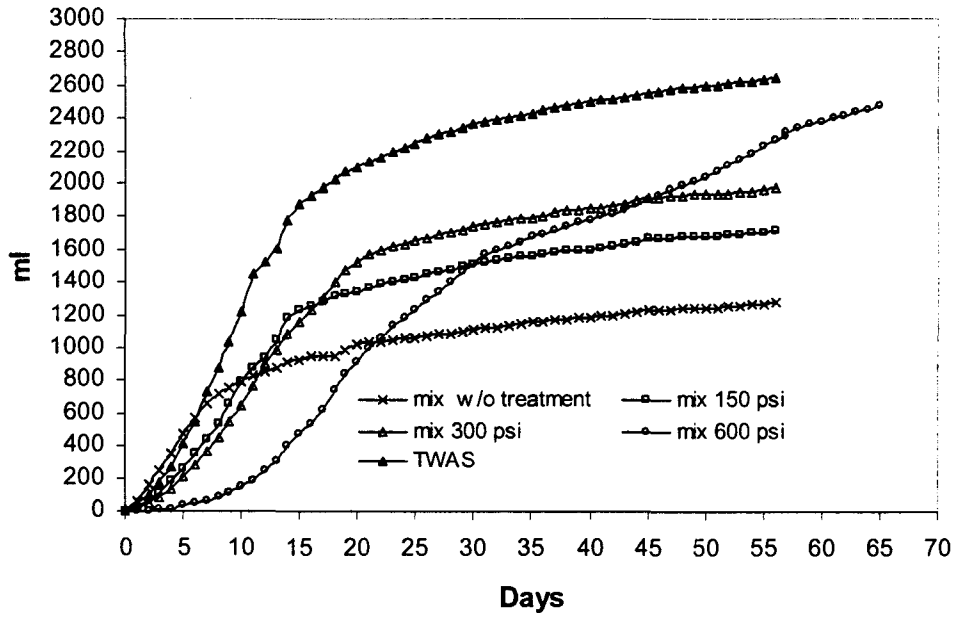

Figure 4.9 Cumulative methane volume TWAS/biosolids mixture and TWAS

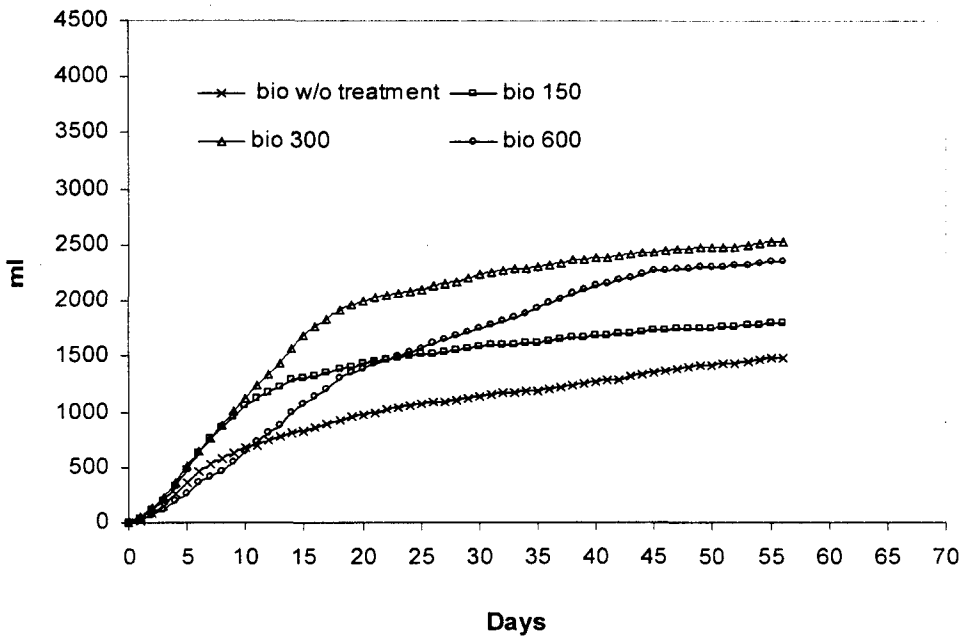

Figure 4.10 Cumulative biogas production for biosolids

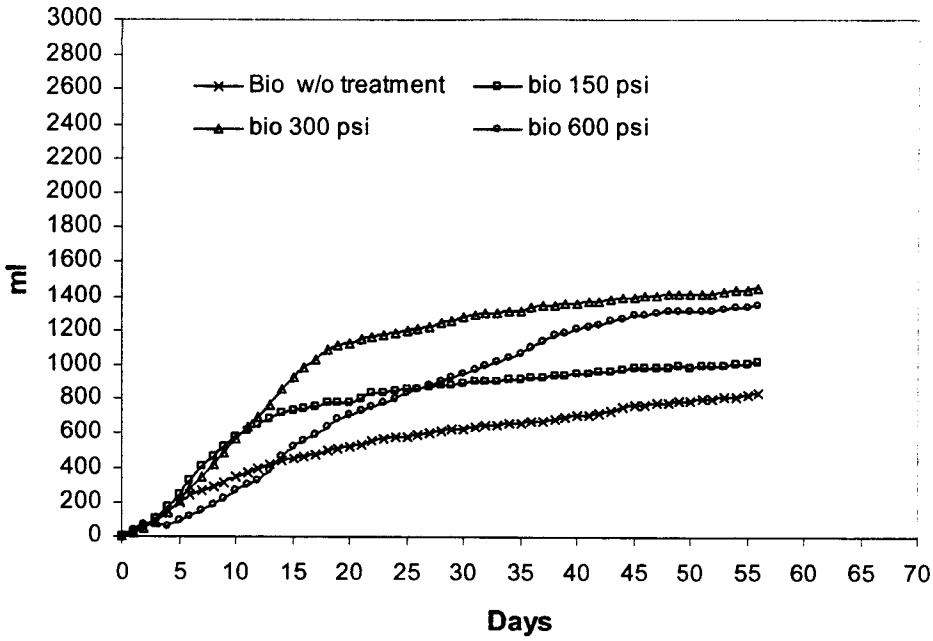

Figure 4.11 Cumulative methane volume for biosolids

From Figure 4.8 it can be observed that the initial biogas production rates were different for all samples. The samples of TWAS and TWAS/biosolids mixture without pretreatment initially produced biogas at an almost constant rate, that was greater than the other samples. For both samples this was expected because the innoculum used for the batch reactors was collected from the anaerobic reactor at ROPEC that was treating TWAS and primary sludge. The innoculum was therefore well acclimated to the feeds that were present in these reactors.

The mixture without pretreatment continued to produce at the initial rate for about 10 days and continued after that at a low biogas production rate until the end of the test. At day 56, the mixture without pretreatment had the lowest biogas production among all samples. The TWAS continued producing biogas at a high constant rate for around 15 days and then started to gradually reduce to a lower rate. The TWAS without pretreatment had the highest total biogas production at the end of the test. This result was expected because the samples

of mixture had less potential for biogas production because of their high content of biosolids, which had already been digested.

The mixture with pretreatment at 150 and 300 psi initially had slower biogas production rates as compared to the mixture without treatment. However, the onset of reduced biogas production was later than the control and both samples achieved higher total biogas production than the control. The slowest initial biogas production rate was observed for the samples that were pretreated at 600 psi. This suggests that at the highest pretreatment pressure some inhibitory substances may have been produced. It may also indicate an acidification of these reactors due to high VFA concentrations that might result from the high SCOD available after pretreatment at 600 psi. The biogas production rate of the mixture pretreated at 600 psi tended to vary with time duirng the test. Nonetheless, at the end of the digestion period this sample produced more total biogas than the other pretreatment conditions and was still producing biogas at a higher rate than the other samples.

As may by observed in Figure 4.9, the trends of methane gas production for the TWAS/biosolids mixture were generally quite similar to those of the biogas production. There was only some difference during the acclimation period because the methane fraction of the biogas increased gradually during this period until it was stabilized and remained constant throughout the test. For the mixture pretreated at 600 psi sample the methane production showed more lag than the biogas production suggesting there was some inhibition of the methanogenic bacteria. After the initial days of acclimation the biogas composition for all the samples remained between 60 to 70% methane and 30 to 40% CO_2.

The biogas production for the biosolids samples shown in Figure 4.10 indicated that samples after pretreatment at 150 and 300 psi had a higher initial biogas production rate than the control, which was different from the samples of the mixture that were pretreated at these conditions. The reduced biogas production rate observed for the biosolids without

pretreatment are an indication that most of the available organics had been digested in the previous digestion. Most probably, only organics that were not readily available for the microorganisms were present in the untreated biosolids.

Pretreatment at 150 psi improved the digestion as more organics became available for digestion. At this pretreatment intensity the biogas production rate was constant for the first 10 days of the test and then gradually decreased to at a low biogas production rate and reached a total biogas volume that was higher than the control at the end of the test.

Pretreatment of biosolids at 300 psi generated the greatest quantity of biogas for this type of sludge. The initial biogas production rate was high and continued at a high rate for almost 20 days. Biogas production for biosolids pretreated at 600 psi showed a similar response to that of the mixture pretreated at the same pressure. A long acclimation period and less constant production were observed throughout the test. Again this may be due to inhibitory substances produced during pretreatment at 600 psi or the production of high VFA concentrations due to a high load of soluble organic substrate.

The methane gas production for the biosolids presented in Figure 4.11 shows that the trend of methane production was generally similar to the biogas production. This was because the methane gas content of the biogas remained essentially constant throughout the test with the exception of the first 10 days of digestion. Overall, the methane gas content was somewhat lower than that observed during the digestion of the TWAS/biosolids mixture. Biogas composition was stable at 55 to 60% methane gas, 30 to 40% CO_2 and a small amount of nitrogen until the end of the test.

The duration of the initial lag phase for all the samples is presented in Figure 4.12. The lag phase was defined as the time in days required to produce 200 ml of methane gas. Depending on sample pre-treatment this volume of methane gas represented 10 to 20 percent of the total methane production. The lag phase for the different pretreatment

conditions is indicative of how easily the anaerobic bacteria become acclimated to the substrate. Even though the digestion in batch reactors differs from the digestion in continuous operation, the duration of the lag phase in the batch reactors can give an indication of how difficult it would be to start an anaerobic digester at full-scale operation with a specific substrate.

Figure 4.12 shows that there is a clear prolongation of the lag phase after pretreatment at 600 psi. For the mixture, as the intensity of the pretreatment increased the lag phase became longer. This may have been due to the formation of new compounds that are toxic to the microorganisms and require some acclimation or it may also have been due to an acidification of the reactors because of the high concentration of new soluble organics that were rapidly transformed to VFAs.

For the biosolids, digestion of the control sample and samples pretreated at 150 and 300 psi had the same lag phase while pretreatment at 600 psi resulted in a significant increase in the lag phase.

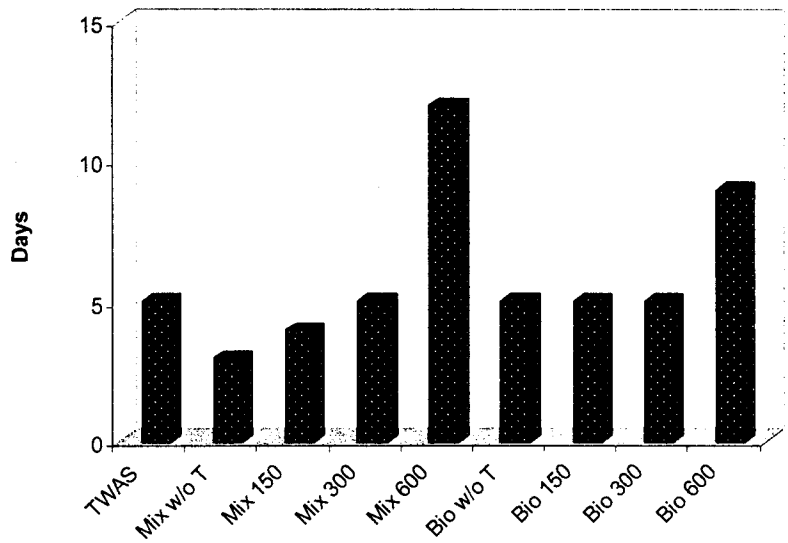

Figure 4.12 Duration of lag phase

After the initial acclimation period, the microorganisms start consuming the organics that were present in the sludge at a constant rate. The rate of biogas production in this phase indicates how well the organics were being consumed by the bacteria. A high biogas production rate indicates that the organics are easily digested by the microorganisms. Figure 4.13 presents the biogas production rate during the period of high biogas production. Once most of the available organics were consumed, the biogas production rate decreased significantly. The daily biogas production rate decreased to around 10% or less of the maximum daily biogas production, until biogas production was minimal.

Minimal biogas production in this last phase is due to lack of substrate availability and is mostly due to the endogenous decay of the microorganisms. When biogas production was minimal the reactors were stopped since most of the available organics were digested.

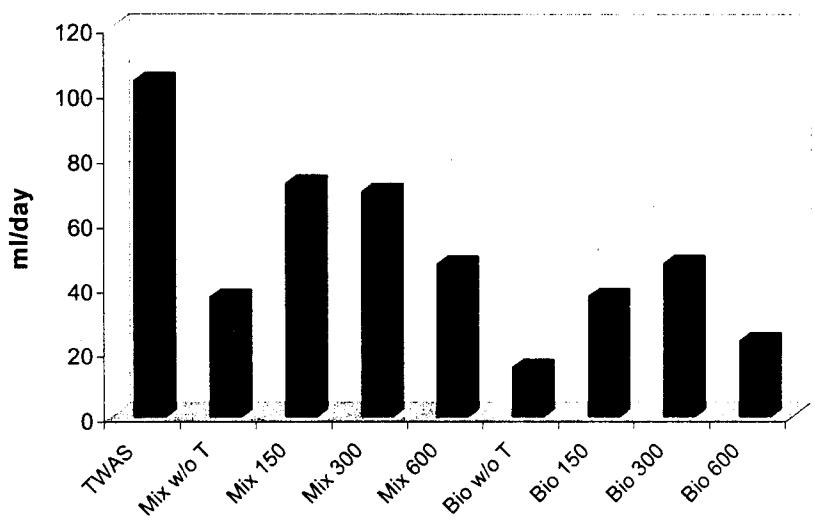

Figure 4.13 Biogas production rates during period of fast production

From Figure 4.13 it can be observed that the highest affinity to the substrate occurred with the TWAS without pretreatment. The mixture without pretreatment had a lower biogas

production rate than the TWAS because of the high proportion of biosolids in the mixture, which were not expected to produce biogas at a high rate. Pretreatment of the mixture at 150 and 300 psi improved the rate of biogas production compared to the control. This indicates that organics were more easily consumed by the microorganisms after treatment at these intensities. At 600 psi the mixture had a slower biogas production rate than it had with the other pretreatments. Again, this is probably an indication that some inhibitory compounds were formed during pretreatment at the highest pressure or an inhibition due to high VFA concentrations occurred during digestion.

The rate of biogas production for the biosolids without pretreatment was the lowest among all the samples as expected. Pretreatment of the biosolids at 150 and 300 psi improved the biogas production rates, which indicates that some of the organics that were difficult to degrade and remained after the first digestion can be transformed into more available organics with the pretreatment. At 600 psi, the biogas production rate for the biosolids was low, again showing inhibition after this pretreatment.

Total biogas production expressed per gram of TS initially in the bottles are presented in Figure 4.14. This figure presents the biogas yields for the TWAS/biosolids mixture, the biosolids, and also an estimate of the biogas yield for the TWAS which was calculated by subtracting the expected contribution of biogas produced by the biosolids from the biogas of mixture. The calculation of the TWAS biogas production is shown in Table D.3. The following equation was used,

$$\frac{V_{TWAS}}{TS_{TWAS\_in\_mix}} = \frac{V_{mix} - (TS_{bio-in\_mix} \times R_{bio})}{TS_{TWAS\_in\_mix}} \qquad \textbf{Equation 4-4}$$

Where,

$R_{bio} = \frac{V_{bio}}{TS_{bio}}$, ratio of biogas production per TS added for the biosolids, ml/g

V_{TWAS}: Cumulative biogas volume, ml (expected from TWAS in mixture)

V_{mix}: Cumulative biogas volume, ml (measured during digestion of mixture)

V_{bio}: Cumulative biogas volume, ml (measured during digestion of the biosolids)

TS_{bio} : TS added to reactors with biosolids, g

$TS_{TWAS\_in\_mix} = TS_{mix} \times 0.3$ (mixture had 30% solids from TWAS, by weight), g/l

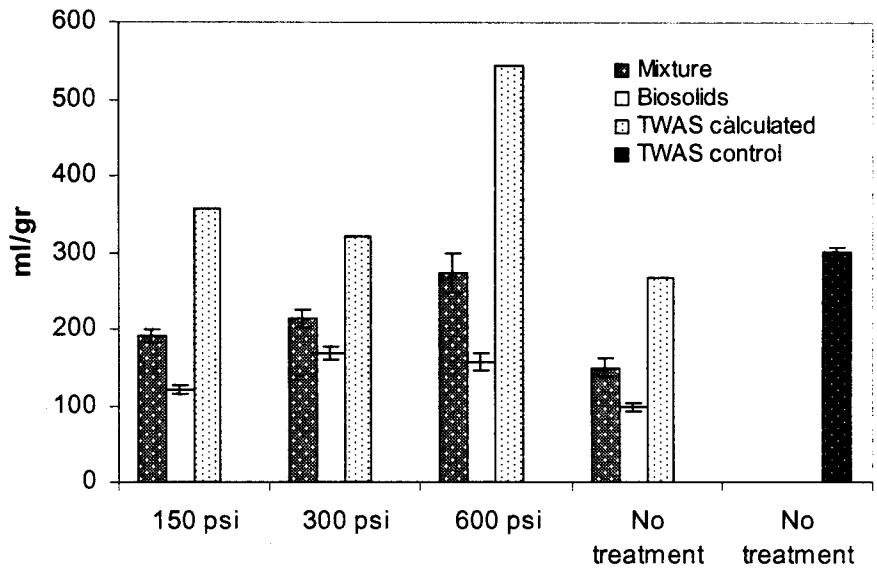

Figure 4.14 Biogas yield per gram of TS influent for batch tests

Figure 4.14 shows an improvement of biogas yield for all the pretreatment conditions over the control samples. For the mixture, the highest total biogas production was observed with pretreatment at 600 psi while for the biosolids the highest production was observed at 300 psi. The calculated TWAS biogas yield shows that the best pretreatment intensity for increasing the total biogas production of the TWAS was 600 psi. This sample had the best improvement on biogas yield over the control. The calculated value for TWAS without

pretreatment was similar to the value obtained for the TWAS that was digested as a control, which validates the calculation of total biogas yield for the TWAS in the mixture.

