

THERMOPHILIC, BATCH, HIGH-SOLIDS BIOGASIFICATION OF SUGAR BEET
TAILINGS

By

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To my mother who has always been supportive of my education

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LIST OF ABBREVIATIONS

ABCR	Anaerobic batch composting reactor
ACSC	American Crystal Sugar Company
ADF	Acid detergent fiber
AFR	Anaerobic filter reactor
ARS	Analytical research systems
BMP	Biochemical methane potential
C1	CR10X 1 controller
C2	CR10X 2 controller
C/N	Carbon-to-nitrogen ratio
COD	Chemical oxygen demand
CSTR	Continuous stirred tank reactor
DM	Dry matter
FID	Flame ionization detector
GC	Gas chromatograph
HRT	Hydraulic retention time
ISR	Inoculum-to-substrate ratio
MSW	Municipal solid waste
NDF	Neutral detergent fiber
NFC	Non-structural carbohydrates
OFMSW	Organic fraction of municipal solid waste
SBR	Sequencing batch reactor
SCOD	Soluble chemical oxygen demand
SEBAC	Sequential batch anaerobic composting
SS	Suspended solids

SSR	Solid state relay
SWWT	Separate wash water treatment
STR	Stirred tank reactor
TS	Total solids
UASB	Up-flow anaerobic sludge blanket
VFA	Volatile fatty acids
VS	Volatile solids
VSS	Volatile suspended solids

Abstract of Thesis Presented to the Graduate School
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Tailings from sugar beet processing are currently managed by landfilling or land application. For example, American Crystal Sugar Company generates 400 tons per day of sugar beet tailings and spends close to \$1 million dollars per year disposing them. Anaerobic conversion of sugar beet tailings into energy would not only generate biogas for energy, but also reduce the quantity of waste stream that requires disposal.

The concept of flooded Sequential batch anaerobic composting (SEBAC-2) technology, developed at the University of Florida was initially implemented for the biogasification of sugar beet tailings. Preliminary experiments were conducted at mesophilic (37°C) temperatures and it was found that daily methane production rates and methane yield failed to increase even after 40 days of digestion. Persistent high volatile fatty acids build up and high soluble COD during biogasification were perceived to be significant reason for the failure.

This thesis presents findings related to the implementation of single-stage and two-stage thermophilic high-solids systems for enhanced biogasification of sugar beet tailings. The single stage system was operated in different modes: no pre-treatment, pre-treatment, no bulking, bulking and maceration. The methane yields varied between 170 to 285 L kg VS⁻¹ and time required to achieve 95% of methane potential varied between 8 to 15 days. Single-stage with pre-

treatment and bulking showed the highest methane potential, the shortest retention time and low volatile fatty acids accumulation. Two-stage system was operated by sequencing a single-stage high solids system with an anaerobic filter reactor. The methane yields varied between 293 to 315 L kg VS⁻¹ and time required to achieve 95% of methane potential varied between 7.5 to 10 days. The volatile fatty acid accumulation was also found to be low. The advantages of operating a two-stage system was the elimination of pre-treatment, and bulking, in addition to reduced retention times and higher loading rates. The retention time in the two-stage thermophilic system was reduced to almost 1/3 from previously operated SEBAC-2 mesophilic system.

CHAPTER 1 INTRODUCTION

1.1 Background

Management of organic wastes generated by human activities is increasingly one of the most pressing concerns confronting a developing society. Increased awareness and stricter environmental policies and regulations have translated to re-examining and enhancing conventional practices. High demands to establish an environmentally-acceptable and sustainable technology platform for organic wastes has prompted the interest of research, development and commercialization sectors. Industries producing significant organic wastes as part of their processing practices are becoming in tune with modern waste management strategies. In-vessel conversion technologies provide a sensible, on-site solution to organic waste management, especially in many nations where it is becoming increasingly difficult to landfill biologically degradable waste (Fricke et al., 2005). The sugar beet industry (American Crystal Sugar Company, ACSC) was recently targeted as a promising candidate for implementing a sustainable technological solution to their significant sugar refining organic byproduct: sugar beet tailings.

Nearly forty percent of all refined sugar consumed in the USA annually is made from beets grown in the north central and north western regions of the United States. Sugar beet processing generates significant quantities of both solid and liquid organic waste. Post-harvest operation begins when beets are brought into the processing plant from storage in outdoor stockpiles and are washed; sugar beet “tailings,” which mainly consist of sugar beet (10-30%), weeds, sugar beet tops, debris and soil are dislodged from sugar beets during this washing process. Subsequently, sugar beet tailings are stockpiled outside the processing plant and are hauled away for disposal into landfills or applied on nearby farmland at a cost to the plant. For example,

ACSC spends approximately \$1 million per year disposing 400 tons of tailings that are generated daily at its East Grand Forks, Minnesota processing plant (Teixeira et al., 2005).

Organic waste management begins with identifying feedstock characteristics and evaluating plausible conversion technologies for handling such feedstock. Commercial conversion processes include combustion, thermochemical gasification, thermochemical liquefaction, aerobic composting and anaerobic digestion. These processes yield conversion to various products which include electrical/heat energy, steam, low-to-high energy gases, liquid fuels and chemical feedstocks. If the organic waste is abundant, and if collection and transportation is economically feasible, major criteria for the selection of conversion technologies include (Chynoweth et al., 1980):

- Feedstock characteristics such as moisture content or biodegradability
- Energy product desired
- Effluent streams (byproducts, residues)
- Environmental impact
- Economics

A lack of literature on the disposal of sugar beet tailings indicated that not much attention had been devoted towards processing this waste residue for value addition. Selection among the available residual waste conversion technologies was evaluated initially based on the intrinsic moisture. Appearing as a solid, sugar beet tailings (Figure 1-1) actually have a moisture content of 84 to 87 %, and a biodegradable fraction approximately 80 to 90 % of dry matter content. Generally, a feed moisture content of more than 50% is not preferred for thermal conversion processes; implementation of conventional combustion, liquefaction or gasification would be practical only if a vigorous and costly pre-drying stage was implemented into the overall waste management scheme.

Biological conversion technologies provide a conventional approach to management of high moisture and biodegradable feedstocks and are generally classified as either aerobic or anaerobic processes. Aerobic processing (composting) is the biological transformation in the presence of oxygen whereas anaerobic processes (anaerobic digestion or biogasification) occurs in the absence of oxygen and also yields a valuable product: biogas fuel (a mixture of methane and carbon dioxide). Practical biodegradability of an organic feedstock utilizing each process may vary under similar conditions: particle size, time, and environmental conditions (temperature, nutrient requirements, etc.) will influence the outcome of biodegradation (Kayhanian, 1995). Though waste minimization and recycling can be fully exploited with both biological transformation schemes, there is still a residual fraction which has to be disposed of (Fricke et al., 2004).

Biological gasification (biogasification) of sugar beet tailings via the anaerobic process is a very attractive method that would not only generate biogas, but also reduce the volume of waste stream that requires disposal. Preliminary studies on feasibility of biogasification were conducted at the University of Florida. Biochemical methane potential (BMP) assays of sugar beet tailings yielded 250 L of methane/kg VS. Based on this methane yield, a simple economic analysis showed that taking into account the reduced cost of disposal, electricity revenues, and natural gas savings, a conservative net savings from biogasifying 400 tons/day of tailings was \$4,873 per day (Teixeira et al., 2005).

Among the various technologies that are available for anaerobic digestion, the Sequential Batch Anaerobic Composting (SEBAC) was initially chosen for the biogasification of sugar beet tailings. The SEBAC process is a patented high solids, batch, leachbed process that uses a combination of solid state fermentation and leachate recycle to provide a simple and reliable

process (Chugh et al., 1999; Chynoweth and Legrand, 1993; Chynoweth et al., 1992). As compared to other waste management technologies, SEBAC offers numerous technical and economic advantages, which include:

- Simple operation protocols
- Flexible designs, such as tanks, trench or cells
- Relatively low initial capital investments

The SEBAC process has been tested on organic fraction of municipal solid waste (OFMSW), woody biomass, yard wastes and mixtures of yard wastes and biosolids. Recently, the SEBAC process was modified (termed SEBAC-2) for improved kinetics and reduced solids processing time by incorporating flooded operation and periodic redirection of leachate flow (Luniya et al., 2005).