The increase in biogas production as compared to the controls is presented in Figure 4.15. The increase in biogas over the control was calculated using Equation 4-5

$$\%Biogas_{Increase} = \frac{\frac{V_{sample}}{TS_{sample}} - \frac{V_{control}}{TS_{control}}}{\frac{V_{control}}{TS_{control}}} \qquad \textbf{Equation 4-5}$$

where,

V_{sample}: Cumulative biogas volume of sample, ml

$V_{control}$: Cumulative biogas volume of control, ml

TS_{sample}: TS of sample, g

$TS_{control}$:TS of control, g

In Figure 4.15 it can be observed that for the mixture the improvement in biogas production increased as the pretreatment intensity increased. However, for biosolids there was a higher improvement in biogas production after pretreatment at 300 psi. The calculated increase in biogas production for the TWAS was better after pretreatment at 600 psi with respect to the other pretreatments and also with respect to the samples of the mixture and the biosolids. The estimated increase in TWAS biogas production after pretreatment at 300 psi was low because the expected biogas production from the biosolids at this pretreatment intensity was high. For pretreatment at 150 psi the improvement over the control for the TWAS was better than for the mixture and the biosolids.

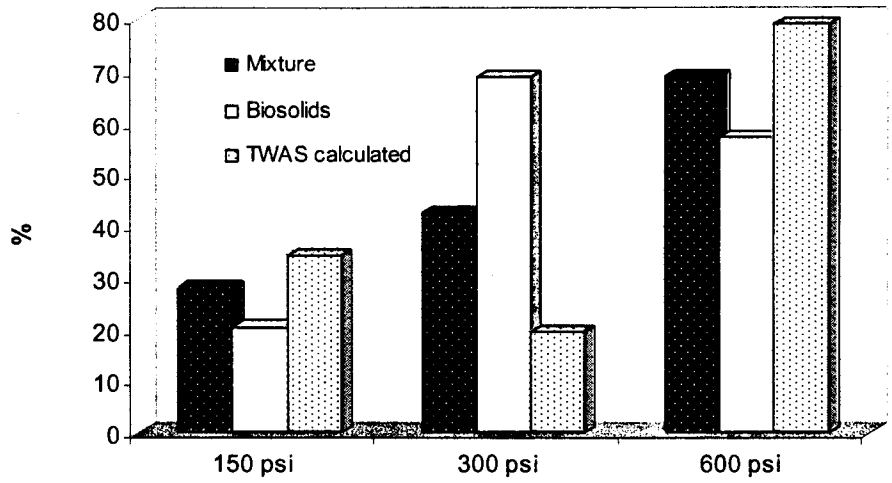

Figure 4.15 Increase in cumulative biogas production over control samples

4.2.2 VS REMOVAL DURING BATCH DIGESTION AND METHANE YIELD

VS destruction during the batch digestion was measured to asses the extent of organic matter conversion to methane. As shown in Figure 4.16 the mass of VS initially added to the batch reactors was similar for all the samples except for the TWAS control. The initial VS values were an average of duplicate analyses. The error bars presented for the initial VS are the difference between duplicate analyses, which was a maximum of 6%. After digestion, the VS were measured for duplicate reactors and in duplicate analyses. The error presented for the final VS values are the difference between duplicate reactors. This difference generally varied from 6 to 17%. However, the values of VS concentrations observed for one of the two reactors with biosolids pretreated at 300 psi and one of the reactors with biosolids pretreated at 600 psi were discarded because they differed considerably from the duplicate reactor and after inspection of the data it was observed that the TS values in those reactors were higher than the input values. Therefore, in these cases the values presented are those of only one reactor. The error presented for these samples was the difference of duplicate analyses. In general, from Figure 4.16 it a reduction of VS is observed in all the samples during digestion.

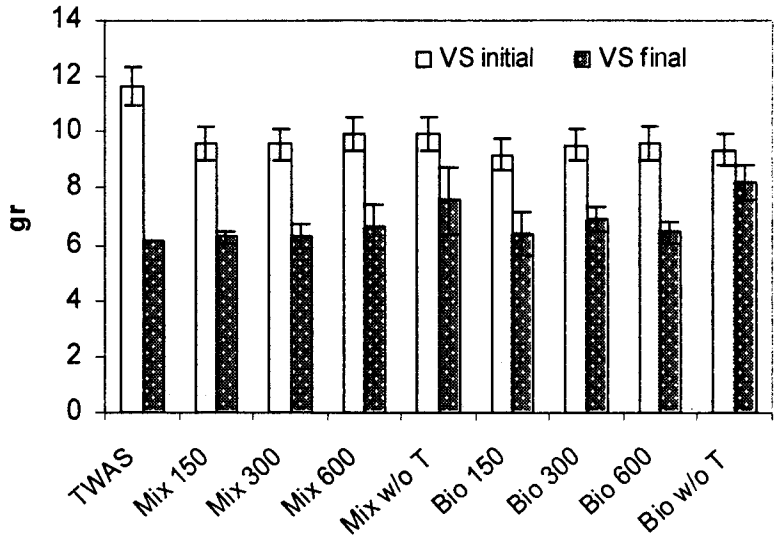

Figure 4.16 Initial and final VS.

Figure 4.17 presents the VS reduction during digestion. The values are the average VS destruction of the duplicate reactors and the errors presented are the difference in VS removals from the duplicate reactors. The VS removals for the biosolids pretreated at 300 and 600 psi are the result of only one reactor and the error was that of duplicate analysis. It can be observed that for the mixture at all the pretreatment conditions the VS destruction was similar, at around 38% while for the mixture without pretreatment it was only 28%. Biosolids also showed similar VS removals at all the pretreatment intensities at around 34% while the biosolids without pretreatment had a much lower VS destruction of 19% which was expected for this sludge. It is recognized that the trend of VS removals according to the treatment intensity was not in perfect agreement with the trend of biogas production. Nonetheless, the VS removal results consistently show a significant improvement over the untreated samples. The VS results at 300 psi pretreatment also agree with the biogas results in the sense that the observed improvements in VS removals relative to the control samples were better for the biosolids than for the mixture.

The calculated VS destruction for the TWAS showed the best improvement over the control at pretreatment of 300 psi, with similar improvement at 600 psi. The VS reduction for TWAS pretreatment at 150 psi did not seem to improve the VS removals of the TWAS compared to the control. The value calculated for TWAS without pretreatment was close to the VS destruction achieved during digestion of the TWAS control, both being within the typical range of 30 to 50% VS destruction that might be expected for this type of sludge. In general, the VS destruction for the mixture and biosolids was low, even after pretreatment. These results were expected because the biosolids had been previously digested and the mixture had a large proportion of biosolids.

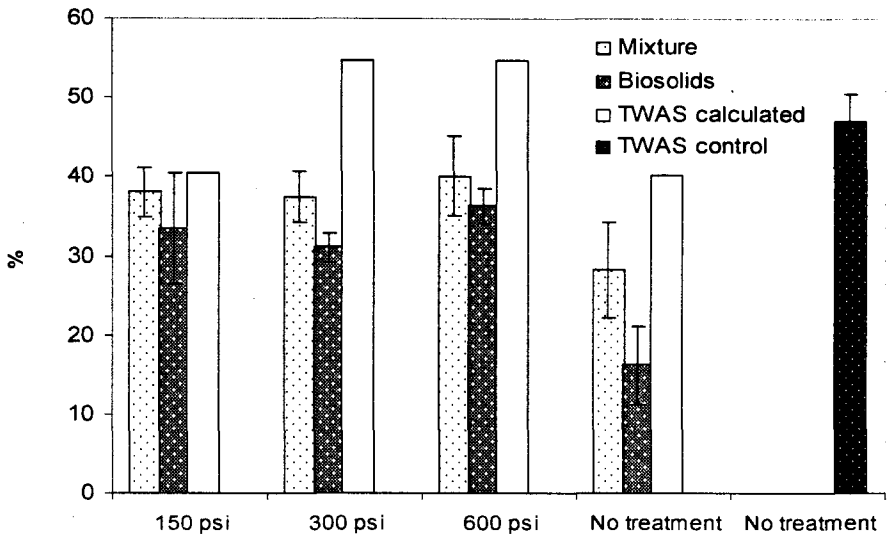

Figure 4.17 Percentage VS removed during digestion.

Figure 4.18 presents the methane yield calculated as the average total cumulative methane production of duplicate reactors divided by the average total VS destroyed during digestion of duplicate reactors. The error represents a combined error from the differences in methane yield and VS destroyed in the duplicate reactors. The VS removed for samples of biosolids pretreated at 300 and 600 psi were the values for one reactor. Typical biogas production rates range from 750 to 1000 ml of biogas per gram of VS destroyed (Malina and Pohland,

1992). Assuming an average of 60% methane gas composition of the biogas, the methane gas production should be in the range of 450 to 600 ml CH_4 per gram of VS destroyed. As observed in Figure 4.18 most of the samples had methane yields that were reasonably close to the theoretical value. The overall average methane yield of all samples was 490±100 ml CH_4 per gram of VS destroyed. From Figure 4.18 it can also be observed that the calculated TWAS yield for the samples without pretreatment was very close to the yield of the TWAS control.

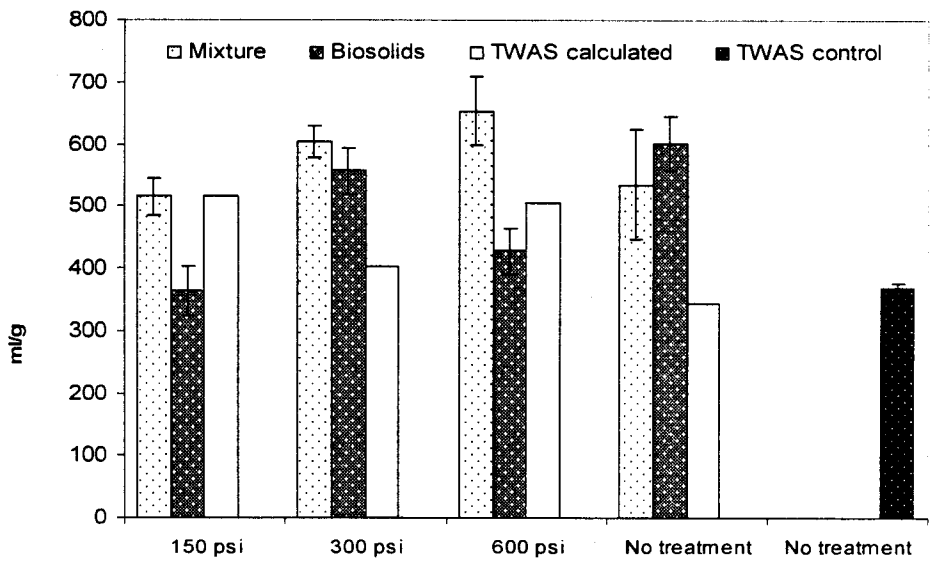

Figure 4.18 Methane yield per gram of VS removed

Table D.4 presents the calculation of VS removal for the TWAS and Table D.5 presents the calculation of methane yield for the TWAS. The following equations were used,

$$\%VS_{TWAS\_rem} = \frac{VS_{TWAS\_rem}}{VS_{TWAS\_in\_mix}} \qquad \textbf{Equation 4-6}$$

$$VS_{TWAS\_rem} = VS_{mix\_rem} - (VS_{bio\_in\_mix} \times R_{bio}) \qquad \textbf{Equation 4-7}$$

Where,

$$R_{bio} = \frac{VS_{bio\_rem}}{VS_{bio\_in}}$$

VS_{TWAS_rem}: VS of TWAS removed during digestion of the mixture, g

VS_{mix_rem}: VS removed during digestion of the mixture, g

$VS_{bio\_in\_mix}$: Initial VS of biosolids in the mixture, g

VS_{bio_rem}: VS removed during digestion of the biosolids, g

VS_{bio_in}: Initial VS of biosolids for biosolids digested alone, g

$$VS_{TWAS\_in\_mix} = (VS_{mix\_in} - VS_{bio\_in\_mix}) \quad \textbf{Equation 4-8}$$

$VS_{TWAS\_in\_mix}$: Initial VS of TWAS in the mixture, g

VS_{mix_in}: Initial VS of mixture, g (for mixture digestion)

$$VS_{bio\_in\_mix} = (TS_{mix\_in} \times \%TS_{bio\_in\_mix} \times \%VS) \quad \textbf{Equation 4-9}$$

TS_{mix_in}: Initial TS of mixture for mixture digestion, g

$\%TS_{bio\_in\_mix}$: percentage of solids from biosolids in the mixture , i.e., 70%

$$\left(\frac{V_{CH4}}{VS_{rem}}\right)_{TWAS} = \frac{V_{CH4\_TWAS}}{VS_{TWAS\_rem}} \quad \textbf{Equation 4-10}$$

$$V_{CH4\_TWAS} = (V_{CH4\_mix} - V_{CH4\_bio\_in\_mix}) \quad \textbf{Equation 4-11}$$

$$V_{CH4\_bio\_in\_mix} = (VS_{bio\_in\_mix\_rem} \times R_{bio}) \quad \textbf{Equation 4-12}$$

where,

$$R_{bio} = \frac{V_{CH4\_bio}}{VS_{bio\_rem}}$$

V_{CH4_TWAS}: methane volume produced from TWAS during digestion of mixture, ml

V_{CH4_mix}: methane volume produced during digestion of mixture, ml

$V_{CH4\_bio\_in\_mix}$: Methane volume produced from biosolids during digestion of mixture, ml

$VS_{bio\_in\_mix\_rem}$: VS of biosolids removed during digestion of the mixture, g

V_{CH4_bio}: methane volume produced during digestion of biosolids, ml

VS_{bio_rem}: VS removed during digestion of biosolids, g

4.2.3 SOLUBLE COD REMOVAL DURING BATCH DIGESTION

Figure 4.19 presents the initial and final SCOD concentrations for the anaerobic batch digestion. The error presented for the initial values was the difference between duplicate analyses. The difference between duplicate analyses of the SCOD measurements was relatively small. Most of the duplicate analyses differed from each other by only 3 to 6% and the maximum difference was 10%. The error for the final values is the difference between duplicate reactors which also had similar SCOD concentrations. Differences in SCOD concentrations between duplicate reactors were between 3 to 9%. The accuracy of the data allowed for a meaningful observation of SCOD changes during the digestion.

As observed in Figure 4.20 there was a significant improvement in SCOD removals for both the TWAS/biosolids mixture and the biosolids after pretreatment, especially at 300 and 600 psi as compared to the controls. Pretreatment of both the mixture and the biosolids at 150 psi showed an improvement over the control but they were not as significant as with the other pretreatments. Samples pretreated at 600 psi had slightly lower SCOD removals than samples pretreated at 300 psi. This suggests that some of the soluble organics produced during pretreatment at 600 psi were not easily degraded during the digestion.

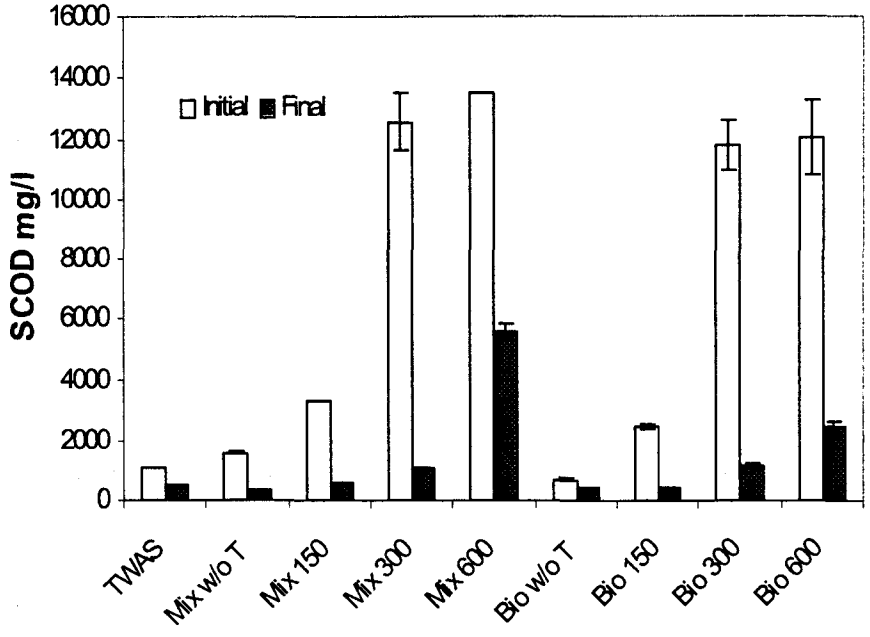

Figure 4.19 SCOD initial and final

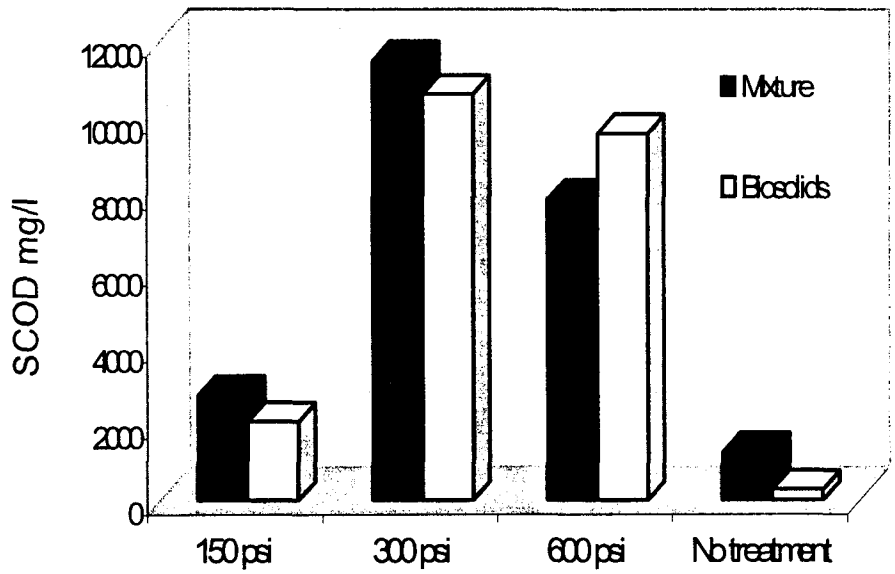

Figure 4.20 SCOD removed during batch anaerobic digestion

4.2.4 AMMONIA DURING BATCH DIGESTION

Ammonia is produced during anaerobic digestion due to the digestion of organic nitrogen present in the sludge. Hence higher concentrations of ammonia in the reactors indicates a higher conversion of organics during digestion. However, excessively high ammonia concentrations can become toxic to the methanogenic bacteria. Ammonia concentrations of 3000 mg/l have been reported to be partially inhibitory and concentrations of 4000 mg/l to cause complete inhibition at high pH values (Malina and Pohland, 1992). The difference between the initial and the final ammonia concentration in the reactors indicates the ammonia that was released during digestion. Figure 4.21 presents the ammonia released during digestion for the control samples and for the samples after steam explosion. The error bars represent a combined error of the differences between duplicate reactors and the difference of duplicate analyses. From Figure 4.21 it can be observed that for the mixture the highest release of ammonia was observed after pretreatment at 600 psi. This sample produced significantly higher ammonia than the control. Pretreatment at 300 psi had higher release of ammonia than the control but it was not as significant as with the 600 psi pretreatment and the sample pretreated at 150 psi had a similar ammonia release to that of the control. For the biosolids the ammonia released after pretreatments at 300 and 600 psi was very similar, both being higher than the control. The biosolids pretreated at 150 psi produced a slightly lower amount of ammonia than the control. In general, the trends of ammonia production are in agreement with the biogas production observed during digestion (Figure 4.14). Although the increased biogas production over the control after pretreatment of the mixture at 600 psi was not as significant as the increase in ammonia production.

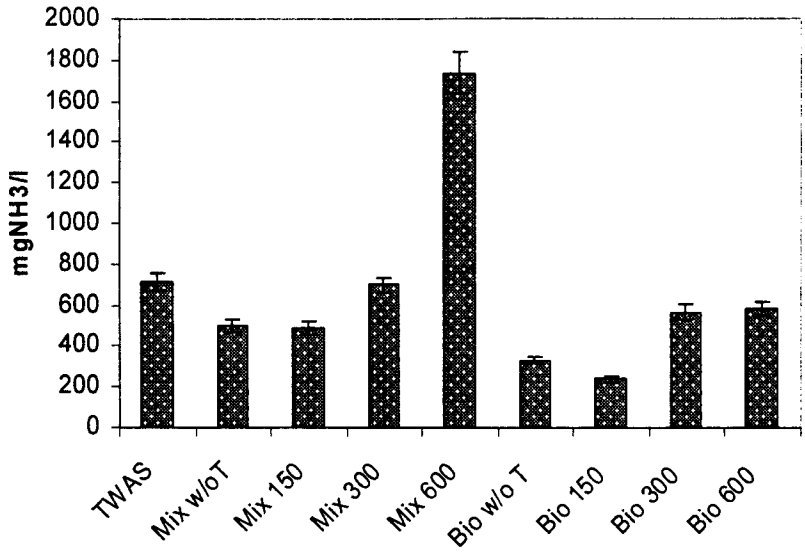

Figure 4.21 Ammonia concentrations released during batch digestion

According to the biogas production data of the batch reactors, steam-explosion pretreatment enhanced the anaerobic digestion of the TWAS/biosolids mixture and the biosolids compared to the controls. Among the different parameters measured for the batch digestion tests, the data of biogas production and SCOD removal showed the most consistent responses for the effects of the different pretreatment intensities.

From these two parameters, it was concluded that the pretreatment at 300 psi was the optimum condition for the pretreatment of the biosolids. For the mixture, pretreatment at 600 psi had a higher cumulative biogas production than the mixture at 300 psi. However, the digestion of the sample treated at 600 psi was observed to be somewhat problematic mainly due to the long duration of the initial lag phase and the slow rate of biogas production. Additionally, considering the higher energy required for pretreatment at 600 psi, pretreatment at 300 psi was selected as the optimum condition to treat the TWAS/biosolids mixture.

Pretreatment at 150 psi required less energy. However, the improvements over the controls for both samples pretreated at 150 psi were not as significant as with the other two pretreatments. Given the above batch digestion results, in the second experimental phase, semi-continuous reactors were prepared with samples of TWAS/biosolids mixture and biosolids pretreated at 300 psi and controls.

The pretreatment temperature at 300 psi (220°C) was higher than the optimum temperatures reported in the literature for other thermal pretreatments. Haug (1978) and Li and Noike (1992) reported a temperature of 175°C to be the optimum for pretreatment of TWAS. Haug (1978) reported inhibition during digestion of the TWAS pretreated at 225°C that resulted in low biogas production. However, it should be noticed that in the present study pretreatment was not performed directly on TWAS but on digested sludge and a mixture of TWAS and digested sludge. Results by Pinnekamp (1989) suggest that higher temperatures can be used to improve the digestion of digested sludge than for TWAS. Pinnekamp (1989) reported pretreatment temperatures from 135 to 170°C to be the optimum for WAS while for anaerobically digested sludge, temperatures up to 180°C were reported to improve the digestion. However, temperatures higher than 180°C were not tested by Pinneknamp (1989).

4.3 PERFORMANCE OF SEMI-CONTINUOUS ANAEROBIC REACTORS

4.3.1 BIOGAS PRODUCTION OF SEMI-CONTINUOUS REACTORS

The daily biogas production measured during the semi-continuous flow anaerobic digestion of the TWAS/biosolids mixture and the biosolids with steam explosion pretreatment at 300 psi and without pretreatment are presented in Figure 4.22 to Figure 4.25. From these figures it may be observed that the daily biogas production of the duplicate reactors was similar to each other for all samples and that there was only a reasonably small variability in the daily values of biogas production after the initial start-up.

The variability between the average daily biogas production of duplicate reactors was slightly different for the reactors treating different samples. For the reactors digesting the mixture pretreated at 300 psi (Figure 4.22) the differences were 0.4 and 3.5% at SRT's of 14- and 8-day respectively. Duplicate digesters treating the mixture without pretreatment (Figure 4.23) had similar average biogas production at the SRT of 14-day, with only 0.1% difference and a 6% difference at the SRT of 8-day. The duplicate reactors digesting biosolids with pretreatment at 300 psi (Figure 4.24) and without pretreatment (Figure 4.25) had more variability than the reactors treating the mixture. The average daily biogas production of the duplicate reactors treating biosolids pretreated at 300 psi differed by 2 and 16% at SRT's of 14 and 8-day respectively. The duplicate reactors treating biosolids without pretreatment had 3 and 8% differences in the average daily biogas production at SRT's of 14 and 8-day, respectively.

In general there was more variability in the digestion at the 8-day SRT. This can be explained by the higher organics load and the shorter residence time that resulted in a less stable digestion. From Figure 4.22 to Figure 4.25 it can also be observed that at the 14-day SRT all the reactors took around 30 days to reach a stable daily biogas production, after which the reactors were considered to be at steady-state. An increase in daily biogas production as the SRT was reduced to 8 days can be clearly observed. More biogas production was expected at the 8-day SRT because of the higher organics loads.

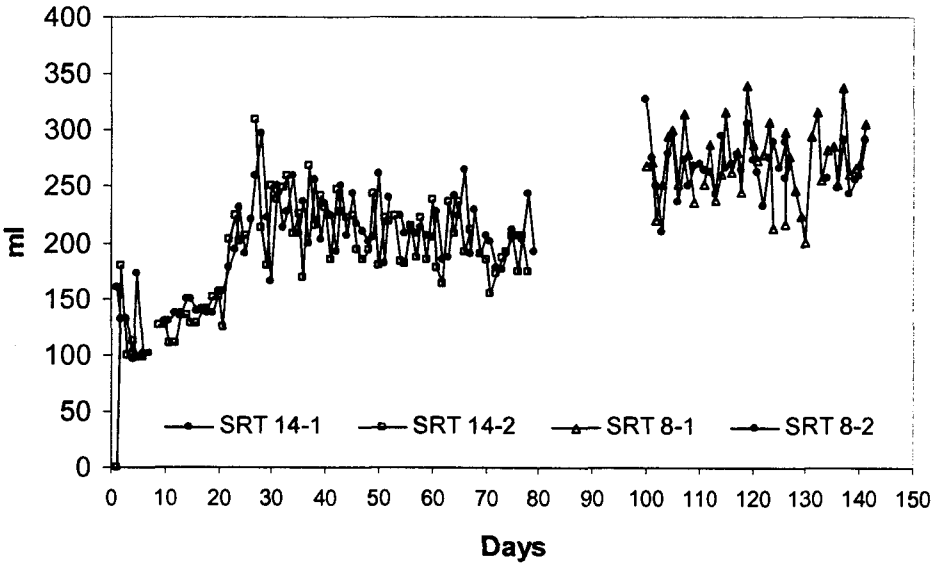

Figure 4.22 Daily biogas production of mixture at pretreated 300 psi

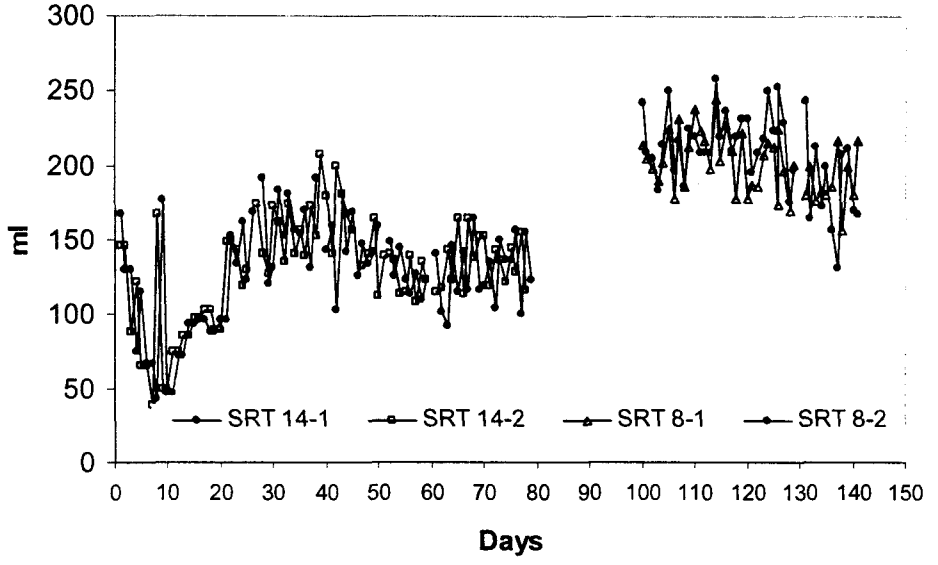

Figure 4.23 Daily biogas production of mixture without pretreatment

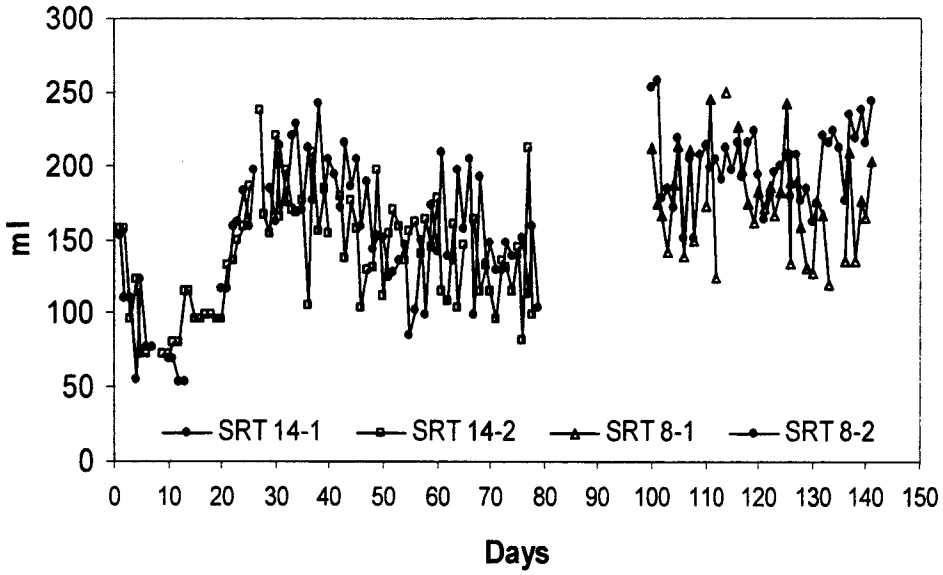

Figure 4.24 Daily biogas production of biosolids pretreated at 300 psi

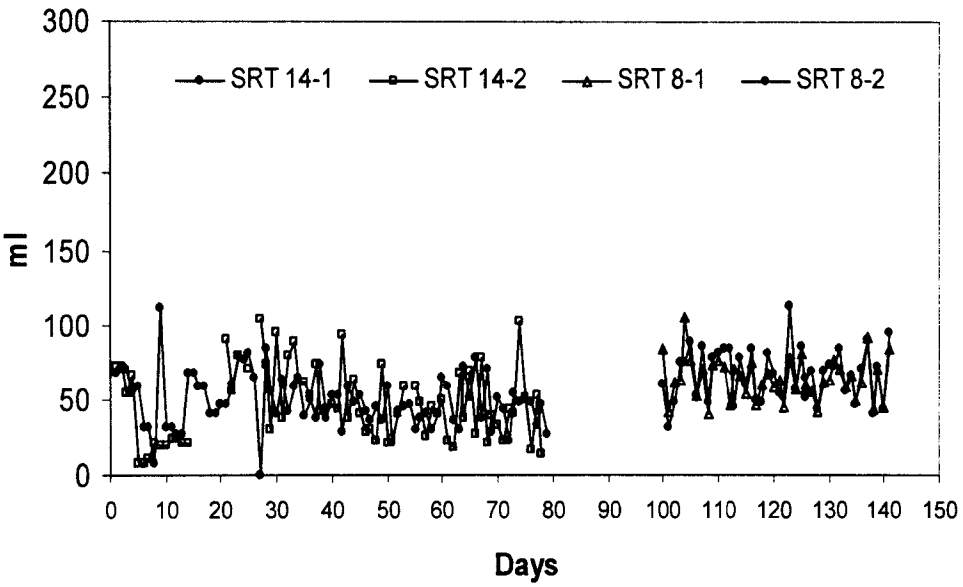

Figure 4.25 Daily biogas production of biosolids without pretreatment

The average daily biogas productions from the duplicate reactors at steady-state are presented in Figure 4.26. The average daily biogas production for the mixture with pretreatment at 300 psi was 211±26 ml at the 14-day SRT and 270±31 ml at the 8-day SRT. The mixture without pretreatment had daily biogas production of 142±23 ml at the 14-day SRT and 205±25 ml at the 8-day SRT. The average daily biogas production for the TWAS/biosolids mixture pretreated at 300 psi was 49 and 31% higher than the control at 14 and 8-day SRTs, respectively. Biosolids pretreated at 300 psi had daily biogas productions of 155±22 ml and 188±30 ml at 14 and 8-day SRTs, respectively. As expected, biosolids without pretreatment produced significantly less biogas than the other samples. At the 14 day SRT, the average production was 47±30 ml while at the 8-day SRT it was 66±16 ml. The increases over the control for the biosolids were 229 and 184% at the 14 and 8-day SRTs, respectively. Similar to the results of the batch reactors, the improvements in biogas production compared to the controls were higher for the sample of biosolids than for the TWAS/biosolids mixture.

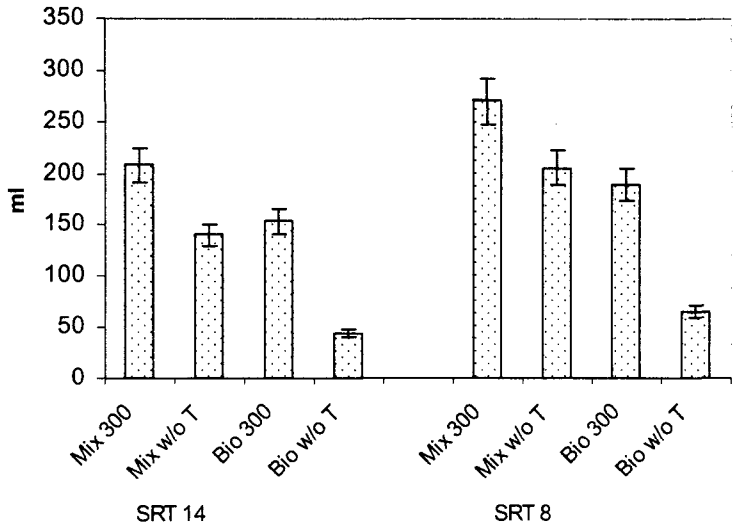

Figure 4.26 Average daily biogas production during semi-continuous digestion

The biogas yields per gram of TS in the influents of the semi-continuous digesters are presented in Figure 4.27. The error presented is the combined error of the difference between biogas production of the duplicate reactors and the difference between duplicate TS analysis. As expected the biogas yields for the TWAS are higher than the yields of the biosolids and the mixture. It can be observed that for both the TWAS/biosolids mixture and biosolids after pretreatment at 300 psi, the biogas yield was higher than for the controls at both the 14 and 8-day SRTs. However, the yields calculated for the TWAS at both SRTs were slightly lower than the control. For all the samples the yields remained stable with the change of SRT, as was expected. The biogas yields for the TWAS/biosolids mixture, the biosolids and the calculated TWAS pretreated at 300 psi and without pretreatment were very similar to the respective yields observed during the batch digestion (Figure 4.14).

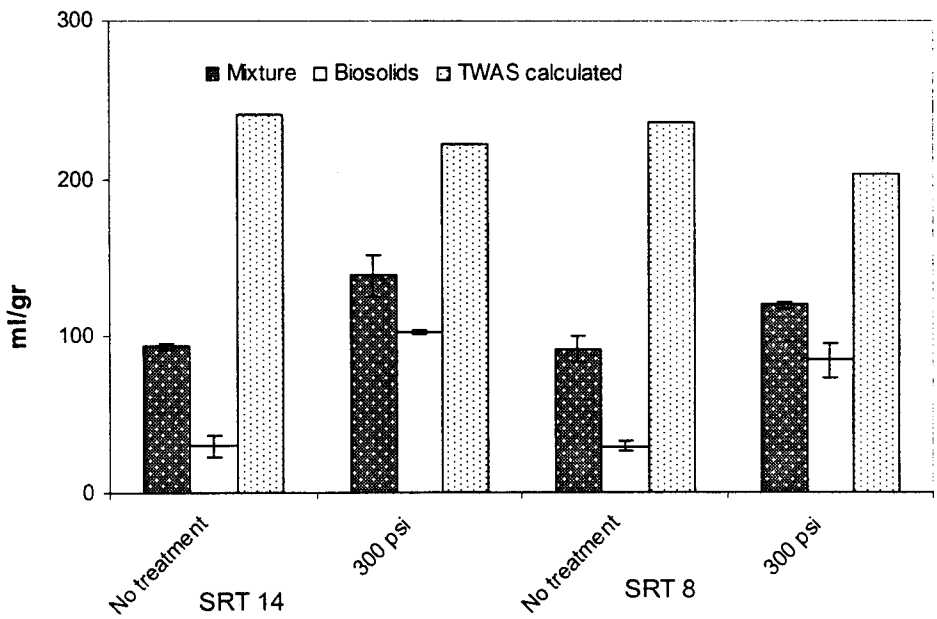

Figure 4.27 Biogas yield per gram of TS in the influent.

The calculation of TWAS biogas yield is shown in Table D.6. This calculation was performed using Equation 4.3

4.3.2 VS REMOVALS AND METHANE YIELD DURING SEMI-CONTINUOUS DIGESTION

The VS removals observed during semi-continuous digestion are presented in Figure 4.28 to Figure 4.31.The influent VS values were calculated according to the %VS of each sample and the TS of the feed. The feed was always prepared at 3% TS and the %VS was assumed to remain constant throughout the test since the feed was kept refrigerated to prevent any significant changes. The VS values of the effluents of the reactors were measured regularly. It can be observed from Figure 4.28 to Figure 4.31 that there was some variability in the measured effluent values of VS for the duplicate reactors. The standard deviation of daily values of VS in the effluents ranged from 2 to 11% for the different reactors. The average VS concentrations and standard deviations are shown in tables E.1 and E.2. Despite the variability in the daily effluent VS it was still possible to clearly observe a trend of VS destruction for the different samples.