In preliminary experiments, sugar beet tailings were anaerobically digested using SEBAC-2 at mesophilic conditions; findings showed that the methane generation rates were poorer compared to that from digestion of other organic residues (Chynoweth et al., 2002). Persistently high volatile organic acid concentrations were measured in leachate and daily methane production rates failed to increase even after 40 days of digestion. Therefore, if biogasification of tailings were to be successfully implemented at full-scale there was need for further investigations to determine the factors affecting the degradation of tailings and to develop a scalable process. These investigations and their outcomes are presented here.

1.2 Objective

The objective of this research was to effectively carry out bench-scale studies on the biogasification (also known as anaerobic digestion) of sugar beet tailings in an effort to identify critical factors and performance measures during batch operation. The research findings would ultimately lead to a proposal of a system design and operation concept for full-scale application

of biogasification. This objective was chosen as a point of study on an on-going industrially-oriented project (Conversion of Biomass into Energy and Compost through Sequential Batch Anaerobic Composting) at the University of Florida in partnership with Xcel Energy and American Crystal Sugar Company. The goals of this research work were divided into six objectives.

- **Objective 1:** Design, construct, and successfully operate a bench-scale system for batch, high-solids biogasification of sugar beet tailings.
- **Objective 2:** Investigate the effect of single stage operation on sugar beet tailings
- **Objective 3:** Investigate the leaching and pre-treatment of readily soluble fraction of sugar beet tailings
- **Objective 4:** Investigate the effect of bulking on the biogasification of sugar beet tailings
- **Objective 5:** Investigate the effect of two-stage operation on the biogasification of sugar beet tailings
- **Objective 6:** Achieve accelerated biogasification of sugar beet tailings and highlight operation techniques that can be implemented in scale-up studies.



Figure 1-1. Raw sugar beet tailings received from American Crystal Sugar Company

CHAPTER 2 MATERIALS AND METHODS

2.1 Introduction

In this chapter, the systems that were employed to perform well-controlled experiments in biogasification of sugarbeet tailings are described. The design, fabrication and operation of reactors, the instrumentation and software, the operation of gas meters, the implementation of temperature control, and supporting equipment are described in detail. Protocols followed regarding preparation of feedstock, reactor loading, unloading and operational schemes are also described in detail.

The chapter proceeds in describing the preliminary acclimatization stage of building a microbial population necessary to carry out well-controlled experiments. Thereafter, a platform of four studies was designed to address key factors affecting high-solids biogasification digestion of sugar beet tailings. The chapter concludes by describing the analytical techniques used to carry out measurements on critical biogasification parameters; this includes the work conducted by an external laboratory – Dairy One Forage Lab (Ithaca, New York).

2.2 Reactor Design

Experiments were carried out in three, 20-liter Pyrex glass carboy bottles converted specifically to meet the design needs of batch anaerobic leachbed/ high-solids reactors. Two vessels were designated for solids digestion, named as anaerobic batch composting reactors 1 and 2 (ABCR1 & 2). The third vessel for liquid digestion was named anaerobic filter reactor (AFR). Design issues addressed included: the need for a large cross-sectional opening to facilitate solids loading and unloading efficiently; the need for an adjustable bed volume to experiment with a range of bulking densities; Adjustable leachate re-circulation lines to account for level increases/decreases of settled solids and working liquid volumes; the need for a top-

plate lid that would keep the vessel gas-tight; and an efficient strategy for flushing and performing maintenance on the vessel. To adequately tailor a vessel with such needs, collaborative design and custom fabrication was provided by Analytical Research Systems (Micanopy, FL, USA) in conjunction with University of Florida's Agricultural and Biological Engineering machine shop.

Solids handling during loading and unloading of vessels received forefront attention in design considerations. Each carboy bottle was thermally cut at its base and a flanged lip was curled, resulting in an inverted carboy bottle with a complete cross-sectional opening. The neck of the bottle was adjusted by thermally fusing a glass flange and couple to increase overall length. A custom-build glass Duran O-ring flange bottom (ABCR's only) was machined to fit the carboy flange, secured by a stainless steel, quick-release clamp. Carboy modifications (Figure 2-1) to construct bioreactors were regarded as simple and low-cost solutions to constructing lab-scale anaerobic equipment.

To facilitate easy loading and unloading of sugar beet tailings, the next phase of design focused on a top lid adequate to seal each vessel. Several design concepts were drafted for a top lid to cover the cross-sectional area of the modified carboy bottle. The glass flange design on the carboy bottle gave impetus to a clamp-seal strategy; clearance on the glass flange (0.75 inches) provided enough surface area for a gasket to sit in between the proposed lid and glass flange. A flange ring was conceptualized and fabricated to press against the underside of the carboy flange, whereas the lid would press on the upside of the glass flange. The lid would clamp to the flange ring at twelve points; bolts and wing nuts were used to fasten the parts together (Figure 2-2).

Aluminum was chosen as the material of construction for the top lid. This versatile metal provided certain beneficial properties such as; strong metal characteristics which made it suitable

for clamping; a light weight, minimizing force on the glass structure; and metal with low oxidative properties to withstand humid environments. The lid included ports and an adjustable perforated plate suspended on the “in” side of the lid; tapered holes were fabricated to meet the needs of four ports (1/2 inch NPT-F) and three support-rod holes (Figure 2-3). Ports were fitted with fluid system piping components, which included Swagelok press fittings for 1/4 inch tubes (liquid inlets) and hose barbs for 3/8 inch silicon tubing (gas outlet); additional holes were plugged with appropriate brass caps. Three 6-inch stainless steel support rods were screwed on the inside part of the lid; a 1/8 inch 316 stainless steel perforated plate (11 inches in diameter) was suspended from the rods and served as the adjustable top barrier for the leach bed. A similar perforated plate was machined as a bottom barrier of the leach bed, sitting on the shoulders of the glass carboy. Finally, a Viton gasket was cut to 1 1/2 inches in area (twice as wide as the glass carboy flange) to serve as the sealant between the lid and gasket. A high heat, inert and chemical resistant silicone lubricant (Dow Corning High Vacuum Grease) was applied to both sides of the gasket to assure proper sealing. The lubricant was re-applied after each experiment.

Support stands were fabricated by ARS to adequately erect each biogasification vessel.

Design criteria that were considered included:

- A stand that can support a 20-kg load
- A glass-friendly material that would support the full weight of the carboy, lid and contents sufficiently
- A stand that would enable easy access to sample/process ports and maintenance
- A stand that would not impede loading and unloading of vessels.

A custom tri-pod support stand was tailored to the design criteria for each vessel. Each consisted of an adjustable UHMW-PE base support ring with an 11-inch ID chamfered hole and three

hollow aluminum legs; base mounts (Base Flange #4UG93, Grainger) were fitted on the ends of each leg to secure to a base plate (Figure 2-4).

Slight modifications in design were implemented on the AFR, fabricated by ARS. A short-neck, 20-L Pyrex carboy bottle (CLS 15955, Sigma-Aldrich) was ordered specifically for this vessel. A special request was made to ARS glass-blower to minimize the volume of reactor below the bottoms perforated plate. This design modification translated to minimal “dead” volume that would not contribute to the active reactor volume; in contrast, solids reactors were designed with long necks to accommodate particulates to accumulate during degradation without clogging re-circulation lines. The Duran o-ring flange design was substituted by Teflon wide-mouth threaded plug. Finally, four press-fittings (SAF 2507 Swagelok) were machined and screwed into the Teflon plug to serve as inlet/outlet ports.

2.3 Instrumentation and Equipment

2.3.1 Introduction

In order to achieve proper understanding of the process characteristics in anaerobic digestion, each biogasification vessel was instrumented for data acquisition of biogas production rate, temperature and pH; Logger Net (v 3.1) software and CR10-X measurement/controller module (products of Campbell Scientific Inc, USA) were used to monitor such parameters. The effects of variation of measured parameters would help to optimize the system performance within the system’s operation boundaries.