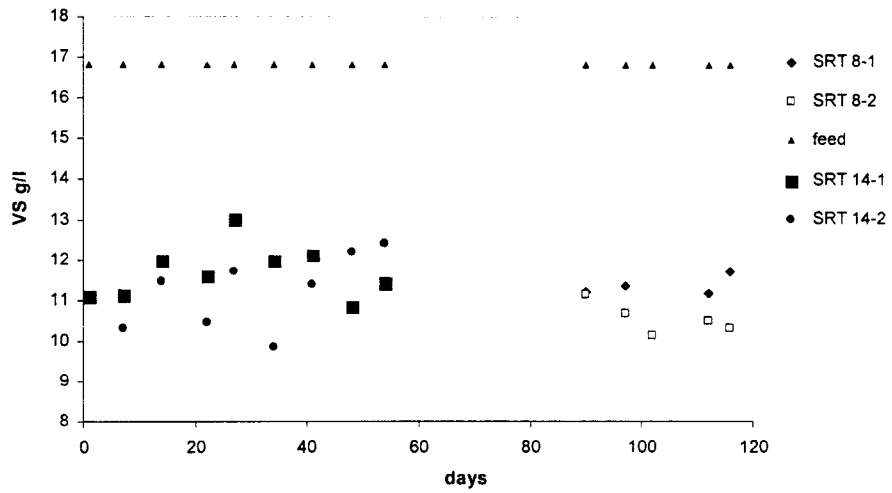

Figure 4.28 VS influent and effluents of mixture at 300 psi

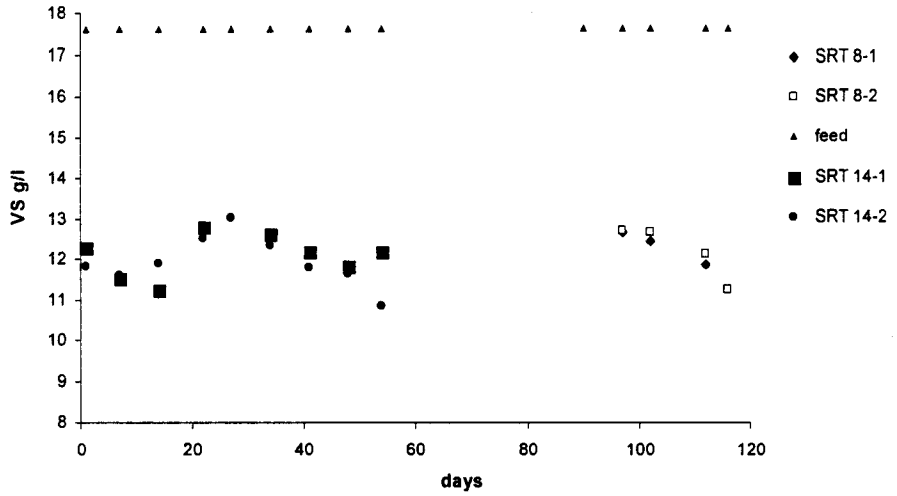

Figure 4.29 VS influent and effluent of mixture without pretreatment

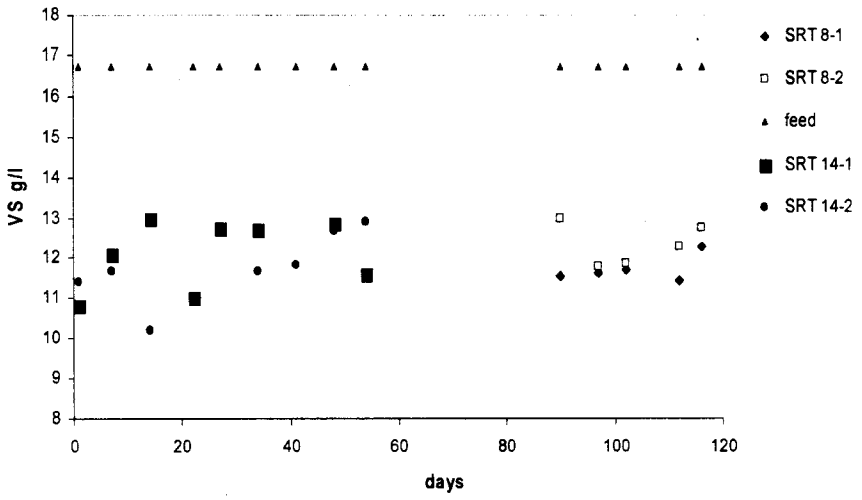

Figure 4.30 VS influent and effluent of biosolids at 300 psi

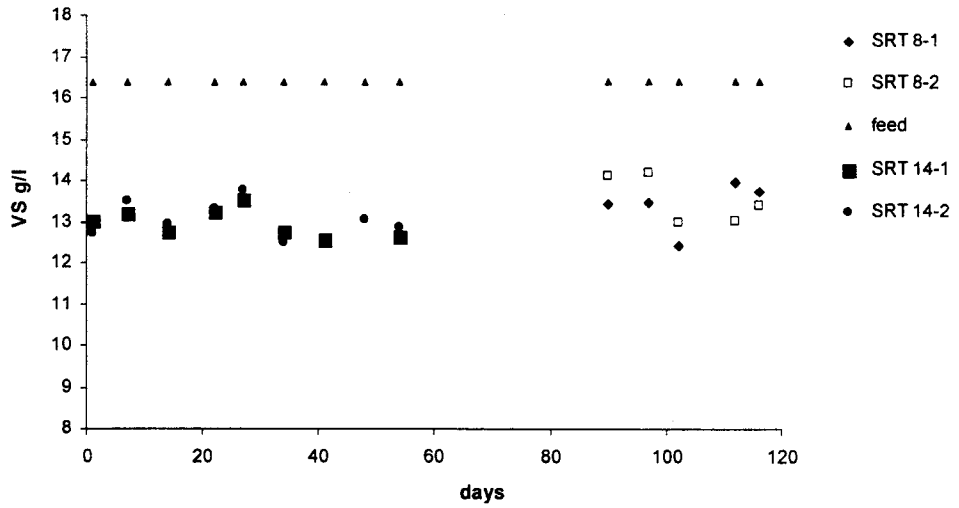

Figure 4.31 VS influent and effluent of biosolids without pretreatment

The average VS values in the influent and effluents of the semi-continuous digestion at SRT of 14 and 8 days are presented in Figure 4.32, corresponding percentage reductions are presented in Figure 4.33.The influent VS values were an average of duplicate analyses performed on the feed at the beginning of the test and the effluent VS were the average of all the VS measurements performed during digestion on each sample and its duplicate. The error for the influent values represents the difference between duplicate analyses. For the effluents the error represents the standard deviation of all VS measurements for the duplicate reactors. It can be observed that the VS in the influents were very similar for all the samples and that there was a significant reduction of VS during digestion for all the samples. The VS reduction at the lower SRT were similar to the reduction achieved at the 14 day SRT despite the higher initial loads.

From Figure 4.33 it can be observed that for the TWAS/biosolids mixture VS destruction tended to remain almost constant at around 30% with only slight improvements of the treated samples with respect to the controls. At the 14 day SRT the VS destruction improved

from 31 to 34% while at the 8 day SRT it increased from 29 to 35%. For the biosolids a more significant improvement over the controls was observed for both SRTs with changes from 20 to 29% at the 14-day SRT and 18 to 28% at the 8-day SRT. In general, the improvements for treated samples over the controls were more significant at the reduced SRT.

The calculation of VS destruction for the TWAS had somewhat unexpected results because at both SRTs the VS destruction calculated for the TWAS was higher for the control reactors than for the pretreated samples. However, TWAS VS removals for all the samples were between 35 to 50% which is within the range of expected values for this type of sludge. The unexpected results observed for the TWAS may possibly be attributable to inaccuracies in the assumption involved in the calculation, which is that the steam-explosion treatment would have the same effect on the biosolids treated alone than on the biosolids in the TWAS/biosolids mixture. One reason why this assumption may not be entirely accurate is because the biosolids alone were treated at 30% solids concentration while the TWAS/Biosolids mixture was treated at 15% solids concentration. The different water content in the two samples could affect the treatment.

In general, the VS removals observed for the mixture and the biosolids pretreated at 300 psi and without pretreatment were similar to the observed VS removals for the respective samples during the batch digestion. The exception was the pretreated mixture, which had a slightly lower reduction during semi-continuous digestion (Figure 4.17).

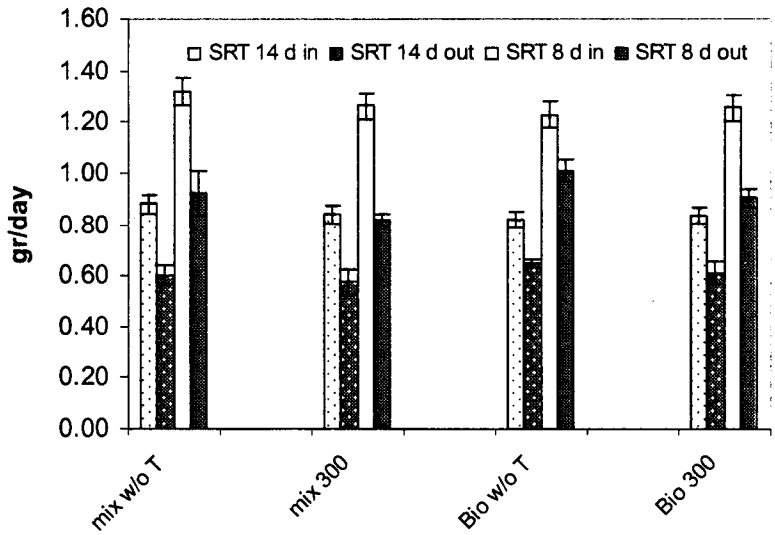

Figure 4.32 VS initial and final semi-continuous reactors

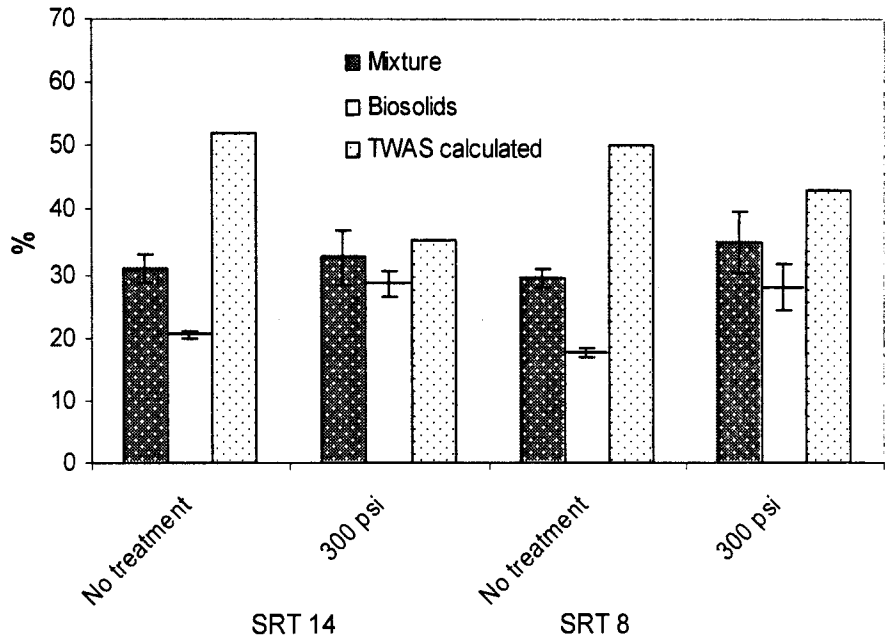

Figure 4.33 VS reduction during semi-continuous digestion

Figure 4.34 presents the methane yield per gram of VS removed during the semi-continuous digestion. The error bars represent the combined error of the differences of methane gas production and VS destruction between duplicate reactors. The overall average methane yield for the semi-continuous digestion was 370±119 ml CH_4 per gram of VS destroyed.

This value was 24% lower than the average methane yield for the corresponding samples of the batch test. This difference was possibly due to a small but systematic error in the biogas readings from the tedlar bags. It can be observed from Figure 4.34 that for most of the samples the yields were close to 400 ml/gr which are slightly lower that the theoretical value, which ranges from 450 to 600 ml/g (Malina and Pohland, 1992). The samples of biosolids without treatment showed very low yields at both SRTs. It is suspected that the biogas production from these reactors was higher than what were actually measured. Possibly the biogas measurements from the tedlar bags at smaller volumes was less accurate. The much higher biogas production observed for the pretreated biosolids as compared to the untreated biosolids also suggests that the untreated biosolids could have produced more biogas than what was recorded.

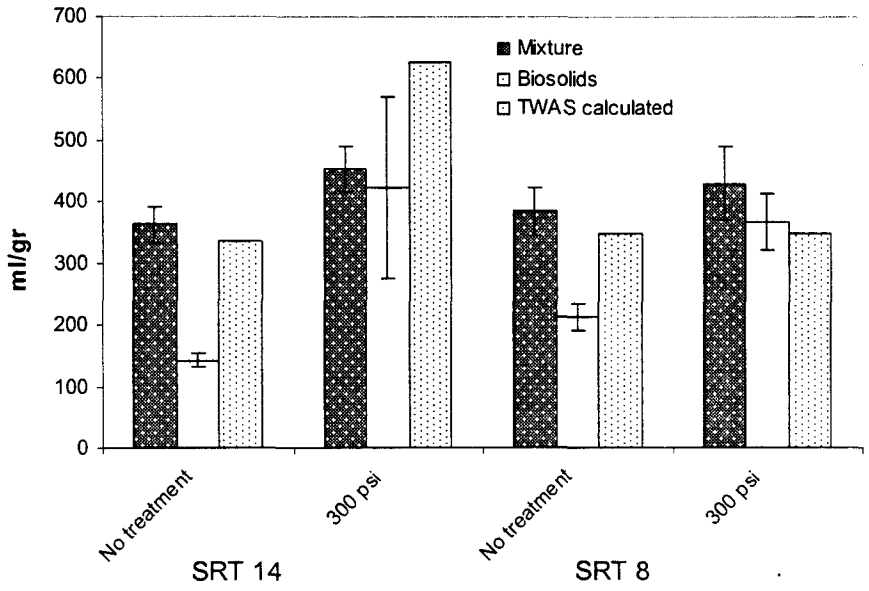

Figure 4.34 Methane yield per gram of VS removed.

Table D.7 presents the calculation of VS removal and methane yield for the TWAS during the semi-continuous digestion at SRT 14. This calculation was performed similarly to the calculation performed for the batch test using equations 4.6 to 4.12.

4.3.3 TOTAL AND SOLUBLE COD REMOVALS DURING SEMI-CONTINUOUS DIGESTION

Average TCOD concentrations of the influent and effluent of the semi-continuous reactors are presented in Figure 4.35. The influent TCOD concentrations are the average of 5 measurements performed at different times during digestion. The effluent TCOD concentrations for the 14 day SRT are the average of 4 measurements performed in the month that the digesters were run at steady-state for SRT 14-days. The average TCOD concentrations and standard deviations for the 14 day SRT are shown in table E.1. After the change to the 8-day SRT, the analysis of TCOD was done more frequently. The concentrations of TCOD for the 8-day SRT are the average of 9 measurements performed during the operation at this SRT. The average TCOD concentrations and standard deviations for the 8 day SRT are shown in table E.2. The error shown in Figure 4.35 represents the standard deviation of all the TCOD results obtained during the digestion.

From Figure 4.35 it can be observed that the initial TCOD concentration was slightly higher for the mixture pretreated at 300 psi than for the other samples; however, the initial TCOD concentration was reasonably similar for all the samples. It can also be observed that for all the samples there was a significant reduction in the TCOD concentration during digestion at both 14 and 8 day SRTs.

Figure 4.36 presents the TCOD removed during semi-continuous digestion at both the 14 and 8-day SRTs. It can be observed that at the 14-day SRT the TCOD removals were better for the control reactors than the reactors with the mixture pretreated at 300 psi. However the TCOD removal for the untreated mixture appears to be overly high given the biogas and VS results. The pretreated biosolids had a higher TCOD removal than the control at the 14-day SRT. At the 8-day SRT both the pretreated mixture and biosolids had higher TCOD removals than the controls.

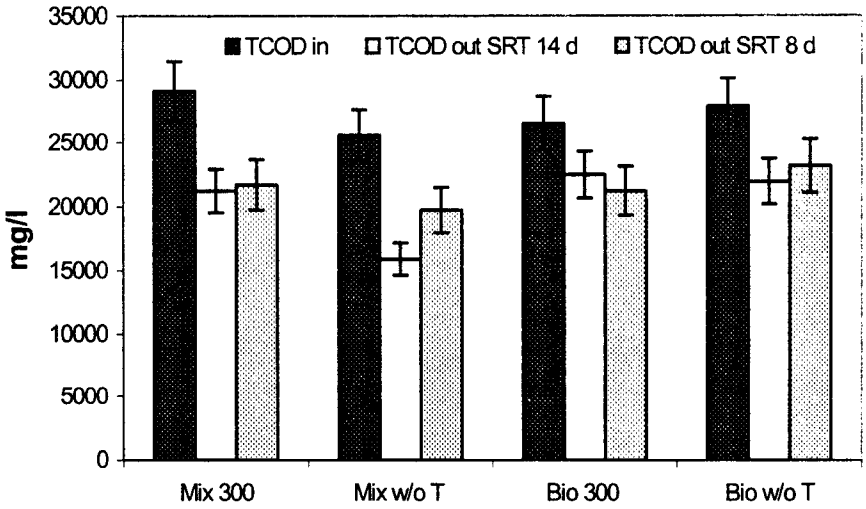

Figure 4.35 Average input and output TCOD concentration

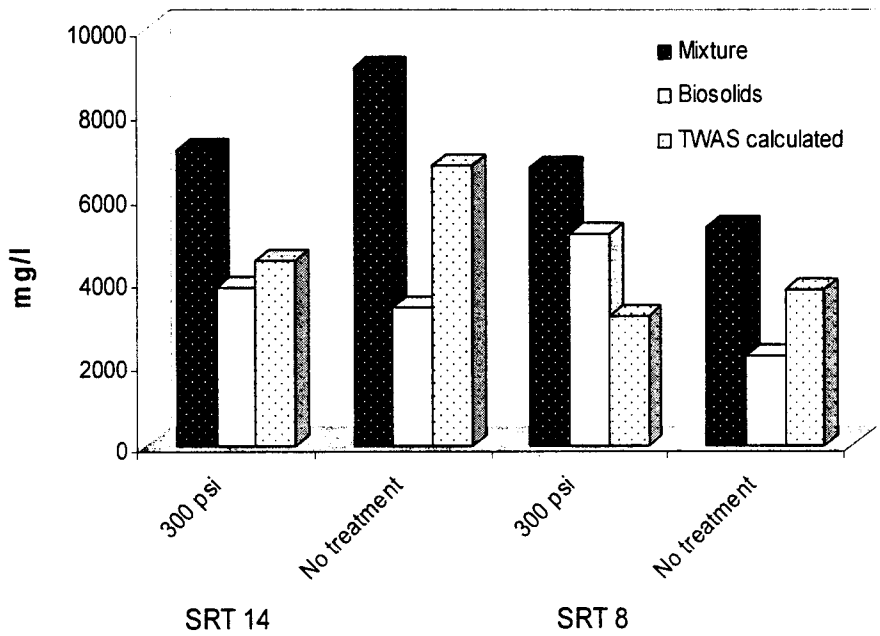

Figure 4.36 TCOD removed during semi-continuous digestion

Table D.8 presents the calculation of the TWAS TCOD removed during semi-continuous digestion at SRT 14. The following equations were used,

$$TCOD_{TWAS\_rem} = TCOD_{mix\_rem} - TCOD_{bio\_in\_mix\_rem} \quad \textbf{Equation 4-13}$$

$$TCOD_{bio\_in\_mix\_rem} = TCOD_{bio\_in\_mix} \times R_{bio} \quad \textbf{Equation 4-14}$$

Where,

$R_{bio} = \frac{TCOD_{bio\_rem}}{TCOD_{bio\_in}}$, measured for digestion of biosolids alone

$$TCOD_{bio\_in\_mix} = \left(\frac{TCOD}{TS}\right)_{bio} \times TS_{bio\_in\_mix} \quad \textbf{Equation 4-15}$$

$TCOD_{bio\_rem}$: TCOD removed during digestion of biosolids alone, mg/l

$TCOD_{bio\_in}$: TCOD added for the biosolids digestion, mg/l

$TS_{bio\_in\_mix}$: 70% of the TS added for the digestion of the mixture, g

SCOD analyses were performed with the same frequency as the TCOD analysis. Thus the average SCOD concentrations presented in Figure 4.37 are average values of the same number of measurements as mentioned above for the TCOD. The error is presented as the standard deviation of all the measurements. The average SCOD concentrations and standard deviations are shown in tables E.1 and E.2. From Figure 4.37 it can be observed that the influent SCOD concentrations for the samples pretreated at 300 psi were higher than the controls as expected. It is also observed that for all the samples there was a significant reduction in the SCOD concentration during digestion.