2.3.2 Datalogger and Controller

The CR10-X is a compact, modular datalogger with a measurement and control module, external power supply and keyboard display. The low-power design allows it to operate up to one year on a 7 Amp-hr, unregulated 12 Vdc source. It is designed for unattended network applications and can measure, record and display data (62000 non-volatile points) without

operator or computer intervention. In addition, the CR10-X's built-in intelligence helps to setup test routines and specify the parameters of each channel. The channels available include: 12 single-ended or 6 differential, individually configured; two pulse counters; switched voltage excitations; and eight control/digital ports. A wide range of sensors compatible with the CR10X were available on the market to meet the specific needs of measuring or controlling experimental parameters.

Two CR10X controllers were available for this biogasification study- C1 and C2. With three units constructed for biogasification experiments, C1 would serve ABCR 1 whereas C2 would serve ABCR 2 and AFR. This arrangement was especially beneficial when dual-stage experimentation was conducted on the latter part of this work (Chapter 6). Two, 12-V batteries supplied power to both controllers; each day they were closely monitored, measured and recharged if voltage fell below 11.8 volts. Controllers left online with a power source of < 11.5 volts would shift to an indeterminate state and malfunction. This led to potential loss of temperature control in reactors and datalogging failure. A fail-safe diagnostic was coded in the CR10X program (Appendix A) in the event of power supply outage to prevent the worse case scenario when heating tape fails to turn-off when set point is exceeded. This would lead to temperatures above the thermophilic range in the reactor causing irreversible inactivation of microorganisms. Controllers C1 and C2 were encased in a wiring panel (Figure 2-5) for protection of any outside interferences or liquid spills..

2.3.3 Datalogger Support Software

LoggerNet 3.2-series software was used in conjunction with the CR10X datalogger and control module. It supports programming, communication, and data retrieval between Campbell Scientific dataloggers and a PC. It is considered the standard software package recommended

for those who have single or network dataloggers that do not require the more advanced features offered by competitors (e.g. Labview). Some software features include the ability to:

- Create custom datalogger programs using Edlog compiler
- Display or graphs real-time or historic data
- Build custom display screens to view data or control flags/ports
- Collect data on demand or schedule
- Retrieve data using various telecommunications options
- Process data in LoggerNet's Split program
- Export data to third party analysis package

In this project, LoggerNet served well in handling programs needed to monitor, log and control biogasification experiments. Edlog is the programming tool for Campbell Scientific mixed-array and table-data dataloggers. It was used to create new programs, edit existing programs, or convert existing code into a file that could be edited. It provided the necessary tools to write execution files that enabled measurements of temperature, pH, biogas production as well as frequency of sampling and final data storage allocation.

Case-specific programs for biogasification experiments were written and compiled in Edlog; the execution and sampling interval for adequate resolution was chosen as one minute. Programs were then uploaded from the PC's CS I/O 9-pin port via a cable to the CR10X datalogger, and initiated to run. Within 24-36 hours, data would be manually downloaded from each controller and parametrically sorted into array tables. Microsoft Excel was used as an offline, third-party data base for analysis of parameters and system operation.

2.3.4 Sensor for Biogas Production

Many conventional technologies exist when gas flow measurement is a parameter of interest. Diaphragm, rotary and turbine gas meters are common in many industrial and commercial applications, but are limited for high and steady flow conditions. Raw biogas produced from anaerobic digestion of organic matter can cause erroneous flow readings on

conventional devices due to moisture and other impurities in the biogas and flow that is intermittent and delivered in packets. For such a purpose, a special U-tube gas meter was used to efficiently measure the gas flow by liquid displacement (Figure 2-6).

2.3.4.1 Biogas meter operation

A liquid displacement flow meter (U-tube design) was used to measure gas flow through a process line. This design circumvents the deficiencies of the conventional meters by having error free operation even if gas flow is intermittent, high in moisture and contains impurities. The active components of the circuit include a 3-way solenoid valve, a float switch, an electromechanical counter, a time delay relay and a U-tube monometer component. A low volatility fluid antifreeze brand was filled inside the u-tube and the entire apparatus was sealed properly.

The biogas from the reactor accumulated in one limb of the U-tube and displaced the liquid inside; when the liquid in the second leg rose to a certain level, the float switch tripped, causing three events to occur simultaneously: a signal was sent to the counter to record the reading for display; the biogas from the first leg was vented into the atmosphere, causing a reset of both liquid levels in both legs; and a timer kept the vent line open long enough to equilibrate the levels. During the vent cycle, the reactor's biogas was isolated from the gas meter. With each switch closure, the counter continued to increment the amount of gas flowing through the meter; cumulative counts per given period would yield a volumetric gas flow rate.

2.3.4.2 Calibration of biogas meter

Biogas flow was measured by determining the relationship between the counter increment and the volume of incoming gas required to trigger one counter increment. To simulate biogas, which primarily consists of two gas-phase components (methane and carbon dioxide), a specialty, high purity standard was used; 60.00% CH₄ and 40.00% CO₂. A glass syringe of

known volume and accuracy (100 ± 1 mL) was used to determine the amount of simulated biogas required to induce one counter increment.

Calibration protocol included injecting a series of simulated biogas doses into a biogas meter via a sealed septum and observing at what volume switch closures occurred. Protocol was conducted in both off-line mode (stand-alone gas meter) and on-line mode (gas meter connected to reactor vessel) during low or no biogas production. The final result of the calibration was an input-output relationship, called a calibration factor with units- mL of gas/count. The precision of calibration factors were characterized by reporting the standard deviation of a population of repeated measurements. Typically, a series of ten injections were deemed as adequate population for determining a gas calibration factor. Values of 55 ± 3.2 mL per count were obtained regularly during calibration protocols. This level of measured resolution (one gas click) on each gas meter was sufficient to provide insight about biogas production trends within a period of study (100 minutes).

In gas measurement applications, the relationship between intensive properties (e.g., temperature and pressure) and gas behavior were considered. The ideal gas law can be applied to real gases when pressures are lower than an atmosphere and when temperatures are not close to the liquefaction point. With near ambient pressures and a 55°C operating temperature, this equation of state was adequate in characterizing and predicting the behavior of biogas.

The strong relationship between gas temperature and volume received attention during calibration of biogas meters. During experimentation, Biogas was produced at 55°C in each vessel and measured externally at a lower temperature. As a result, a cooling affect translated to a variable delivery of volume of gas than what actually was produced in each vessel. To take account of measurement errors due to gas cooling, a conservative correction factor was

implemented in all measurements: normalizing measured gas to standard temperature and pressure (STP) conditions. This factor was conservative because it assumed that gas was collected at 55 °C. The final calibration factor was multiplied by a correction factor (273.15/328.15 °C) to conservatively estimate gas produced in each biogasification vessel.

2.3.4.3 Connection to data acquisition

Previous biogas monitoring (SEBAC) was conducted by off-line measurements with the U-tube gas meter. Counts were typically cumulated for an extended interval of time (typically one day) and a cumulative gas production rate was calculated only then. To better study the evolution of intermittent gas in each vessel, a real-time gas generation concept was implemented to read counts every minute of operation. This real-time measurement approach probed further into the dynamics of gas release during biogasification and map out periods of high/low productivity at a higher resolution.

The U-tube meter operated on a switch-closure mechanism that was actuated by a float switch trigger. When the trigger is activated, a change in voltage was expressed across the two terminals on the 11-pin time relay socket; this switch closure could be picked up as a pulse input (± 2.5 V) by the CR10X datalogger. A dual-wire line was used to connect the datalogger with the gas meter to precisely measure the switch closure. Hence, each count was logged through a pulse port and stored in the final storage. The datalogger provided switch closure resolutions of 1.2 μ s for signals up to 400 kHz.

2.3.5 Sensor for pH

The use of a real-time sensor suitable to measure the pH of leachate during biogasification was incorporated into each system. Luniya 2005 adapted an off-line method of measuring pH to depict the progression of biogasification; one sample was taken each day for measurement. However, further resolution in pH profiling would enhance the insight into the dynamics of pH

change, and become useful in process control applications. This gave impetus to find a pH probe suitable for robust, biological applications that can interface with the CR10X datalogger.