Figure 4.38 presents the SCOD removed during semi-continuous digestion at both SRTs of 14 and 8 days. It can be observed that the SCOD removals were better for the pretreated samples than for the controls. The change of SRT from 14 to 8 days did not seem to have any significant effect on the SCOD removals. The SCOD removals calculated for the TWAS

were relatively low. This result did not correspond to the higher biogas yields calculated for the TWAS.

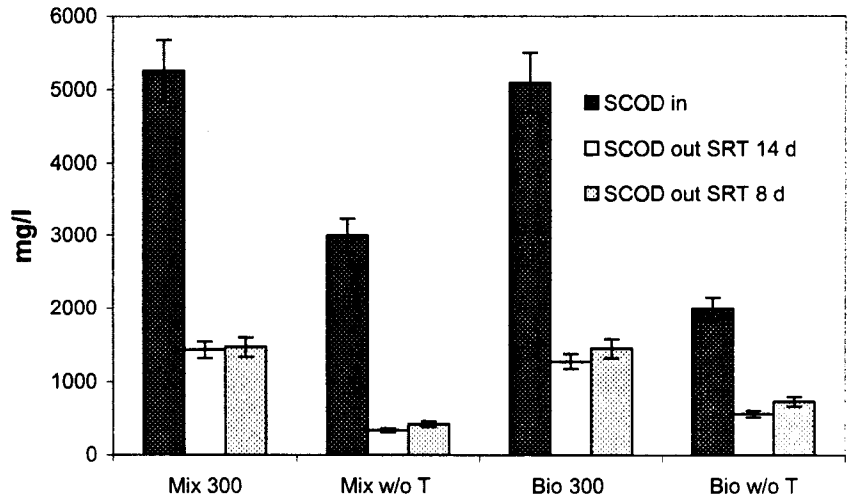

Figure 4.37 Influents and effluents average SCOD concentration

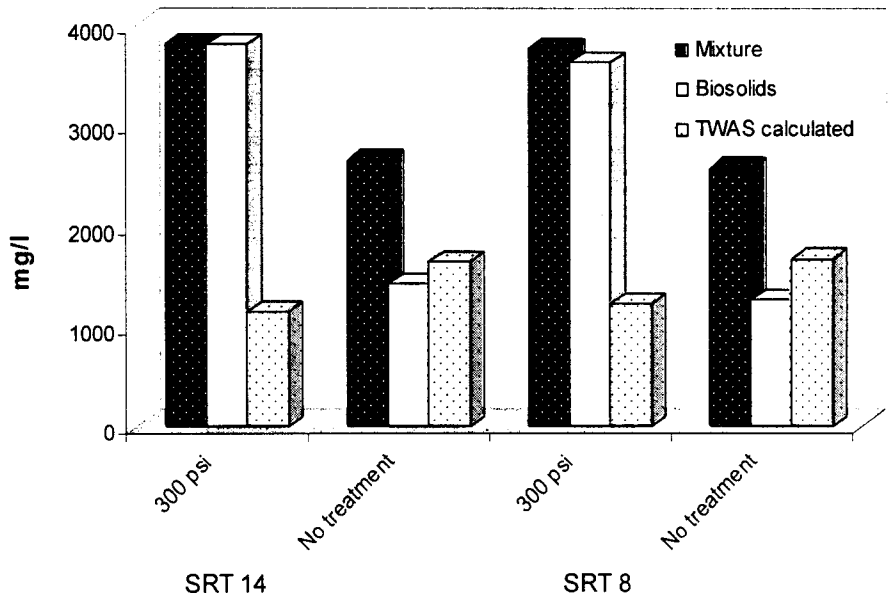

Figure 4.38 SCOD removed during semi-continuous digestion

The theoretical methane yield per gram of TCOD removed for anaerobic digestion at 35°C is 390 ml CH_4 per gram TCOD removed (Parkin and Owen, 1986). However some variability

has been observed in the yields reported in the literature with values ranging from 100 to 350 ml/g COD removed at STP (Droste, 1997). The methane yields for the semi-continuous digestion of the TWAS/biosolids mixture and the biosolids after pretreatment at 300 psi and controls are presented in Figure 4.39. The TWAS yields calculated based on the expected contribution of the biosolids in the mixture are also shown in Figure 4.39. The error presented is the combined error of the differences between TCOD and methane gas values of duplicate reactors. It can be observed that most of the samples had methane yields that were reasonably close to the theoretical value. However, the mixture without pretreatment had a low yield at the 14-day SRT. This occurred because the COD removals for these reactors were unexpectedly high. The yield for the biosolids without pretreatment at the 14-day SRT was also quite low. For these reactors the COD removals were not high but the biogas production was relatively low. This suggests again that the biogas production for the biosolids without pretreatment could have been higher that what was actually measured, as discussed earlier.

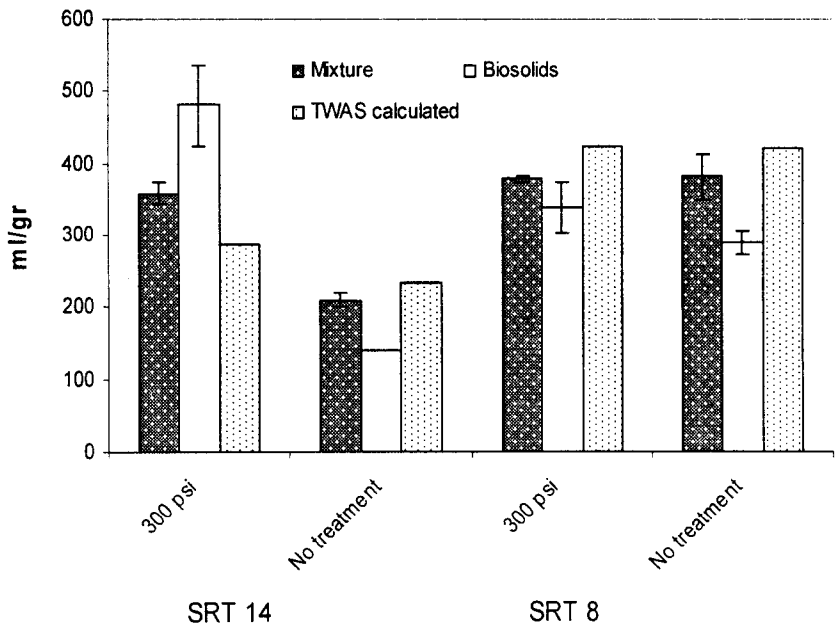

Figure 4.39 Methane yield per gram of TCOD removed during semi-continuous digestion.

4.3.4 EFFLUENT VFA, ALKALINITY AND AMMONIA

The influent VFA concentrations for the pretreated samples of the mixture and biosolids were relatively high at 1500 and 1200 mg/l respectively. The sample of mixture without pretreatment had a lower TVFA concentration of 500 mg/l and the biosolids without pretreatment had a low TVFA concentration of just 50 mg/l. During start-up the TVFA concentrations in the effluents of the reactors were similar to the influent TVFA concentrations, which indicated that there was no removal of VFA during this period. After the first 20 days of operation the VFA concentrations were significantly lower than the influent concentrations and then they were relatively constant throughout the test. The total VFA concentrations in the effluents of all reactors were in the range of 50–500 mg/l which is within the normal range for anaerobic digestion operation (Table 2-2).

Figure 4.40 to Figure 4.43 present the VFA concentrations in the effluent of the reactors, during the runs at 14 and 8-day SRT, after the start-up period. Butyric and propionic acid, known to be the most toxic volatile acids to the methanogenic bacteria, had low concentrations throughout the digestion. For all reactors the concentration of butyric acid was lower than 40 mg/l and propionic acid was not measured in any of the reactors. This suggests that there was a healthy environment for the microorganisms throughout the test.

By comparing Figure 4.40 and Figure 4.41 it can be observed that the effluents of the reactors with mixture pretreated at 300 psi had higher VFA concentrations than the effluents of the reactors with the mixture without pretreatment at both 14 and 8-day SRTs. However the VFA removals were higher for the reactors with the mixture pretreated at 300 psi because the influent VFA concentration for these reactors was much higher than for the control reactors. The higher methane production observed during digestion of the mixture pretreated at 300 psi as compared to the control also indicates that there was a higher conversion of acetic acid to methane gas in the reactors with the pretreated mixture.

By comparing Figure 4.42 and Figure 4.43 it can be observed that the effluents of the reactors with biosolids pretreated at 300 psi had higher VFA concentrations than the effluents of the reactors with biosolids without pretreatment which had very low VFA concentrations. Again there was a much higher VFA concentration in the influent of the reactors with the pretreated biosolids. Thus in these reactors there was a higher removal of VFA, which also corresponded to the higher biogas production, observed for the reactors with the pretreated biosolids.

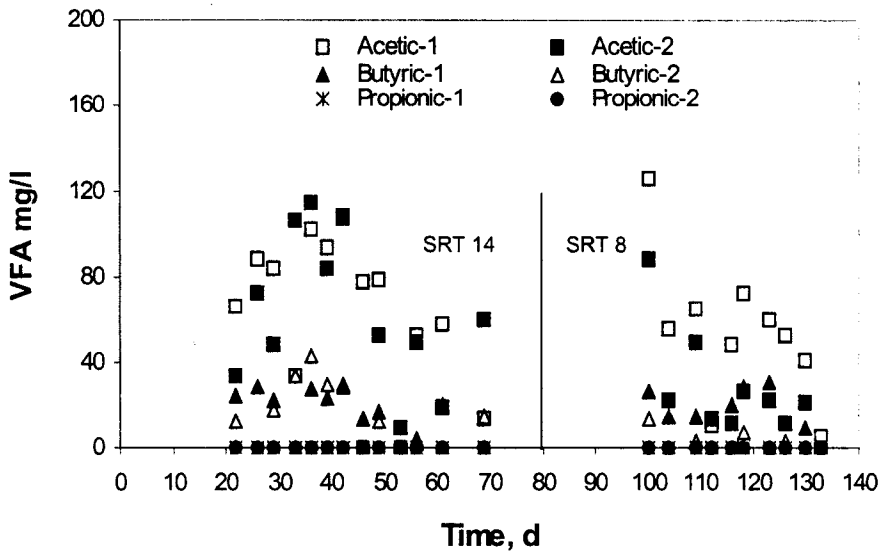

Figure 4.40 VFA concentrations during digestion of mixture pretreated at 300 psi

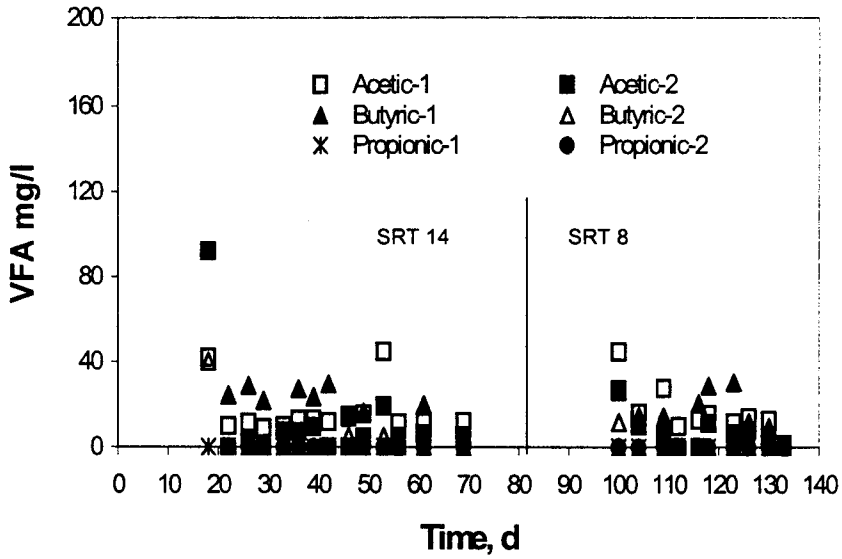

Figure 4.41 VFA concentrations during digestion of mixture without pretreatment

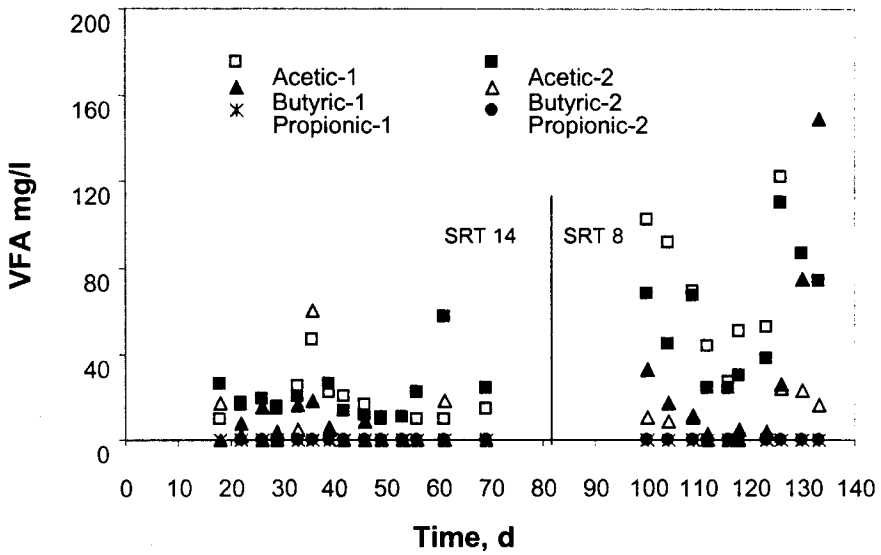

Figure 4.42 VFA concentrations during digestion of biosolids pretreated at 300 psi

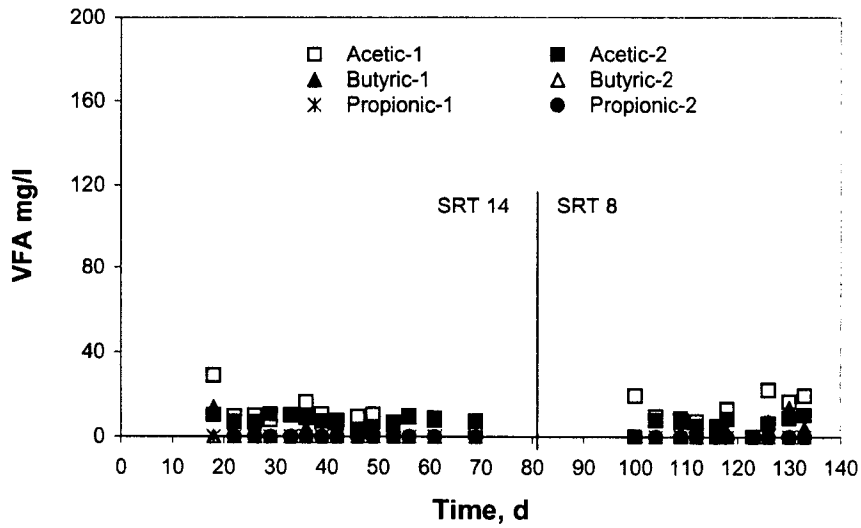

Figure 4.43 VFA concentrations during digestion of biosolids without pretreatment

Bicarbonate alkalinity was added initially to the reactors to provide enough buffer capacity to avoid acidification of the reactors due to VFA production. All reactors were started with a concentration of 4000 mg/l in addition to the alkalinity that was already present in the sludge. Therefore there was a high initial alkalinity concentration at the starting of the digestion for all the samples.

Figure 4.44 to Figure 4.47 present the bicarbonate alkalinity measured in the effluent of the reactors digesting the samples pretreated at 300 psi and the control samples at both 14 and 8-day SRTs. It can be observed that for all the samples the duplicate reactors showed almost identical effluent alkalinity values throughout the test. The initial high alkalinity concentration was reduced after approximately 40 days of digestion for all the samples. In general, the alkalinity concentrations that were maintained throughout digestion were within the optimum range of 2000 to 3000 mg/l suggested in the literature (Table 2-2). The exception was the reactors treating the biosolids without pretreatment for which the alkalinity

concentration was slightly lower than the optimum range. However, these reactors were never in an extreme operational condition.

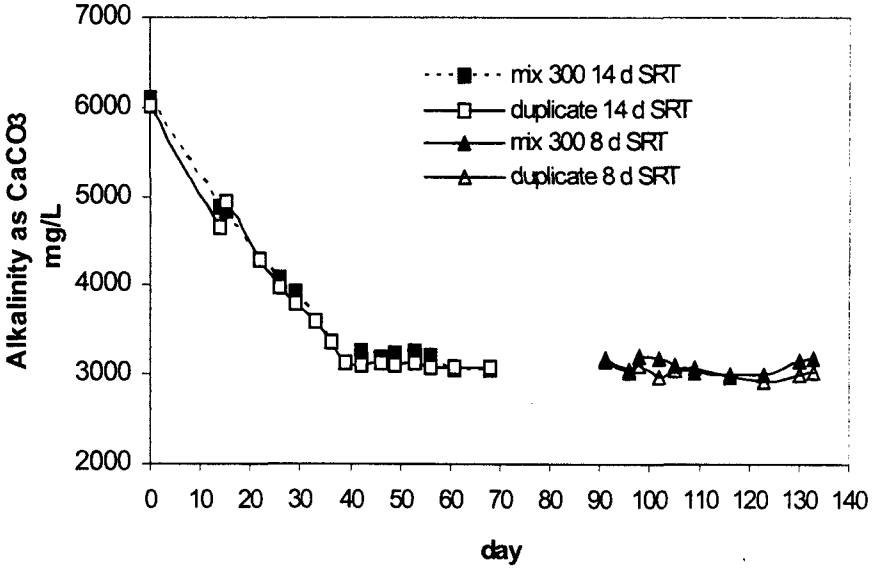

Figure 4.44 Bicarbonate alkalinity during digestion of mixture pretreated at 300 psi

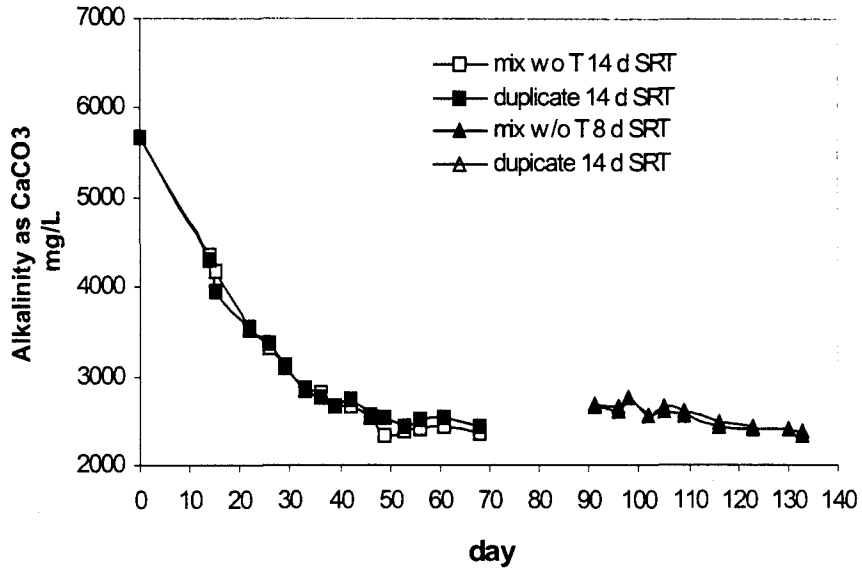

Figure 4.45 Bicarbonate alkalinity during digestion of mixture without pretreatment

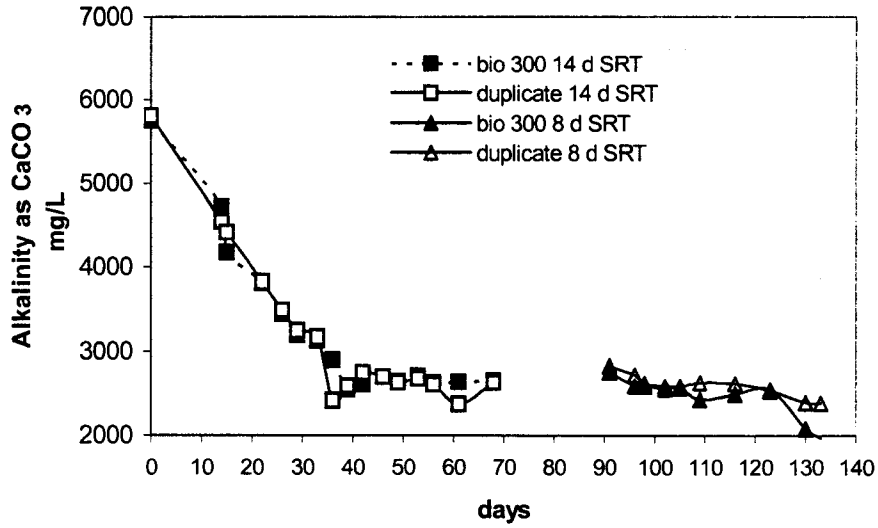

Figure 4.46 Bicarbonate alkalinity during digestion of biosolids pretreated at 300 psi

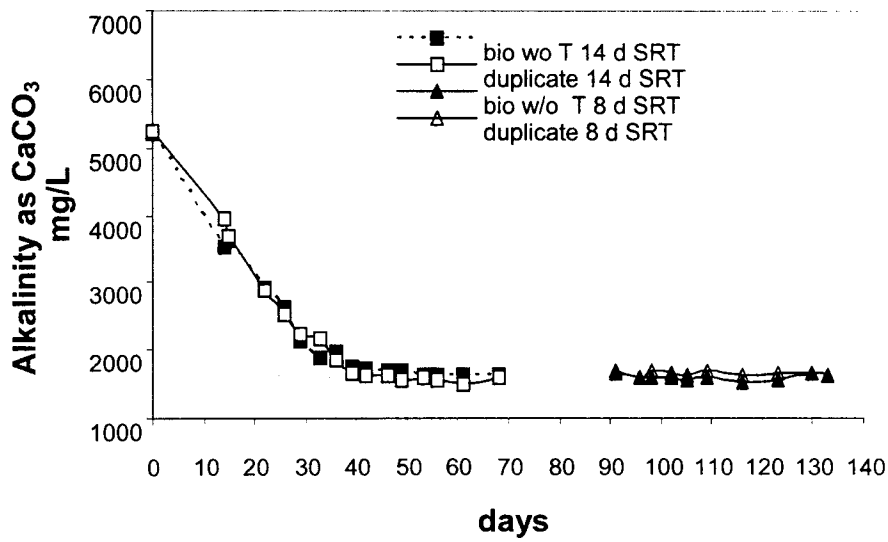

Figure 4.47 Bicarbonate alkalinity during digestion of biosolids without pretreatment

Figure 4.48 shows the effluent ammonia concentrations of reactors treating the TWAS/biosolids mixture and biosolids pretreated at 300 psi and without pretreatment, during digestion at the 14-day SRT. The average ammonia concentrations and standard deviations for the 14 day SRT are shown in table E.1. Figure 4.49 shows the effluent ammonia concentrations during digestion at the 8-day SRT. The average ammonia concentrations and standard deviations for the 8 day SRT are shown in table E.2. The ammonia concentrations of duplicate reactors are shown in separate series. From Figure 4.48 and Figure 4.49 it can be observed that the duplicate reactors had very similar effluent ammonia concentrations and that the ammonia concentrations for all samples remained reasonably stable during the digestion.

Since ammonia results from the hydrolysis of organic nitrogen present in the sludge, then higher release of ammonia during digestion indicates a higher digestion of organics in the reactor. Figure 4.50 presents the ammonia released during semi-continuous digestion of the control samples and the pretreated samples. From Figure 4.50 it can be observed that the pretreated biosolids and the TWAS/biosolids mixture released more ammonia than the controls during digestion. The biosolids samples had greater increase over the control than the mixture. This result corresponds with the trends of biogas production observed during digestion (Figure 4.26).

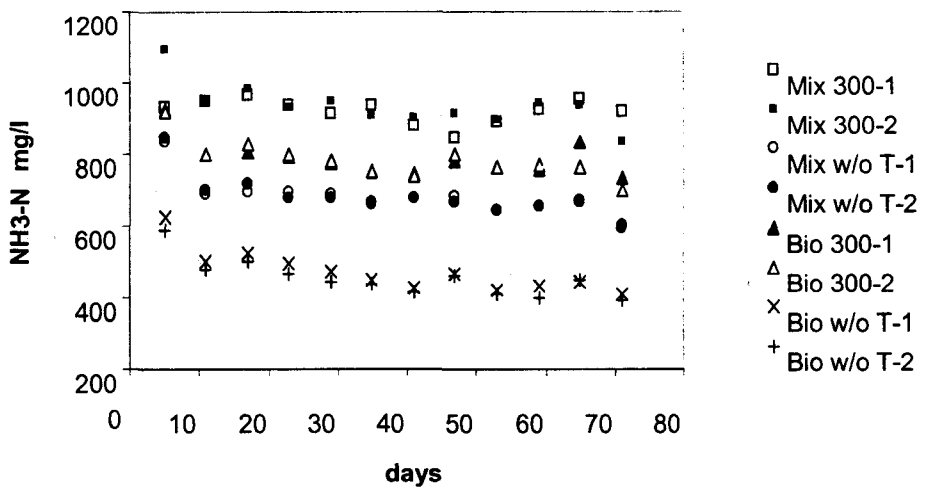

Figure 4.48 Ammonia concentration during digestion at 14-day SRT

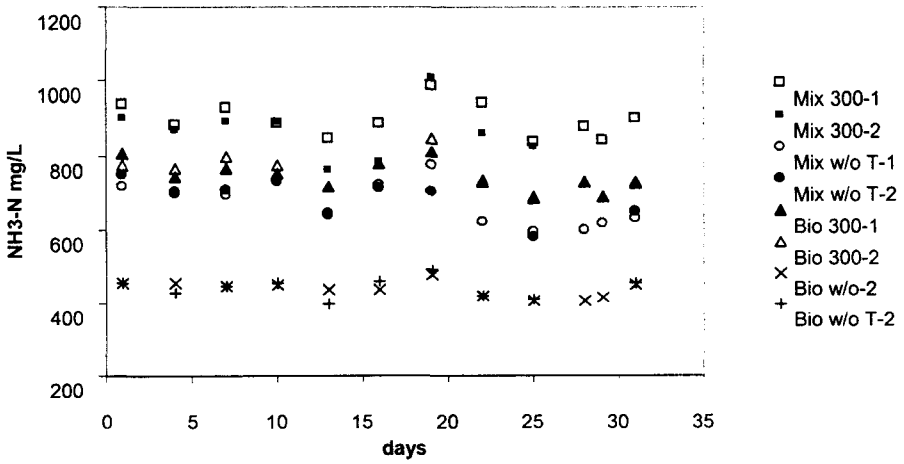

Figure 4.49 Ammonia concentration during digestion at 8-day SRT

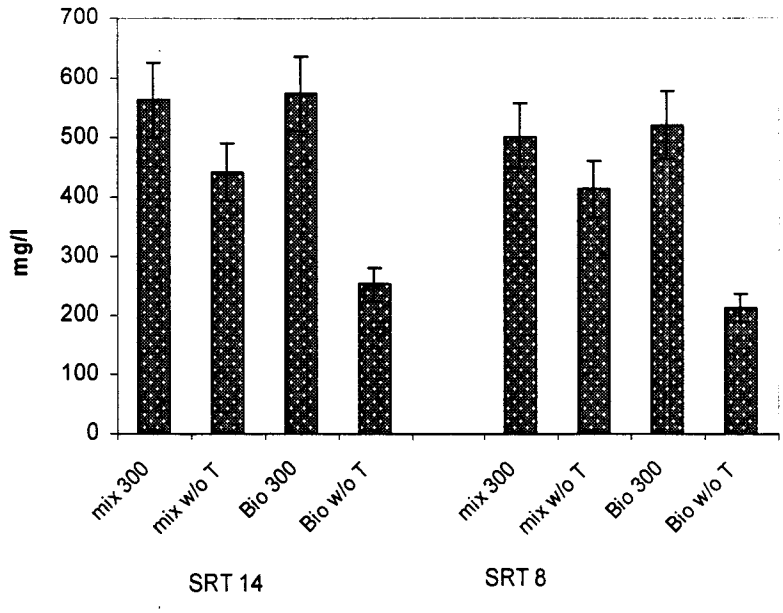

Figure 4.50 Ammonia released during digestion

4.3.5 DEWATERABILITY OF DIGESTED SLUDGE

The CST test was performed in order to evaluate the effect of pretreatment on the dewaterability of the sludge. The CST value is a measure of the time that a sludge takes to release its water. Therefore, a low CST indicates a rapid release of the sludge's water and a better expected performance during dewatering. Figure 4.51 presents the average CST values measured in the effluents of the semi-continuous reactors. The values presented are an average of 15 measurements. The measurements were performed on five different samples of the effluent and for each sample three readings were performed. The error bars represent the standard deviation of the 15 measurements.

Figure 4.51 shows that there was a significant improvement in the CST values for the pretreated samples over the control reactors. The mixture pretreated at 300 psi had a CST value that was 32% less than the control and the biosolids pretreated at 300 psi had a CST

value that was 45% less than the control. These results indicate that the steam-explosion pretreatment at 300 psi improved the dewaterability of the sludge.

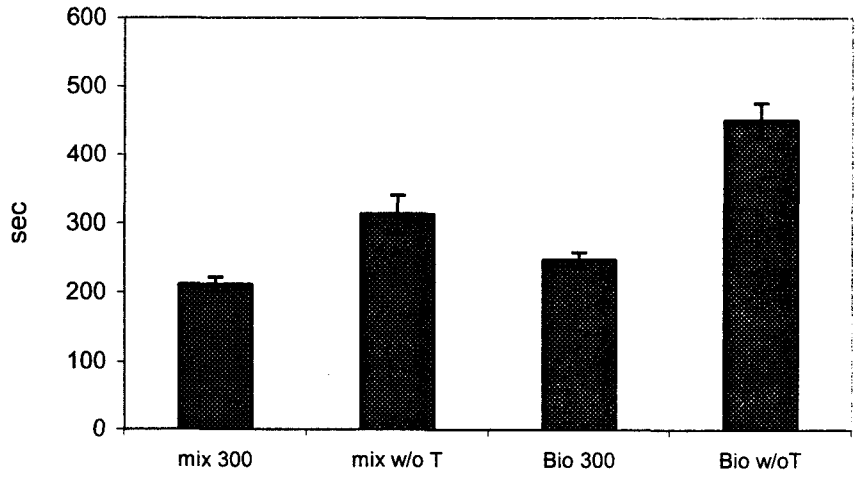

Figure 4.51 Average capillary suction time of semi-continuous digestion effluents

4.3.6 ENERGY CONSUMPTION AND GENERATION

Energy requirement

One factor that must be considered when evaluating sludge pre-treatment technologies is the energy consumed to pretreat the sludge. For this study the energy requirements for the steam-explosion pretreatment were provided by SUBBOR. Table 4-1 presents the energy requirements to treat one tonne of sludge at three different steam-explosion conditions.

Table 4-1 Energy requirement for steam-explosion.

Pressure (psi)	Cooker temperature (°C)	Energy requirement (*MBTU/tonne sludge)
150	186	285
300	216	360
600	254	476

*MBTU = million BTU

Source: Personal communication with HuaWu Liu from SUBBOR, February 2004.

The energy requirements presented in Table 1 were calculated for a sludge with 30% solids concentration. Therefore these values are representative of the energy used during the pretreatment of the biosolids, which were exploded at 30% solids.

Energy production

Knowing that the energy content of methane is about 1000BTU/ft^3 (35315 BTU/m^3) (Malina and Pohland, 1992) the surplus energy production during anaerobic digestion of pretreated samples can be easily estimated from the additional methane gas that was produced during digestion of pretreated samples over the control samples.

The additional energy production per tonne of sludge that would be produced from the enhanced methane gas production during anaerobic digestion of the pretreated biosolids is presented in Table 4-2. The calculation of the additional energy produced was performed as follows:

$$CH_{4\_sample}(ml/g) = \frac{CH_{4\_produced}(ml)}{TS_{added}(g)}$$

$$CH_{4\_add}(ml/g) = (CH_{4\_sample} - CH_{4\_control})$$

$$CH_{4\_add\_per\_ton\_sludge}(m^3/ton) = CH_{4\_add} \times \frac{300000gTS}{ton\_sludge} \times \frac{1m^3}{10^6 ml}$$

$$E(MBTU/ton) = CH_{4\_add\_per\_ton\_sludge} \times \frac{0.035315MBTU}{m^3}$$

where,

CH_{4_sample}: Methane volume produced per gram of TS added to the digester.

CH_{4_add}: Additional methane volume produced per gram of TS during digestion of pretreated sample over control sample.

$CH_{4\_add\_per\_tonne\_sludge}$: Additional methane produced per tonne of biosolids

Table 4-2 Surplus methane and energy production during digestion of pretreated samples.

Sample	Methane production (ml)	Methane production per gram TS (ml/g)	Additional methane production (ml/g)	Additional methane per tonne sludge (m^3/tonne)	Additional energy produced (MBTU/tonne sludge)
Control	837	56	-	-	-
150 psi	1021	68	12	3.7	0.1302
300 psi	1451	97	41	12.3	0.4338
600 psi	1350	90	34	10.3	0.3622

The results show that the input energy required by the steam-explosion pretreatment was much greater than the additional energy gains obtained from the digestion of the treated biosolids. Even for the optimum treatment condition of 300 psi the energy input was 800 times greater than the additional energy production. However it should be noted that the pretreatment apparatus employed in this study did not have any kind of energy recycling. The steam-explosion was conducted in batch operation releasing the steam after each explosion. If the steam was recycled there would have been substantial energy savings. In addition, if the steam-explosion were to be implemented in a continuous full-scale operation, the heating of the sludge to thermophilic temperatures would no longer be required since the heat produced by the steam-explosion could be used for this purpose resulting in significant energy savings. Also due to the high temperatures used during pretreatment extra heat would be available from the treated sludge for recirculation into the system, e.g. to preheat incoming sludge. The viability of the pretreatment must consider the energy balance in a

closed-loop system with steam recirculation and also could possibly require an optimization of the pretreatment apparatus for increased efficiency.

The energy balance conducted in this study only considered steam explosion of the digested biosolids as this was the only stream that could be directly employed in the steam explosion process with the existing dewatering equipment. If the TWAS stream could be thickened sufficiently, the energy balance may have been much more favourable.

It should be noted that despite the high improvements in methane production observed for the pretreated biosolids as compared to the control, the additional methane gas that can be produced from the biosolids is still relatively low in absolute terms because a high percentage of the organic matter in the biosolids has already been degraded in previous digestion. Hence the additional energy that can be produced is also relatively low.

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The high pressures and temperatures of the steam-explosion treatment were found to cause solubilization of particulate substrate as shown by the increases in SCOD. Pretreatment at 150 psi increased the SCOD by roughly 2-fold for the TWAS/biosolids mixture, by 4-fold for the biosolids as compared to the controls, while the calculated increase over the control for the TWAS was 41%. Pretreatment at 300 psi increased the SCOD by 8, 18 and 4 fold for the TWAS/biosolids mixture, the biosolids and the TWAS respectively as compared to the controls. Pretreatment at 600 psi caused similar SCOD improvements as those observed with pretreatment at 300 psi, which indicates that most of the sludge organics were already solubilized with pretreatment at 300 psi and there was no need for additional pressure.

Overall, we may conclude that the degree of solubilization of the sludge was significantly increased with pretreatment. After pretreatment at 300 and 600 psi, around 40% of the organics were soluble for both the TWAS/biosolids mixture and the biosolids. After pretreatment at 150 psi the degree of solubilization did not improve significantly, although it was higher than that of the untreated sludge; around 15% of the organics were soluble after pretreatment at 150 psi while a degree of solubilization lower than 10% was observed for all untreated sludges.

In general, ammonia and VFA concentrations increased after pretreatment for both the TWAS/biosolids mixture and the biosolids, which was an additional indication of organic matter solubilization during pretreatment.

Batch anaerobic digestion of pretreated TWAS/biosolids mixture and biosolids showed a clear improvement in biogas production compared to the controls. This result indicates that the organics that were solubilized were converted to methane gas during digestion. Higher

SCOD removals observed during the digestion of the pretreated samples also indicated that the soluble organics generated during pretreatment were transformed to methane.

For the TWAS/biosolids mixture there was a higher increase in biogas production as the pretreatment intensity increased. However, despite the higher increase in biogas production for the mixture pretreated at 600 psi, the acclimation period of the bacteria to this sample was longer than for the other pretreatments and the biogas production rate was also slower. Given these drawbacks and the fact that more energy is required for pretreatment at higher pressure (600 psi), pretreatment at 300 psi was found to be the optimum condition for the TWAS/biosolids mixture. Pretreatment at 150 psi required less energy but the improvement in biogas production after this pretreatment was not as significant.

For the biosolids, pretreatment at 300 psi represented the best improvement in biogas production. The sample pretreated at 600 psi had a lower biogas production than the pretreatment at 300 psi and also required a longer acclimation period and showed a slower biogas production rate. Improvement in biogas production after the 150 psi pretreatment was not as significant as the improvement obtained with the 300 psi pretreatment. Therefore the latter was selected as the optimum pretreatment intensity for the biosolids.