The CSIM 11 pH probe (manufactured by Innovative Sensors, Inc.) was found to be the most appropriate for experimental conditions in biogasification. The probe was built for field and industrial use; it contains a pre-amplifier that practically eliminates the hypersensitive characteristics of ion specific probes. Some important specifications include:

- A 0°C to 80°C temperature range
- A 0 to 100 psig pressure range
- Accuracy of $\pm 0.1\%$ over full range
- Response time as 95% of reading in 10 seconds
- Drift less than 2 mV per week
- Mounting at any angle

The CSIM11 pH sensor was incorporated to measure the pH of digester and anaerobic filter effluent via an external flow-cell method; liquid leachate was pumped from the bottom of each vessel, allowed to flow through a flow cell containing the pH probe, and subsequently returned to the top of the reactor. A bypass line was incorporated in the pH flow cell to assist in inspection, maintenance and calibration of sensors. As a result the flow cell concept (Figure 2-7) circumvented any re-circulation downtime during routine checks on the pH probe

The CSIM 11 pH probe was connected to the CR10X's analog differential channels and was set to measure and store pH every minute during experiments. Temperature compensation of pH measurements was programmed into Edlog code; the pH value was adjusted in real time by using the measured vessel temperature. Appendix A includes the program code that was written to program the pH sensor.

Calibration was carried out on pH sensors on a regular basis to ensure accurate measurements. The frequency of calibration depended on the level of accuracy required and the coating/fouling nature of the samples measured. A trial operation that was conducted revealed

the need to check electrodes that were continuously monitoring leachate checked about once a week. The inspection process included: cleaning the electrode to remove any bacterial films or hard coatings; visually inspecting the reference junction inside the probe; confirming that the bulb was filled with reference solution; and a calibration check.

Calibration check of the pH sensor was conducted by measuring pH of three buffer solutions- pH of 4, 7 and 10. The datalogger was programmed to read pH in each buffer solution and their temperatures. The Nernst temperature compensation was calculated for the probe and an appropriate value of multiplier was used in the datalogger measurement to correct for temperature (Figure 2-8). Each buffer solution was measured within $\text{pH} \pm 0.2$. If a drift was observed, then the value of multiplier was adjusted accordingly. Once the protocol was completed, the pH probe was screwed back into the flow cell to begin monitoring leachate; necessary changes were made to compensate for possible offsets in the program compiler.

2.3.6 Sensor Temperature

Temperature monitoring and control was conducted by T-type thermocouples. The CR10-X had the capabilities of connecting either six thermocouples (differential channels) or twelve (single-ended channels). Each thermocouple contained two dissimilar metals (copper and constantan) that produced a voltage drop when subjected to different thermal contact. Edlog's control toolbox provided a template for reading T-type thermocouple voltage output and converting into a temperature. Thermocouple designs used included extension thermocouple wire and a 1/8 inch junction probe thermocouple manufactured by Omega Scientific, Inc.

Thermocouples were tested for accuracy and precision of measurement. The CR10X internally contains a thermocouple reference that was suitable to use as a standard. To make a thermocouple measurement, the controller reference temperature was converted to equivalent TC

voltage relative to 0° C, and then added to the measured TC voltage; the sum is the reported output temperature, with a polynomial linearization error of $< \pm 0.2^\circ \text{ C}$ from 0°C to + 60 °C.

2.4 Temperature Control

2.4.1 Heating Hardware

Sustaining thermophilic conditions (55°C) in each vessel was addressed after design and fabrication. Heat delivery options that were considered included both internal and external devices; a heating element within the reactor or a leachate re-circulation method which exchanges heat with a warm water bath. The internal heating element option was eliminated on the basis that a completely filled solids bed would impede convection of heat. Also, the possibilities of fouling and scaling heating elements (as seen in SEBAC-2 heating vessels, UF Energy Park Site) during prolonged operation were anticipated. The external heating option proved viable for delivery of a thermophilic leachate, but introduced undesired high re-circulation rates (~ 1.5 L/min) to sustain in-vessel thermophilic conditions.

Thermolyne heating tapes (SIL HTQ TP series type, manufactured by Barnstead International) provided trouble-free heating operation for vessels to sustain thermophilic conditions. They are constructed of high quality resistance wire and braided insulation and are designed to provide the user with long life and high performance. Measuring 1 inch wide and 6 feet in length, each vessel was wrapped with two heating tapes in parallel along its exterior glass wall; tape was used to adequately secure each band firmly on the glass (Figure 2-9). To minimize radial heat losses, flexible-fiber insulation was applied over the heating tape. Each vessel was subsequently wrapped with aluminum heating duct to firmly hold the insulation in place. A view window was left un-insulated to serve as a level indicator for filling and dispensing during vessel loading and unloading.

Each heating band had the capability of delivering 418 Watts of power with a 120 V AC requirement; regulation of heat delivery from each band was addressed by conventional control accessories. Solid state relays (SSR) are normally open switching devices with no moving parts, capable of millions of cycles of operation. The SSRL series of solid state relays (manufactured by Omega Engineering, Inc) were used to control the large resistance heating bands in conjunction with the CR10 X datalogger and controller. Each SSR was equipped with Vdc input/Vac output terminals, which sufficiently linked with the CR10X's pulse terminals. When called upon by a program, the normally open SSR would be triggered by a 5 Vdc control signal from the CR10X; subsequently the SSR would close and complete the circuit, providing 120 Vac to each heating band. An LED status input indicator provided visual confirmation of the state each relay was in. Circuit connections between the datalogger, SSR and heating band (Figure 2-10) provided a simple electrical solution to heating lab-scale vessels with adequate control.

To dissipate heat, each SSR was mounted on an aluminum plate, which conducted heat away, circumventing any overloads or failures of the device. All SSR's were monitored using a multimeter on a regular basis to assure that they were functioning normally. A checkpoint inspection of critical locations within the circuit enabled positive identification of faulty performance (e.g, controller failure to excite 5 Vdc or SSR failures to actuate VAC terminals).

2.4.2 Temperature Control

Sustaining thermophilic conditions in each vessel with the aforementioned heating hardware was addressed by a temperature profiling of the system. The simplest form of control (on/off control) was deemed sufficient for robust batch studies. On-off control is usually used where precise control is not necessary, or where the mass of the system is so large that temperatures change very slowly. Some of the observations taken into consideration, while deciding on a control strategy included:

- Temperature and spatial variations (if any) within each vessel
- Acceptable high/low set points for on/off control
- Single, dual-direction and no liquid re-circulation on temperature control
- Warm-up time

Temperature profiling was conducted initially by placing six thermocouples (type-T) at multiple radial and axial positions in conjunction with a liquid re-circulation mode for mild mixing; Rachig rings were packed into the bed area to simulate biomass solids and 12-L of water was poured into the reactor to flood the bed (Figure 2-11).

An on-off controller will switch the output (on or off) only when the temperature crosses a set point. Since the temperature crosses the setpoint to change the output state, the process temperature will be cycling continually, going from below setpoint to above, and back below. As a result, the turn-on and turn-off temperatures were deliberately made to differ by small amounts to prevent noise from switching the heating band rapidly and unnecessarily when the temperature was near the set point. The appropriate Edlog program was coded (Appendix A) for on/off control of the heating bands around a vessel; open loop control tuning was done to determine the optimum on/off set-points within system constraints (packed bed media and constant re-circulation rate). A total of nine profile studies (Figures 2-12 to 2-17) were conducted for development of an adequate heating control strategy.

2.4.3 System Temperature Profiling

The temperature profile studies conducted served as indicators of system performance under experimental conditions; the studies revealed the following:

- The first profile study (Figure 2-12) was conducted to characterize any spatial temperature variations in the vessel. The six thermocouples indicated that it took approximately 230 minutes to elevate the vessel temperature from 25°C to ~ 55°C. Moreover, the difference in temperature after a steady-state on/off control between each thermocouple was ± 2 °C. Such small temperature gradients were deemed tolerable spatially; subsequently, a thermocouple position in the center of the bed was assigned for temperature control.