The long acclimation and slower biogas production rates observed for all samples pretreated at 600 psi suggests that high pressure and temperature may produce organics toxic to the anaerobic microorganisms. On the other hand, it is possible that this inhibition may have resulted from acidification of the reactors due to the higher load of soluble readily degradable organics present in the sludge after pretreatment at 600 psi. There was insufficient information to conclude which was the exact cause of the inhibition observed.

The VS removals observed during the batch digestion for the untreated samples were low as was expected due to the characteristics of the sludge. The biosolids, which had been previously digested, were not expected to have a high VS reduction. The observed VS

reduction for the biosolids was only 19%. Given the high proportion of biosolids in the mixture, this sample was not expected to have a high VS reduction, although somewhat better results than the biosolids could be expected because of the TWAS present in the mixture. A VS destruction of 28% was observed for the mixture without pretreatment while the TWAS without pretreatment had a VS reduction of 48%, which was in the typical range for this type of sludge.

The VS destruction for the pretreated samples was in all cases higher than the controls. The TWAS/biosolids mixture had very similar VS destruction at all the pretreatment intensities, with a VS reduction of around 39% while the control sample had a VS reduction of only 28%. For the biosolids, VS destructions of around 34% were observed for all the pretreatments intensities while the control had only a 19% VS reduction. The VS destruction calculated for the TWAS was similar after pretreatment at 300 and 600 psi, with a high VS reduction of around 55%, while the control TWAS had a VS destruction of 40%. The calculated value for the TWAS without pretreatment agreed well with the TWAS control. Despite the higher VS removals observed for the pretreated samples as compared to the controls the similar responses observed for the samples pretreated at different intensities did not correspond to the observed biogas production. Consequently, the methane yield per gram of VS destroyed showed some variability. However for most of the samples the yields were reasonably close to the theoretical values.

The SCOD removed during batch digestion was significantly better for the samples pretreated at 300 psi than the controls for both the TWAS/biosolids mixture and the biosolids. At 150 psi pretreatment both samples had higher SCOD removals than the control but the removal was not as significant as with pretreatment at 300 psi. The high SCOD removal for samples pretreated at 150 and 300 psi suggests that the organics solubilized during pretreatment were easily digested in the anaerobic digestion. The SCOD removals

after pretreatment at 600 psi were slightly lower than with pretreatment at 300 psi. This seems to indicate that during digestion of the samples pretreated at 600 psi the microorganisms were not able to digest some of the soluble organics that were produced after this pretreatment. The results of SCOD reduction during batch digestion corroborated that pretreatment at 300 psi was the optimum to enhance anaerobic digestion.

Digestion in semi-continuous reactors showed that the results observed for the TWAS/biosolids mixture and the biosolids during batch digestion were sustainable during prolonged operation. The mixture pretreated at 300 psi presented 49 and 31% higher average daily biogas production over the controls at the 14 and 8-days SRT respectively. The increases over the controls for the biosolids were 229 and 184% at the 14 and 8-day SRTs respectively. The biogas yields were better for the pretreated TWAS/biosolids mixture and the biosolids as compared to the controls at both 14 and 8-day SRT. On the other hand the biogas yield calculated for the TWAS did not show improvement over the control at both 14 and 8-day SRT.

The ammonia, VFA and alkalinity concentrations monitored during the semi-continuous digestion showed that all the reactors were operating at optimal conditions all throughout the test. This was correlated well with the stable biogas and methane production during digestion.

The VS removals during semi-continuous operation were similar at both the 14 and 8-day SRT. The pretreated TWAS/Biosolids mixture had slightly better VS reduction than the control, with values of around 30% for the control sample and around 35% for the pretreated sample. For the biosolids, the VS reduction improvements as compare to the controls were better than those observed for the TWAS/biosolids mixture. This correlated well with the better biogas production relative to the controls observed for the biosolids. Control samples of biosolids had VS reduction of around 19% while the pretreated biosolids had a VS

reduction of around 29%. The calculated VS removals for the TWAS were better for the control samples at both SRTs. The control sample had a VS reduction of around 50% at both the 14 and 8-day SRT and the pretreated TWAS had a VS reduction of 35 and 43% at the 14 and 8-day SRT respectively.

Similarly to the batch test results, SCOD removals during semi-continuous digestion were significantly better for the pretreated TWAS/biosolids mixture and biosolids than the controls. This result agrees well with the higher biogas production observed during the digestion of pretreated samples.

The digestion in semi-continuous operation showed that it was possible to maintain stable digestion even at a relatively short 8-day SRT, which means that the anaerobic bacteria were able to rapidly process the organics that resulted from the pretreatment at 300 psi. Digestion of samples without pretreatment was also stable at 8-day SRT, however the biogas production and VS destruction were relatively poor.

The methane yields per gram of VS destroyed observed during the semi-continuous digestion were somewhat lower than the corresponding methane yields of the batch digestion. This difference was possibly the result of a small but systematic error in the biogas readings from the tedlar bags. The biosolids without pretreatment had a particularly low methane yield. This was suspected to be the result of smaller reading of biogas than the actual biogas production due to an error in the biogas measurements from the tedlar bags for small biogas volumes. The methane yield per gram of TCOD destroyed was also low for the biosolids without treatment. This again suggests that the biogas measurement for these samples were low. The methane yield for the mixture without treatment at the 14-day SRT was low because the TCOD removal for this sample was unexpectedly high. For the other samples the methane yields per gram of TCOD removed were reasonably close to the theoretical value.

From the batch test results, the estimation of the effect of the pretreatment on the TWAS based on the effect of pretreatment on the TWAS/biosolids mixture and the biosolids seemed to be reasonably accurate since, for most parameters the calculated value for the TWAS without pretreatment was reasonably close to the TWAS control, which validated the result of the calculations for the TWAS for those parameters. The batch test results showed that there was a significantly positive effect of the pretreatment on the TWAS, at both 300 and 600 psi but more significantly at 600 psi. These results generally corresponded well to the solubilization results observed after pretreatment.

In contrast, the results of the semi-continuous digestion tests did not corroborate the results of the batch test for the TWAS. The parameters calculated for the TWAS based on the effect of pretreatment on the TWAS/biosolids mixture and the biosolids during semi-continuous digestion consistently showed that there was no improvement for the treated TWAS over the controls. The most likely explanation for these unexpected results is that the contribution of the pretreated biosolids in the pretreated TWAS/biosolids mixture was consistently overestimated resulting in an underestimation of the TWAS contribution. The overestimation of the biosolids contribution most likely resulted from the pretreatment being more effective on the biosolids alone than on the biosolids in the TWAS/biosolids mixture because of the higher solids content of the biosolids (30% TS) as compared to the mixture (15 % TS) at the moment of pretreatment. The higher water content in the TWAS/biosolids mixture resulted in less energy applied to the solid particles for the same treatment intensity. Another factor that may contribute to the low values obtained for the parameters of the treated TWAS during semi-continuous digestion is the fact that this experiment was only carried out with samples treated at 300 psi which was the optimum treatment intensity for the biosolids (batch tests) and not for the TWAS. This may reinforce the overestimation of the biosolids contribution in the TWAS/biosolids mixture.

In general, the pretreatment was observed to produce significant improvements for both the TWAS/biosolids mixture and the biosolids. This observation was consistent in all phases of the study, including the batch and semi-continuous tests. The treatment solubilized organics present in the biosolids, which were then readily converted to biogas during digestion. In regards to the TWAS, based on the results of solubilization and the results of the batch test and despite the results of the semi-continuous digestion, the pretreatment is considered to be promising for improving the digestability and methane production of this type of sludge.

In regards to the dewaterability it was found that pretreatment at 300 psi improved the dewaterability of the TWAS/biosolids mixture and the biosolids as shown by a decrease in the CST values.

The cost-effectiveness of this technology has to be evaluated based on continuous operation of the pretreatment and anaerobic digestion systems. This operation must include the recirculation of steam and the use of the heat from the pretreated sludge. Additionally, other factors such as the reduction of residual sludge disposal due to improved VS destruction and dewaterability of sludge after pretreatment could be considered.

5.2 RECOMMENDATIONS

Further research work could include the following:

Conducting analysis of the organic compounds present in the sludges before and after steam-explosion pretreatment to determine if substances that are potentially toxic for anaerobic microorganisms are formed during the pretreatment.

Performing particle size distribution analysis to the sludge before and after the steam-explosion pretreatment to determine changes in particulate matter during the pretreatment.

Conducting analysis of pathogenic microorganisms such as e. coli and salmonella in order to determine the viability for land application of the pretreated sludge.

Performing energy balances for a system operation with energy recirculation including steam recycling, use of heat from pretreated sludge and use of surplus energy generated from the enhanced biogas production during anaerobic digestion.

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APPENDIX A SUMMARY OF RESULTS WITH VARIOUS DISINTEGRATION MECHANISIMS FROM LITERATURE REVIEW

Table A.1 Research findings for various disintegration mechanisms on different types of sludge.

		After disintegration		Anaerobic digestion				After digestion	
Author	**Method**	**Degree of disintegration. SCOD/TCOD (%)**	**Ammonia concentration (mg/l)**	**VS destruction (%)**	**Biogas production increase over controls (%)**	**Biogas Yield**	**COD removal (%)**	**Dewaterability**	**Water Pollution**
THERMAL TREATMENT OF WAS									
Haug 1978	150 ml pressurized reactor, temperature from 175 to 225°C for 30 min	43%	470 for control 770 for treated sludge		70% increase		10%	b^a value increased from 0.16 to 1.73 after treatment at 175°C and to 106 after treatment at 225°C	
Stuckey and McCarty 1984	634 ml pressure reactor temperatures from 150 to 275°C for 45 min				27% increase in methane production				
Pinnekamp 1989	Autoclave at temperatures from 120 to 220°C and pressure of around 392psi (28 bar)					74% Increase in biogas yield ($l/kgVS_{influ}$) at 170°C, optimum temperature			
Martin and Potts (year	Cambi process at temperature			53%	20%			33% dry	

		After disintegration		Anaerobic digestion				After digestion	
Author	**Method**	**Degree of disintegration. SCOD/TCOD (%)**	**Ammonia concentration (mg/l)**	**VS destruction (%)**	**Biogas production increase over controls (%)**	**Biogas Yield**	**COD removal (%)**	**Dewaterability**	**Water Pollution**
unkown)	of 165°C and 10 bar for 30 min. Type of sludge not specified.							solids after dewatering of hydrolysed digested sludge	
Kepp *et al.* (1999)	Cambi process at temperatures from 130-180°C and pressures from 8 to 12 bar for 30 min Type of sludge not specified.	Brooks (1970) reported 30-50% increase in dissolved solids after thermal treatment at 170°C [b]		Increased by 23% over conventional digestion					
THERMAL TREATMENT OF PRIMARY SLUDGE									
Haug 1978	150 ml pressurized reactor 30 min at 175°C-225°C			No increase over the control			No increase over the control	b^a value increased from 0.36 to 0.90 after treatment at 175°C	
Pinnekamp 1989	Autoclave at temperatures from 120 to 220°C and pressure of around 392 psi (28 bar)					20% Increase biogas yield ($l/kgVS_{influ}$) at 170°C, optimum temperature			
THERMAL TREATMENT OF WAS AND PRIMARY SLUDGE MIXTURE									

		After disintegration		Anaerobic digestion				After digestion	
Author	**Method**	**Degree of disintegra-tion. SCOD/TCOD (%)**	**Ammonia concentra-tion (mg/l)**	**VS destruction (%)**	**Biogas production increase over controls (%)**	**Biogas Yield**	**COD removal (%)**	**Dewater-ability**	**Water Pollution**
Haug 1978	150 ml pressure reactor at temperatures from 175 to 225°C for 30 min Mixture of 1:1 by weight				14% methane production increase			b^a value increased from 0.10 to 95 after treatment at 175°C	
Abraham *et al.* 2003	Cambi process at temperature from 160 to 170°C and 12 bar for 45 min Mixture of primary, WAS and some digested sludge			50% greater than conventional digestion					
THERMAL TREATMENT OF ANAEROBICALLY PREDIGESTED SLUDGE									
Pinnekamp 1989	Autoclave at temperatures from 120 to 220°C and pressure of around 392 psi (28 bar)					269% increase inbiogas yield (l/kgVS_{influ}) at 180°C,			

		After disintegration		Anaerobic digestion				After digestion	
Author	**Method**	**Degree of disintegra-tion. SCOD/TCOD (%)**	**Ammonia concentra-tion (mg/l)**	**VS destruction (%)**	**Biogas production increase over controls (%)**	**Biogas Yield**	**COD removal (%)**	**Dewater-ability**	**Water Pollution**
						optimum temperature			
MECHANICAL TREATMENT OF WAS									
Baier and Schmidheiny 1997	Ball milling and high-speed cutter milling	20%		57%	10% Increase		53% 1.2 to 1.5 times higher than the control		
Dohanyos *et al.* 1997	Adapted thickening centrifuge	5% SCOD, values from 2000-3680 mg/l				28% increase in methane yield, average value of 0.0186 l/g COD			

		After disintegration		Anaerobic digestion				After digestion	
Author	**Method**	**Degree of disintegration. SCOD/TCOD (%)**	**Ammonia concentration (mg/l)**	**VS destruction (%)**	**Biogas production increase over controls (%)**	**Biogas Yield**	**COD removal (%)**	**Dewaterability**	**Water Pollution**
Muller *et al.* (1998)	Ball mill, high-pressure homogenizer, ultrasound homogenizer and shear gap homogenizer of WAS	Hi-pressure homogenizer (200 bar) DR_o[c] = 26% Hi-pressure homogenizer (400 bar) DR_o= 40% Stir ball mill DR_o= 43%			Specific biogas production increase by 10 to 20% for sludge treated with high-pressure homogenizer, as compared to the untreated sludge.			SS content below control after dewatering Values after 7 day digestion: Hi-pressure homogenizer at 200 bar 6.8% Hi-pressure homogenizer at 400 bar 12.2% Stir ball mill 16.2%	Ammonia concentration increased as compare to the control. The mean value of the return flow of TKN was about 20 to 30% higher than usual.

a. Parameter used to estimate dewaterability with a semi-quantitative method. A higher *b* value indicates better dewaterability.

b. Solubilization results reported to be similar to those observed by Brooks (1970).

c. (DR_o): measured oxygen consumption of the treated sludge divided by the oxygen consumption of the untreated sludge.

APPENDIX B SAMPLE PREPARATION

The total volume of mixture required was 80 liters, 20 liters per each of the three steam-explosion conditions and the remaining 20 liters were used as control sample. The quantities of biosolids required for the mixture were measured by weight and the quantities of TWAS were measurements by volume. The following equations define the quantities of TWAS and biosolids required for the preparation of 80 liters of mixture at 15% solids concentration.

$$Mass_{solids\_sample} = V_{sample}(\%solids_{sample})$$

$$Mass_{solids\_mixture} = 80 \times 0.15 = 12kg$$

$$Mass_{solids\_mixture} = Mass_{solids\_Twas} + Mass_{solids\_Biosolids}$$

$$Mass_{solids\_mixture} = V_{TWAS}(\%solids_{TWAS}) + V_{bio}(\%solids_{bio})$$

$$V_{sample} = V_{TWAS} + V_{bio}$$

$$Mass_{solids\_mix} = V_{TWAS}(\%solids_{TWAS}) + (V_{sample} - V_{TWAS}) \times (\%solids_{bio})$$

$$V_{TWAS} = \frac{Mass_{solids\_mix} - V_{sample}(\%solids_{bio})}{(\%solids_{TWAS} - \%solids_{bio})}$$

$$V_{TWAS} = \frac{12 - 80(0.30)}{(0.058 - 0.3)} = 48liters$$

$$V_{bio} = (80 - 48) = 32liters$$

$$Mass_{bio} = V_{bio} \times \rho_{bio} = 32 \times 1.1 = 35.2kg$$

Unfortunately a small mistake during the actual preparation of the TWAS/biosolids mixture led to a slightly lower percentage of biosolids in the mixture and a slightly lower total solids. The actual quantities and percentages have been used throughout the thesis. Actual preparation of the TWAS/biosolids mixture was as follows:

$$V_{TWAS} = 48 liters$$

$$V_{bio} = 21.2 liters$$

$$Mass_{solids\_TWAS} = 48 \times 0.058 = 2.784 kg$$

$$Mass_{solids\_bio} = V_{bio} \times \%solids_{bio} \times \rho_{bio} = 21.2 \times 0.273 \times 1.1 = 6.360 kg$$

$$Mass_{solids\_mix} = 2.784 + 6.360 = 9.144 kg$$

$$\%solids_{mix} = \frac{Mass_{solids\_mix}}{V_{TWAS} + V_{bio}} = \frac{9.144}{48 + 21.1} = 0.132 = 13.2\%$$

$$\%TWAS_{solids\_in\_mix} = \frac{2.784}{9.144} \times 100 = 30.4\%$$

$$\%BIO_{solids\_in\_mix} = \frac{6.360}{9.144} \times 100 = 69.6\%$$

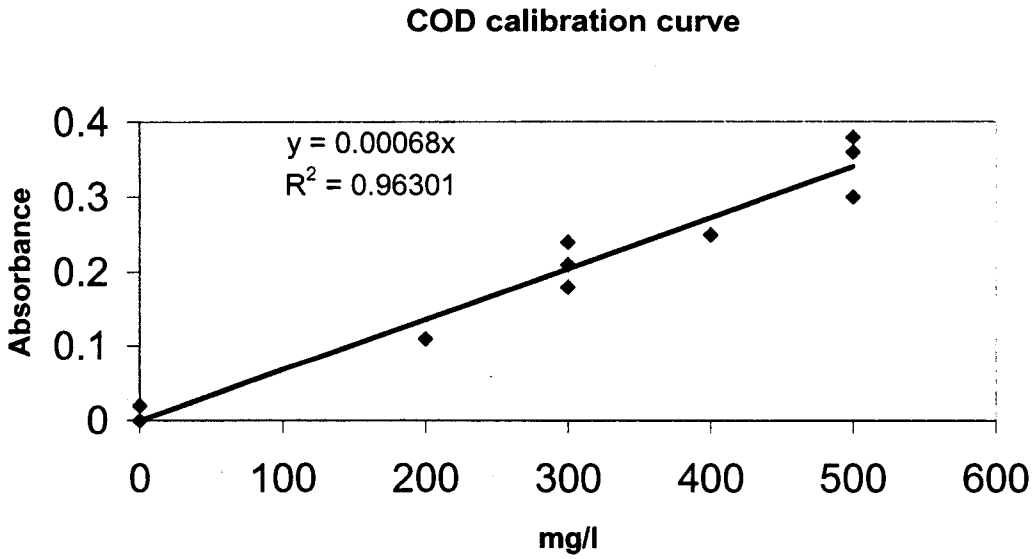
APPENDIX C CALIBRATION CURVES

COD CALIBRATION CURVE

A set of standards with concentrations of 200, 300, 400, and 500 mg/l of COD were prepared for the calibration curve. These set of standards were renewed monthly to avoid deterioration of the standards. The calibration curve was read every time before the reading of the samples. An example of COD calibration curve and calculation of sample COD concentration is given below.