- The second profile study (Figure 2-13) was aimed at determining the on/off set points for heating. At a one-minute interval resolution on data acquisition and a constant re-circulation rate (~ 0.42 L/min), the on/off set-range boundaries were toggled at four different settings. The aim of each study was to converge and confine the bed temperature to or near 55°C. The outcomes demonstrated an inherent lag associated with on/off control. As a result, the minimum amplitude for the saw-tooth profiles under a spatially-centered thermocouple position was approximately 1.5°C.
- The third profile study (Figures 2-14 and 2-15) aimed to characterize the dependency of liquid re-circulation on temperature control. With no re-circulation, the saw-tooth temperature profiles were confined within 54-55.5°C shifted to 54.5-56°C, resulting in a less desired control profile. Spatially, a gradient of approximately 20°C (after 800 minutes) existed from the center of the bed to the re-circulation ports at the bottom of the reactor.
- The last profile study (Figures 2-16 and 2-17) was conducted to validate whether a toggling re-circulation schedule for mixing would sustain or improve the temperature control observed in Figure 2-13(D). The incentives for toggle-mixing were justified during high solids mesophilic digestion of simulated solid waste (Luniya, 2005). In that work, compaction of solid waste bed in a reactor during biogasification was alleviated and dislodged by a toggle re-circulation mode. Five minute cycles were exercised in each direction of re-circulation. Within a 100-minute steady-steady state thermophilic control trial, the toggle-mixing scheme increased the amplitude of the saw-tooth profile to 2°C and introduced sharp changes in temperature/time. From all the temperature characterization studies conducted, profile study Figure 2-13 (D) was the most appealing for on/off control.

2.4.4 Temperature Fail-Safe Protocol

Other matters pertaining to temperature control in each biogasification vessel were also considered. Typically, automated control systems that rely on a power source employ a fail-safe mechanism for managing sudden changes to control or operation. In the case of this work both C1 and C2 depended on a constant power supply provided by two 12-V batteries. Each unit would function optimally when the input source voltage ranged from 11.5 to 12.5 VDC. However, if the voltage power supply fell below 11.5 V, each controller would go into an indeterminate state; the data logging capabilities would become limited and the actuation ports (which controlled heating) would be locked into either an on or off state. Implications of such failure included:

- Temperature control failure in “off” mode, resulting in decreased temperature and kinetics.

- Temperature control failure in “on” mode, resulting in exceeding the tolerable temperature limits of the microbial culture (cell death).
- Failure to log other system parameters, resulting in loss of viable data for biogasification

In addition to daily voltage inspections on both batteries, a fail-safe program was also devised to address the potential consequences of an indeterminate datalogger. Several commands were coded (Appendix A) to systematically check the voltage of each battery and appropriately respond. The primary concern in this work (or for that matter in any anaerobic reactor) was preservation of the microbial culture. As discussed temperature control failure in the “on” mode would result in the destruction of the inoculum, when subjected to high temperature for a prolonged period of time. Thus, a fail-safe command was coded that read the voltage of a battery and systematically commanded actuator ports; if voltage fell below 11.8 V, the program would automatically turn off actuator ports for heating. Justification in kinetic losses outweighed the potential risk of losing batches of inoculum by subjecting to thermal shocks.

2.5 Pressure Testing

2.5.1 Positive Pressure Testing

The performance of biogasification experiments was initially evaluated by the quantity of biogas produced per given time. Biomass is mineralized to a methane and carbon dioxide gas-mixture from available substrate (solid feedstock and soluble constituents) and released from the bed by buoyancy; subsequently, measurements of gas mixture volumes and composition provide explicit insight to biogas production rate and implicit insight to biochemical progression, respectively. With performance measure being so highly dependent on gas collection, efforts were taken to correctly seal and minimize gas leaks.

Each vessel was fabricated to accommodate approximately 2 psi according to ARS engineers; the allowable pressure accumulation (before exhaust) in each vessel when connected to the U-tube displacement meter was approximately 0.25 psi. A protocol was devised that would systematically check if the system leaked. Possible leak areas considered were as follows:

- Brass fittings for re-circulation, thermocouple, and gas outlet (Atop lid)
- U-tube meter
- Biogas tubing (vessel-to-meter line)
- Top-lid gasket

The leak test consisted of pressurizing the vessel and gas meter system to comparable values seen during biogasification experiments. Each system was injected with air through the biogas sampling septum and the liquid-level in the biogas meter was monitored. Enough air was injected to enable the displaced liquid column to just fall short of tripping the float switch. The level of the fluid in the in-going column was marked to detect changes over time; liquid soap was applied at the aforementioned leak areas to detect any leaks. The level of the gas meter was examined after 24 hrs to quantify any pressure loss; typical liquid-level changes observed over that period were approximately 1-inch of water (0.04 psi). With expected biogas production of 500 mL per day, 0.04 psi loss translated to about 25 mL/day of biogas (4.8% of average daily biogas production).

2.6 Liquid Storage Vessels

2.6.1 Inoculum Storage Tank

A storage tank (Figure 2-18) was fabricated for storage of accumulated or excess inoculum produced during biogasification experiments. A simple vessel in design, the storage tank make-up comprised of a cylindrical PVC body, 18 inches in diameter and was placed horizontally. Two PVC caps were glued to each end of the body, completely enclosing the 100-L vessel. Five bulk-head fittings were placed on one face of the vessel and valves were fitted appropriately;

four ports on the top for liquid inlets/gas outlets and one at the bottom as a liquid outlet port.

With the nature of contents being thermophilic anaerobic inoculum, each vessel was kept anaerobic. A 40-L collapsible gas bag was fitted on one valve to monitor any gas production and supply oxygen free gas in cases of vacuum.

2.6.2 High COD Liquid Storage

A storage vessel (Figure 2-19) for wastewater generated from pre-treatment of sugar beet tailings was also constructed. To avoid fermentation of wash water, a refrigeration unit was put in place. A collapsible, 20-L storage bag was suspended inside the refrigeration unit, with inlet and outlet ports at the bottom. This collapsible bag concept provided the means of storing highly degradable liquid feedstocks in oxygen-free and cold environments (4 °C). Liquid was delivered to the storage bag via a ¼-inch tube drilled through the refrigerator insulation, which connected to outlet ports on biogasification units. In experiments where liquid stream was biogasified, a Cole Parmer peristaltic pump was used to pump out contents and deliver them to the appropriate vessel.

2.7 Biogasification System Setup

An operational schematic of the setup of solids (Figure 2-20) and liquids (Figure 2-21) biogasification reactors used in this research aided the construction phase of the project. Schematics highlighted the dimensions of each unit, the reactor sectional volumes and positions of sampling and outlet ports. The re-circulation system in both cases was driven by Masterflex peristaltic pump using Masterflex Tygon (15) tubing, which has very low oxygen diffusivity. For sequencing-experiments (Chapter 6), an *L/S* Masterflex programmable pump was used to exchange leachate between the solids and liquid reactor. The complete biogasification experiment station (Figure 2-22) was optimally positioned on a lab bench to facilitate easy loading/un-loading of solids, daily sampling and safety considerations.

2.8 Feedstock Preparation

Sugar beet tailings were collected by ACSC during the 2005-2006 processing campaign at East Grand Forks Plant, Minnesota. A total of 525 kg of sugar beet tailings were stored in 35 pails and kept in a freezer unit by ACSC. Upon request, feedstock was shipped in five liter pails (frozen) to the University of Florida. Pails of tailings received were mixed together thoroughly to yield a homogenous feedstock sample. Tailings were then packaged in 1.5, 3 or 5-kg aliquots and stored at 0°C in a freezer.

2.9 Protocol for Solids Reactor Loading

2.9.1 Pre-Loading Protocol

Prior to loading a reactor with sugar beet tailings, the empty reactor was thoroughly cleaned. Additionally, the peristaltic pump tubing was replaced, the pH probe was tested for accuracy and all the re-circulation lines were checked for any damage and valves were rinsed free of any particulates or debris. A spot calibration was conducted on the biogas meter to confirm that volumetric counts of gas did not change. Thereafter, a pressure test was also conducted on each reactor before start-up to also assure proper sealing. With satisfactory compliance to pre-loading protocol, each reactor was ready for loading of sugar beet tailings.

2.9.2 Un-Bulked Experiments Loading

The allowable quantity of sugar beet tailings that could be loaded in each reactor permitting a 1.8-L headspace was shown to be approximately 6 kg wet weight. Pre-packaged aliquots of tailings were poured into each reactor, with no external compaction applied, to form a bed of tailings. The top-lid suspended perforated plate was adjusted adequately to intimately make contact with the top of the filled waste bed and the occupied volume was recorded. The packing density of un-bulked experiments ranged from 450 to 650 kg/m³ (wet basis).

2.9.3 Bulked Experiments Loading

Bulked experiments (Chapter 5) were conducted by spatially arranging a bulking agent inside the sugar beet tailings waste bed. Between 1-2 kg of Pumice stones (landscaping rocks, 25 mm in average size obtained from Lowes, Gainesville) were strategically placed in mono-layers during the feedstock loading procedure (Figure 2-23). The aliquot of tailings was divided into 4 sub-samples to assure homogeneous layers between each bulking agent layer.

The top-lid suspended perforated plate was adjusted adequately to intimately make contact with the top-most layer of bulking agent. The packing density of bulked experiments ranged from 250 to 450 kg/m³.

2.9.4 Reactor Start-Up

The reactor was sealed once the loading process was completed. A thin layer of Dow Corning high vacuum grease (976-V) was applied on the glass-flange lip and adjoining gasket. The top lid was brought into position and was fastened in a cross-direction fashion. A thermocouple probe was inserted from the top of the lid into the bed of biomass. Connections between the reactor and gas meter and liquid re-circulation lines were made by Tygon 3/8-inch and hard plastic tubing, respectively. Digester liquor (from previous batch run) was pumped inside to the level of the top perforated plate. The volume of this typically ranged from 8.5 to 12-L, depending on the packing density of an experiment. A viewing glass was used to guide fill-up progress. Sodium bicarbonate was added at 5 g/L to sufficient buffer the system during biogasification. The entire system was pressure tested once more using CH₄/CO₂ gas mixture (60:40 in volume ratio) and the pressure level was monitored over a period of a few hours. The temperature control was then turned on and the reactor was gradually heated until the set range (54.5 to 55°C); this process took approximately 230 minutes. Once the temperature of the reactor had reached the desired temperature range, the experiment was then recorded as being at

day “zero” and the initial gas meter counter noted; datalogging was subsequently initiated by the CR10-X.

2.9.5 Reactor Un-Loading

Upon completion of biogasification, reactors were unplugged from heating and biogas monitoring. Liquid was drained from the bottom, while solids were removed manually from the top. The residue collected was dewatered by gravity and was ready for analysis (see Solids Analysis section). A sample of liquid was tested for analytical parameters and the rest was stored in the inoculum storage vessel.

2.10 Protocol for AFR

2.10.1 Reactor Start-Up

The AFR was constructed for the purpose of treating liquid organic streams, namely COD-rich wastewater produced in the solubilization experiments of sugar beet tailings (Chapter 4). A pre-loading protocol was administered in the loading of the liquids digester, analogous to solids loading. Approximately 10 kg of pumice stones (similar to the ones used for bulking the solids in the solids digester) filled the entire available volume above the perforated plate (approximately 16 L). The pumice stones served as a support for growth media to encourage the growth of biofilms. Approximately 1 kg of sugar beet tailings was also added as part of this packed bed, serving as a way to start up the digester. With no top-perforated plate, the reactor was greased and sealed. Start-up was initiated by gradual heating until the thermophilic set range was attained similar to solids reactors. Datalogging was subsequently initiated.

2.10.2 Feeding

Experiments conducted with liquid streams were conducted in both batch and fed-batch feeding options. In batch feeding mode, wastewater aliquots subjected to treatment were pumped into the system by the AFR e-circulation pump. Firstly, the specified feed volume was

drained from the reactor into the inoculum storage vessel (Figure 2-18); next, the AFR recirculation pump was disconnected from its mixing duties and used for pumping fresh feed. During the procedure, the reactor was vented to atmosphere to avoid any biogas meter failures as a result of not maintaining reactor volume. Finally, the reactor was sealed and injected with CH₄/CO₂ mixture to purge any air out of the system.

In semi-batch feeding mode, an L/S brushless programmable Masterflex pump was used to make scheduled deliveries of feed. A dual-peristaltic head was used to adequately add feed at the top of the reactor while removing effluent liquid at the bottom of the vessel; influent wash water was pumped from the cold liquid storage bag whereas the effluent was pumped into the inoculum storage vessel. With the proximity of 2 feet between liquid storage and reactor, a minimum dose rate (100 ml/min) and dose duration (1 minute) was established for delivery of fresh feed to the system. The mechanism of simultaneous feeding and removal permitted the volume of reactor to remain constant.

2.11 Protocol for Sequencing Experiments

A total of 15 experiments were carried out in this research study. Out of these 15 studies, 4 of them involved the exchange of leachate between the ABCR and AFR. The exchange of leachate between the two reactors is termed as a sequencing process. Sequencing was provided by using the L/S Masterflex programmable pump set a specific delivery schedule; adjustments were made to sequencing throughout the during of studies. Details of the sequencing protocol are further discussed in Chapter 6.

2.12 Inoculum Development

Microbial populations necessary for biogasification were cultured during a 12-month, ongoing acclimatization process. In addition, this extended study time served as a shake-down phase in understanding system responses, tendencies and limitations. It was found that the

appropriate microbial populations required for biogasification were naturally present within the tailings; no external source of inoculum was needed to initiate methanogenesis. A simple incubator method was used to cultivate the present microorganisms by supplying them with appropriate conditions for growth. Sugar beet tailings were initially placed in two, 5-L glass bottles and flooded with water containing sodium bicarbonate. The bottles were placed in an incubator controlled at $55 \pm 1^\circ\text{C}$. Biogasification parameters were monitored on a daily basis. The process was scaled to the 20-L solids reactors (ABCR 1 & 2) after three generations of 5-L incubator trials. A total of 15 acclimatization trials (Figure 2-24) were conducted, resulting in 24 L of a 10th generation microbial population suitable for conducting well-controlled experiments in biogasification. All subsequent experiments were started by using the 24-L inoculum derived from Experiments 15 and 16.

2.13 Design of Experiments

An experimental design was drafted to effectively carry out bench-scale biogasification studies with scopes of ascertaining how quickly sugar beet tailings biodegrade and mineralize to methane and developing methods to accelerate the biodegradation rate. During the inoculum-building process, observations made on biogasification and solubilization characteristics, behavior of the bed of tailings during degradation and other phenomena, gave direction in choosing the appropriate experiments. A total of four studies were chosen as areas of research interest addressed in the design of experiments:

- **Study I:** Single-stage, high solids biogasification of sugar beet tailings
- **Study II:** Pre-treatment effects (solubilization) to enhance single-stage biogasification of sugar beet tailings
- **Study III:** The effect of bulking on the biogasification of sugar beet tailings
- **Study IV:** The effect of two-stage operation on the biogasification of sugar beet tailings

The design of experiments (Figure 2-25) carried out on sugar beet tailings was a systematic tool used to develop a strategy for enhanced biogasification by elimination of unnecessary experiments.

2.14 Analytical Methods

2.14.1 Gas Analysis

Gas samples were taken daily from each reactor using a 20-mL gas tight syringe fitted with an air-tight tee valve. The gas samples were analyzed with a Model 1200 Fisher Gas Partitioner. The GC was fitted with two 6-foot *Haysep* 80/100 mesh columns containing Porapak Q support. Ultra high purity Helium (99.99%) was used as the carrier gas at an operating head pressure of 15 psi. The gas was analyzed for its methane, carbon dioxide, nitrogen and oxygen content. The GC was calibrated with an external standard containing N₂:CH₄:CO₂ in volume ratio of 25:45:30. Gas chromatographs were processed and recorded using a SP 4290 Spectra Physics Integrator.

2.14.2 Liquid Analysis

2.14.2.1 pH

The analysis of pH was conducted using the Campbell Scientific on-line pH probes discussed earlier (See section 2.3.5).