Table B-1 Spectrophotometer absorbance reading of standards

Standard concentration	Absorbance
0	0,00
0	0,02
0	0,00
200	0,11
300	0,24
300	0,21
300	0,18
400	0,25
500	0,36
500	0,38
500	0,30



Calculation of COD concentration:

X = Y/ 0.0068

Where,

X: COD concentration mg/l

Y: Sample absorbance

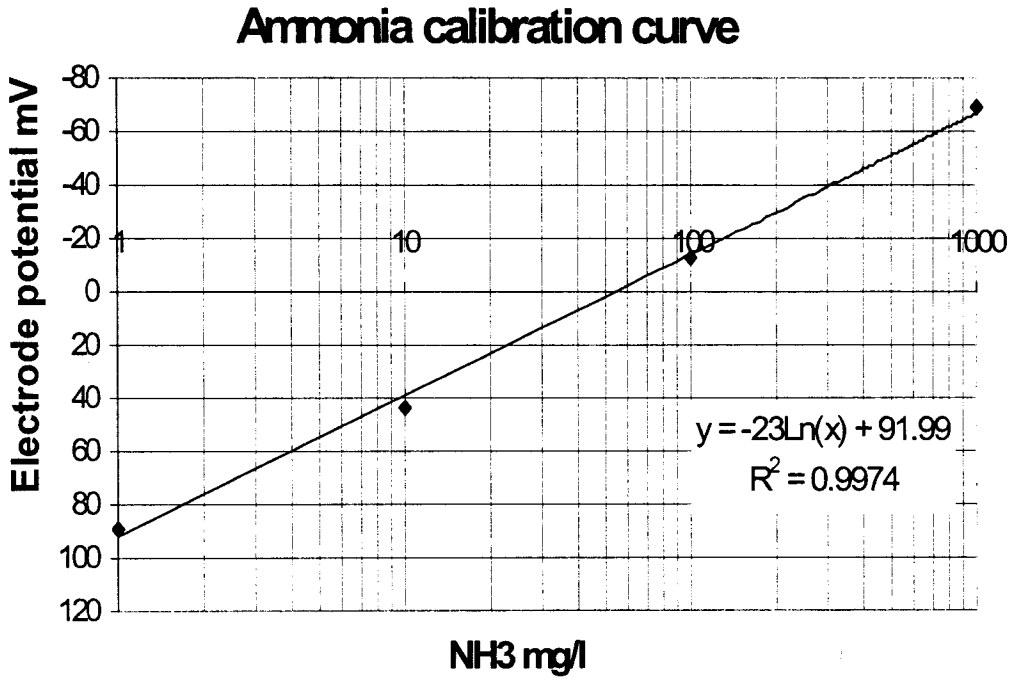
AMMONIA CALIBRATION CURVE

Ammonia calibration curves were prepared with fresh standard every time before the reading of samples.

An example of an ammonia calibration curve and calculation of sample ammonia concentration is given below.

Table B-2 NH_3 electrode potential measurements of standards

NH3 concentration mg/l	Electrode potential mV
1	88,7
10	43,5
100	-13
1000	-69



Calculation of sample ammonia concentration:

X = EXP ((91.99-Y)/23)

Where,

X: NH_3 concentration, mg N/l

Y: Sample electrode potential, mV

APPENDIX D EFFECT OF PRETREATEMENT ON TWAS

Table D.1 Calculation of TWAS TCOD concentration per gram of TS after steam-explosion.

	TCOD (mg/l)	TS (g/l)	$TS_{bio\ in\ mix}$ (g/l)	$TS_{TWAS\ in\ mix}$ (g/l)	TCOD per gram TS (R_{TWAS}, R_{mix}, R_{bio}) (mg/g)	$TCOD_{bio\ in\ mix}$ (mg/l)	$TCOD_{TWAS\ in\ mix}$ (mg/l)	TWAS TCOD per TS (mg/ g)
Sample			TS x 0.70	TS x 0.30	TCOD / TS	R_{bio} x $TS_{bio\ in\ Mix}$	$TCOD_{mix}$ – $TCOD_{bio\ in\ mix}$	$TCOD_{TWAS\ in\ mix}$ / $TS_{TWAS\ in\ mix}$
TWAS	33479	30			1116			
Mix 150	23848	30	21	9	795	14139	9710	1079
Mix 300	30454	30	21	9	1015	23587	6867	763
Mix 600	39679	30	21	9	1323	26652	13026	1447
Mix w/o T	23822	30	21	9	794	16604	7219	802
Bio 150	20198	30			673			1116
Bio 300	33696	30			1123			
Bio 600	38075	30			1269			
Bio w/o T	23719	30			791			

Table D.2 Calculation of TWAS SCOD concentration per gram of TS after steam-explosion

	SCOD (mg/l)	TS g/l	$TS_{bio\ in\ mix}$ (g/l)	$TS_{TWAS\ in\ mix}$ (g/l)	SCOD per gram TS (R_{TWAS}, R_{mix}, R_{bio}) (mg/g)	$SCOD_{bio\ in\ mix}$ (mg/l)	$SCOD_{TWAS\ in\ mix}$ (mg/l)	TWAS SCOD per gram TS (mg/g)
			TS x 0.70	TS x 0.30	SCOD / TS	R_{bio} x $TS_{bio\ in\ Mix}$	$SCOD_{mix}$ – $SCOD_{bio\ in\ mix}$	$SCOD_{TWAS\ in\ mix}$ / $TS_{TWAS\ in\ mix}$
TWAS	1093	30			36			
Mix 150	3329	30	21	9	111	1754	1575	175
Mix 300	12577	30	21	9	419	8268	4309	479
Mix 600	13535	30	21	9	451	8449	5086	565
Mix w/o T	1586	30	21	9	53	466	1120	124
Bio 150	2505	30	30		84			
Bio 300	11812	30	30		394			
Bio 600	12070	30	30		402			
Bio w/o T	666	30	30		22			

Table D.3 Estimation of biogas yield for TWAS after batch digestion

	Cumulative biogas production (V_{bio}, V_{mix}) (ml)	TS (g)	$TS_{bio\ in\ mixture}$ (g)	$TS_{TWAS\ in\ mixture}$ (g)	Biogas per TS (R_{bio}, R_{mix}) (ml/ g)	Biogas expected from TS of bio in mix ($V_{bio\ in\ mix}$) (ml)	Biogas for TWAS in mixture (V_{TWAS}) (ml)	Biogas per TS TWAS (R_{TWAS}) (ml/ g)
			TS x 0.70	TS x 0.30	V / TS	$(TS_{bio\ in\ mix})$ x (R_{bio})	(V_{mix}) - $(V_{bio\ in\ mix})$	V_{TWAS}/ TS_{TWAS}
TWAS	3758	15						251
Mix 150	2406	15	10,5	4,5	160	1053	1353	301
Mix 300	2681	15	10,5	4,5	179	1477	1204	268
Mix 600	3177	15	10,5	4,5	212	1375	1802	400
Mix w/o T	1880	15	10,5	4,5	125	873	1007	224
Bio 150	1504	15			100			
Bio 300	2109	15			141			
Bio 600	1964	15			131			
Bio w/o T	1247	15			83			

Table D.4 VS removal calculation for TWAS after batch digestion

	VS sample (g)	VS innoc (g)	Total VS input ($VS_{mix\ in}$, $VS_{bio\ in}$) (g)	Total VS output (g)	Total VS removed ($VS_{mix\ rem}$, $VS_{bio\ rem}$) (g)	% VS removed	VS bio in mix (g)	VS TWAS in (g)	VS of bio removed/ VS input R_{bio}	VS bio in mix rem (g)	V TWAS rem (g)	%VS removed TWAS
			VS sample + VS innoc		VS input – VS output	(VS input – VS output) x 100/ VS input	TS mix in X 0.70 X %VS	TS mix in X 0.30 X %VS in mix	VS bio rem / VS bio in	R bio x VS bio in mix	VS mix rem – VS bio in mix rem	(VS TWAS rem) x 100/ VS TWAS in
TWAS	10,52	1,16	11,68	6,2	5,51							47
Mix 150	8,44	1,16	9,60	6,3	3,33	35	5,62	3,98	0,31	1,72	1,61	41
Mix 300	8,41	1,16	9,57	6,3	3,27	34	5,85	3,72	0,21	1,23	2,03	55
Mix 600	8,81	1,16	9,97	6,7	3,29	33	5,91	4,55	0,22	1,29	1,99	49
Mix w/o T	8,80	1,16	9,96	7,6	2,39	24	5,73	4,23	0,12	0,69	1,70	40
Bio 150	8,03	1,16	9,19	6,4	2,81	31						
Bio 300	8,36	1,16	9,52	7,5	2,01	21						
Bio 600	8,44	1,16	9,60	7,5	2,10	22						
Bio w/o T	8,18	1,16	9,34	8,2	1,12	12						

Table D.5 Methane yield calculation for TWAS after batch digestion

	Total VS removed (g) ($VS_{mix\ rem}$, $VS_{bio\ rem}$)	$VS_{bio\ in\ mix}$ (g)	$VS_{bio\ in\ mix\ rem}$ (g)	$VS_{TWAS\ rem}$ (g)	Measured methane production (V_{mix}, V_{bio}) (ml)	Methane per gr VS of bio removed R_{bio} (ml/g)	Methane expected from VS of bio in the mixture (ml) $V_{bio\ in\ mix}$	Methane produced by the TWAS in the mixture (ml) V_{TWAS}	Methane per gram VS of TWAS removed (ml/g)
						$V_{bio} / VS_{bio\ rem}$	$R_{bio} \times VS_{bio\ in\ mix\ rem}$	$V_{mix} - V_{bio\ in\ mix}$	$V_{TWAS} / VS_{TWAS\ rem}$
TWAS	5,51				2036				370
Mix 150	3,33	5,62	1,72	1,61	1241		409	833	516
Mix 300	3,27	5,85	1,23	2,03	1441		624	817	402
Mix 600	3,29	5,91	1,29	1,99	1818		559	1259	631
Mix w/o T	2,39	5,73	0,69	1,70	902		317	585	343
Bio 150	2,81				667	238			
Bio 300	2,01				1015	506			
Bio 600	2,10				908	433			
Bio w/o T	1,12				516	462			

Table D.6 Calculation of biogas yield during semi-continuous digestion

	Average daily biogas production (V_{bio}, V_{mix}) (ml)	TS influent (g)	$TS_{bio\ in\ mixture}$ (g)	TS_{TWAS} in mixture gr	Biogas per TS (R_{bio}, R_{mix}) (ml/ g)	Biogas expected from TS of bio in mix ($V_{bio\ in\ mix}$) (ml)	Biogas for TWAS in mixture (V_{TWAS}) (ml)	Biogas per TS TWAS (R_{TWAS}) (ml/ g)
			TS x 0.70	TS x 0.30	V / TS	$(TS_{bio\ in\ mix}) \times (R_{bio})$	(V_{mix})- $(V_{bio\ in\ mix})$	V_{TWAS}/ TS_{TWAS}
SRT 14								
Mix 300	173.4	1.5	1.05	0.45	115.6	91.0	82.4	183.1
Mix w/o T	116.9	1.5	1.05	0.45	77.9	26.1	90.7	201.6
Bio 300	130.0	1.5	1.05	0.45	86.6			
Bio w/o T	37.3	1.5	1.05	0.45	24.8			
SRT 8								
Mix 300	227.1	2.25	1.58	0.68	100.9	110.6	116.5	172.6
Mix w/o T	172.1	2.25	1.58	0.68	76.5	38.6	133.5	197.8
Bio 300	158.0	2.25	1.58	0.68	70.2			
Bio w/o T	55.1	2.25	1.58	0.68	24.5			

Table D.7 Calculation of TWAS VS removal and methane yield during semi-continuous digestion at 14-day SRT

Sample	VS input mixture and Biosolid (VS_{mix}, VS_{bio}) (g)	Average VS removed ($VS_{mix\ rem}$, $VS_{bio\ rem}$) (g)	Average VS removed per VS in (R_{mix}, R_{bio})	VS TWAS in mixture ($VS_{TWAS\ in\ mix}$) (g)	VS Biosolids in mixture ($VS_{bio\ in\ mix}$) (g)	Expected VS of Bio removed from mixture ($VS_{bio\ rem\ in\ mix}$) (g)	VS TWAS removed from mixture ($VS_{TWAS\ rem}$) (g)	% VS removed TWAS	Average measured CH_4 (V_{mix}, V_{bio}) (ml)	CH_4 per gram VS removed (Y_{mix}, Y_{bio} (ml/g)	CH_4 expected from VS of bio removed in mix ($V_{bio\ in\ mix}$) (ml)	CH_4 remaining for TWAS ($V_{TWAS\ in\ mix}$) (ml)	CH_4 per gram VS removed TWAS (ml/g)
				VS_{mix} X 0.30	VS_{mix} X 0.70	R_{bio} x $VS_{bio\ in\ mix}$	$VS_{mix\ rem} - VS_{bio\ rem\ in\ mix}$	($VS_{TWAS\ rem}$ /$VS_{TWAS\ in\ mix}$) x 100		(V_{mix}, V_{bio})/ ($VS_{mix\ rem}$, $VSbio_{rem}$	Y_{bio} x $VS_{bio\ rem\ in\ mix}$	$V_{mix} - V_{bio\ in\ mix}$	$V_{TWAS\ in\ mix}$ / $VS_{TWAS\ rem}$
Mix 300 (1)	0,841	0,269	0,320	0,252	0,585	0,167	0,089	35,4	99,6	370	50,0	50	554
Mix w/o T (1)	0,880	0,272	0,309	0,264	0,573	0,124	0,138	52,1	69,6	256	31,8	38	275
Bio 300 (1)	0,836	0,240	0,286						71,5	299			
Bio w/o T	0,818	0,190	0,217						20,4	114			

Table D.8 Calculation of the TWAS TCOD removed during semi-continuous digestion at 14-day SRT

	TCOD input ($TCOD_{mix\ in}$, $TCOD_{bio\ in}$) (mg/l)	TCOD output (mg/l)	TCOD removed ($TCOD_{mix\ rem}$, $TCOD_{bio\ rem}$) (mg/l)	TS (TS_{mix} TS_{bio}) (g/l)	TS Bio in Mix $TS_{bio\ in\ mix}$ (g/l)	TCOD per TS input ($TCOD/TS_{mix}$, $TCOD/TS_{bio}$) (mg/g)	Input TCOD of Bio in Mix ($TCOD_{bio\ in\ mix}$) (mg/l)	Input TCOD TWAS in Mix (mg/l)	Input TCOD removed per TCOD bio (R_{bio})	TCOD removed of BIO in mix $TCOD_{bio\ in\ mix\ rem}$ (mg/l)	TCOD TWAS removed (mg/l)
SRT 14			$TCOD_{input} - TCOD_{output}$		**TS x 0.70**	**TCOD/TS**	$(TCOD/TS_{bio}) \times TS_{bio\ in\ mix}$	$TCOD_{mix} - TCOD_{bio\ in\ mix}$	$TCOD_{rem\ bio}/TCOD_{in\ bio}$	$R_{bio} \times TCOD_{bio\ in\ mix}$	$TCOD_{mix\ rem} - TCOD_{bio\ in\ mix\ rem}$
Mix w/o T	25610	15917,6	9692	30	21	854	19541	6068		4172,60	5519,37
Mix 300	29133	21257,1	7876	30	21	971	18593	10540		2838,48	5037,71
Bio w/o T	27916	21955,3	5961	30		931			0,214		
Bio 300	26562	22506,9	4055	30		885			0,153		
SRT 8											
Mix w/o T	25610	19741,0	5869	30	21	854	19541	6068		3333,78	2534,79
Mix 300	29133	21709,2	7424	30	21	971	18593	10540		3730,22	3693,90
Bio w/o T	27916	23153,7	4763	30		931			0,171		
Bio 300	26562	21233,0	5329	30		885			0,201		

APPENDIX E INITIAL AND FINAL CONCENTRATION OF VARIOUS PARAMETERS DURING SEMI-CONTINUOUS DIGESTION

Table E.1 Parameters measured in the influent and effluent of the semi-continuous reactors at the 14 day SRT.

Sample	Input							Output									
SRT 14 d	TS		TCOD (4)[a]	Std	SCOD (4)	Std	NH3-N	TS (18)	Std	VS (18)	Std	TCOD (4)	Std	SCOD (4)	Std	NH3-N (12)	Std
	(mg/l)	(mg/l)	(mg/l)		(mg/l)		(mg/l)	(mg/l)		(mg/l)		(mg/l)		(mg/l)		(mg/l)	
Mix 300 #1	30000	16826	28371	2437	5262	894	386	25383	1838	11694	708	20757	1030	1442	110	938	75
Mix 300 #2	30000	16826	28371	2437	5262	894	386	24144	4189	11495	1254	21757	651	1439	111	960	99
Mix w/o T #1	30000	17598	24975	2397	3000	270	262	24446	1764	12358	989	16614	1788	379	49.7	704	82
Mix w/o T #2	30000	17598	24975	2397	3000	270	262	23486	1887	11950	489	14989	416	304	7.4	702	83
Bio 300 #1	30000	16716	26324	912	5098	1035	234	26051	1989	12108	913	22173	2041	1273	95.0	805	84
Bio 300 #2	30000	16716	26324	912	5098	1035	234	25022	2017	11770	821	22757	3026	1297	70.3	808	89
Bio w/o T #1	30000	16363	25292	1100	2003	515	229	25112	2544	12964	340	22317	1785	568	13.6	489	75
Bio w/o T #2	30000	16363	25292	1100	2003	515	229	25960	767	13015	453	21473	3095	564	36.8	474	86

a. Numbers in brackets indicate the number of measurements used to calculate the average value.

Table E.3 Parameters measured in the influent and effluent of the semi-continuous reactors at the 8 day SRT.

	Input							Output									
SRT 8 d	TS	VS	TCOD (4)[a]	Std	SCOD (4)	Std	NH3-N	TS (10)	Std	VS (10)	Std	TCOD (9)	Std	SCOD (9)	Std	NH3-N (11)	Std
	(mg/l)	(mg/l)	(mg/l)		(mg/l)		(mg/l)	(mg/l)		(mg/l)		(mg/l)		(mg/l)		(mg/l)	
Mix 300 #1	30000	16826	28371	2437	5262	894	386	23922	1448	11361	236	21503	1364	1485	56.1	904	44
Mix 300 #2	30000	16826	28371	2437	5262	894	386	22473	686	10548	381	20931	1485	1473	66.1	886	69
Mix w/o T #1	30000	17598	24975	2397	3000	270	262	24204	2623	12288	1388	19789	1990	475	30.5	677	60
Mix w/o T #2	30000	17598	24975	2397	3000	270	262	24714	1823	12527	953	20360	1429	376	16.6	680	54
Bio 300 #1	30000	16716	26324	912	5098	1035	234	24640	476	11713	335	20931	1905	1465	81.0	751	39
Bio 300 #2	30000	16716	26324	912	5098	1035	234	26280	1305	12334	529	19789	2620	1459	84.4	756	48
Bio w/o T #1	30000	16363	25292	1100	2003	515	229	27212	1155	13407	583	23217	1313	745	78.0	441	23
Bio w/o T #2	30000	16363	25292	1100	2003	515	229	27560	959	13533	574	23789	1539	721	63.8	440	28

a. Numbers in brackets indicate the number of measurements used to calculate the average value.