2.14.2.2 Soluble chemical oxygen demand

The soluble chemical oxygen demand (SCOD) analysis was carried out using HACH's United States Environmental Protection Agency (USEPA)-approved dichromate method. The method utilized small micro vials that contained the necessary reagents (silver, chromium and mercury) to carry out the analysis. Leachate samples were withdrawn from each reactor daily; each sample was centrifuged (Fisher Marathon micro H centrifuge), filtered (Whatman micro filter paper, 45 µm) and stored for COD analysis. Precautions were taken to minimize the vaporization of VFA's, which accounted for a fraction of the total SCOD to be measured. Vials

(HACH COD of range: 2 to 1500 mg/L) were filled with leachate sample (diluted if estimated detection limit was approached) and digested for 2 hours at 150°C in a COD reactor (HACH, Model 45600). The SCOD of the digested samples were estimated by measuring their color using a colorimeter (HACH, DR/890) against a blank. Average error of colorimetric COD analysis was quantified as $\pm 4\%$ for samples that range 0 to 20,000 mg/L.

2.14.2.3 Volatile fatty acids

The volatile fatty acids (VFA's) were analyzed on Shimadzu GC- 9AM with a Flame Ionisation Detector (FID) gas chromatograph. The GC-FID was equipped a 1.7 m long by 3 mm inner diameter glass column packed with 100/120 chromosorb WAW coated with 1% phosphoric acid. High purity nitrogen (99.9%) was used as the carrier gas at a flow rate of 20 ml/min. Hydrogen and air were used as the combustion gases, flowing at 0.6 and 1.0 ml/min, respectively. Temperatures of injector, column and detector were 180 °C, 145°C and 200°C respectively.

Four standard solutions were prepared with a fixed concentration (50, 100, 200 and 500 mg/L) of all six VFA's (acetic acid, propionic acid, butyric acid, iso-butyric acid, valeric acid, and iso-valeric acid) to be analyzed. All the standards were stored in air-tight glass jars under refrigeration to prevent VFA breakdown. For the range of interest (50 – 500 mg/L), VFA peak response was shown to be linear; subsequently, calibration was conducted only at 100 mg/L. Analysis of the standard solution yielded acetic acid at 108 mg/L $\pm 12\%$; propionic acid at 104 mg/L $\pm 9\%$; butyric acid at 99 mg/L $\pm 8\%$; iso-butyric acid at 96 mg/L $\pm 8\%$; valeric acid at 93 mg/L $\pm 9\%$; and iso-valeric at 96 mg/L $\pm 9\%$. The GC-FID was calibrated with standard solution prior to analysis of liquid samples.

Liquid samples were withdrawn daily from each reactor; each sample was centrifuged (Fisher Marathon micro H centrifuge), filtered (Whatman micro filter paper, 45 μ m) and stored

(4°C). Sample preparation for analysis of VFA consisted of mixing a 1-mL solution of centrifuged and filtered sample and 20% (by volume) of phosphoric acid for acidification. The solution mixture of 2 µL volume was then injected into the GC-FID (after calibration).

2.14.3 Solids Analysis

2.14.3.1 Moisture content

Aliquots of fresh sugarbeet tailings (0.5 to 1 kg) and digested residue (0.3 to 1.5 kg) were set aside for solids analysis. The moisture content of each aliquot was determined by placing the sample in a constant temperature oven at $105 \pm 1^\circ\text{C}$ for a period of 24 hours. Subsequently, each sample was allowed to cool down to room temperature and weighed with an analytical balance. The percent total solids and moisture was calculated by mass difference.

2.14.3.2 Volatile solids

After a sample was dried for moisture content and total solids, the volatile solids content was determined. Each sample was placed in an evaporation tray (aluminum) or crucible and then placed inside a furnace at $550 \pm 5^\circ\text{C}$ for two hours. After heat treatment, each sample was removed and allowed to cool down at room temperature in a desiccator, before being weighed. The volatile solids content was calculated by mass difference.

2.14.3.3 Solids composition calculation

Calculations for % solids, % volatiles and % fixed solids were carried out according to standard methods (APHA, 1992)

Solids chemical characteristics

The chemical composition of raw sugarbeet tailings and digested residues were tested. Sample aliquots (50 g) were stored in air-tight bags and packed in an insulated envelope for shipment to a forage testing laboratory (Dairy One, Inc., Ithaca, New York). The components tested on the wet and dry matter basis are listed in Table 2-1. Upon receiving forage labs results,

calculations were performed to determine the % solubilization and degradation of the aforementioned components as a result of biogasification. The pertinent definitions regarding components tested were given by Dairy One fact sheet. The definitions for carbohydrates are as follows:

- **Neutral detergent fiber (NDF):** is a measure of hemi cellulose, cellulose and lignin representing the fibrous bulk of the forage
- **Acid detergent fiber (ADF):** is a measure of cellulose and lignin

2.15 Performance Analysis

The performance of the biogasification reactors was evaluated by fitting the cumulative methane production data to the modified Gompertz equation (Lay et al., 1998). The Gompertz equation describes cumulative methane production from batch digesters assuming that methane production is a function of bacterial growth. The modified Gompertz equation is presented as

$$M = P \times \exp \left\{ - \exp \left[\frac{R_m \times e}{P} (\lambda - t) + 1 \right] \right\} \quad (1-1)$$

where M is the cumulative methane production, $L \text{ (kg VS)}^{-1}$ at any time t , P is the methane yield potential, $L \text{ (kg VS)}^{-1}$, R_m is the maximum methane production rate, $L \text{ (kg VS)}^{-1} \text{ d}^{-1}$, λ is the duration of lag phase in days (d), and t is the time (in days) at which cumulative methane production M is calculated.

The parameters P , λ and R_m were estimated data sets by using the ‘Solver’ feature in MS-Excel. The value of parameters which minimized the sum of the square of errors between fit and experimental data were determined.

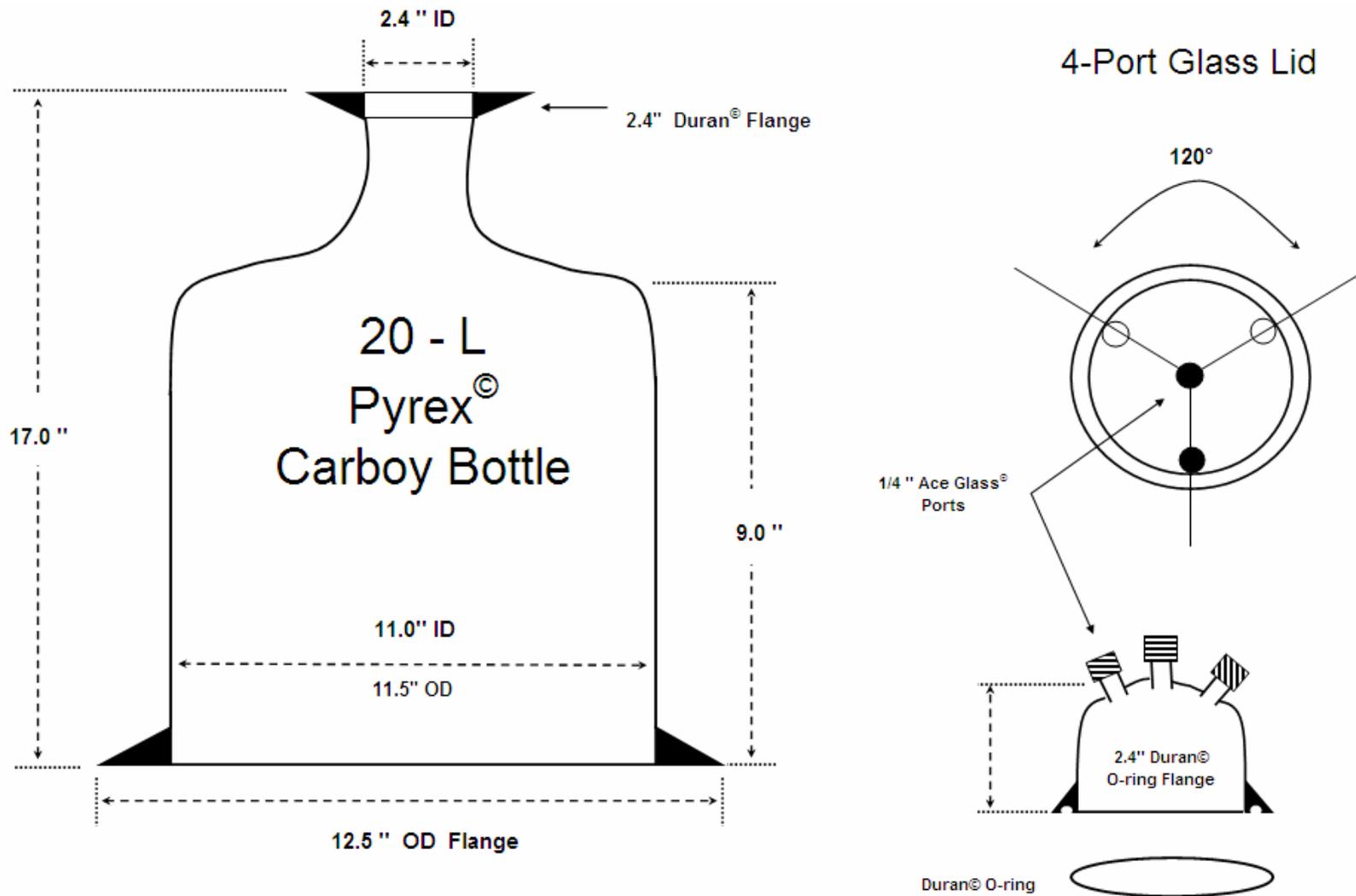


Figure 2-1. Construction of biogasification vessels from 5-gallon carboy bottle

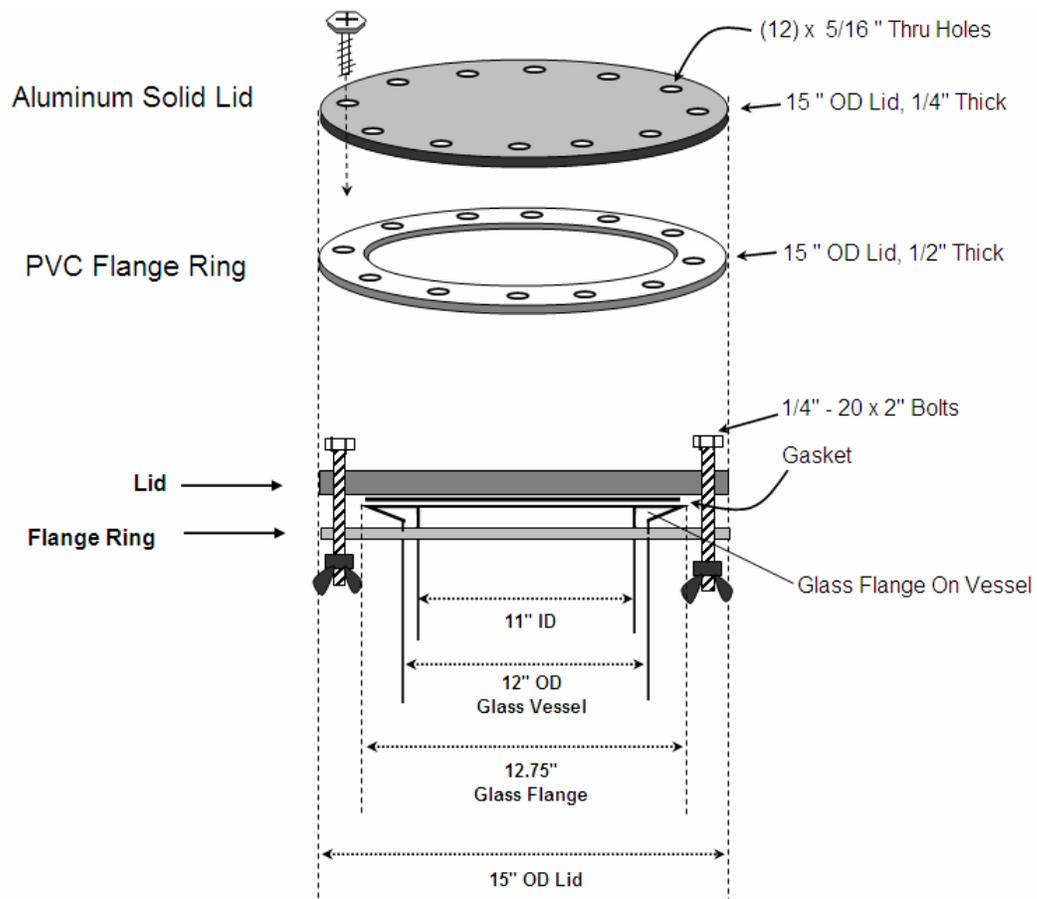


Figure 2-2. Lid components and sealing mechanism for biogasification vessels

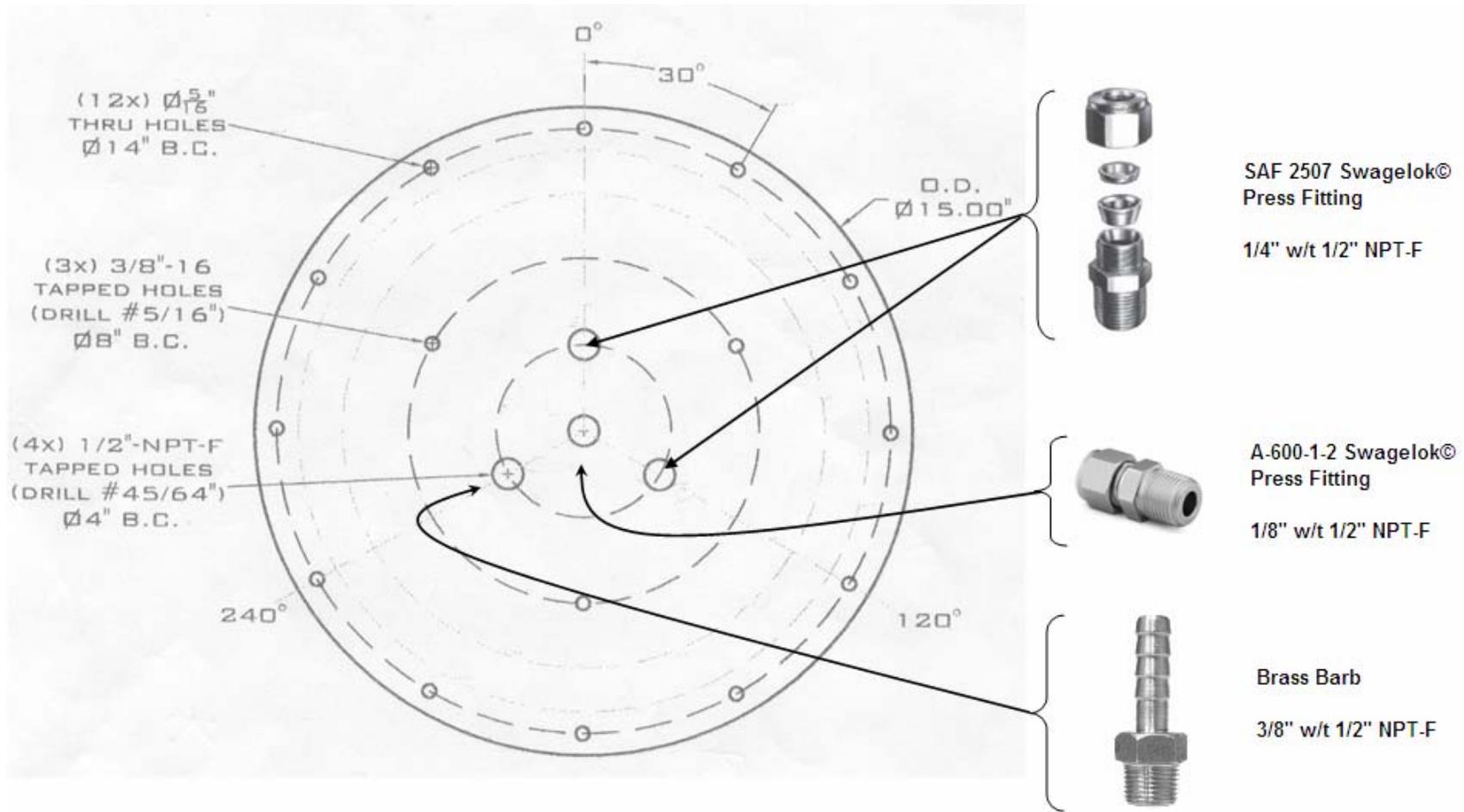


Figure 2-3. Lid specifications and components for biogasification vessels

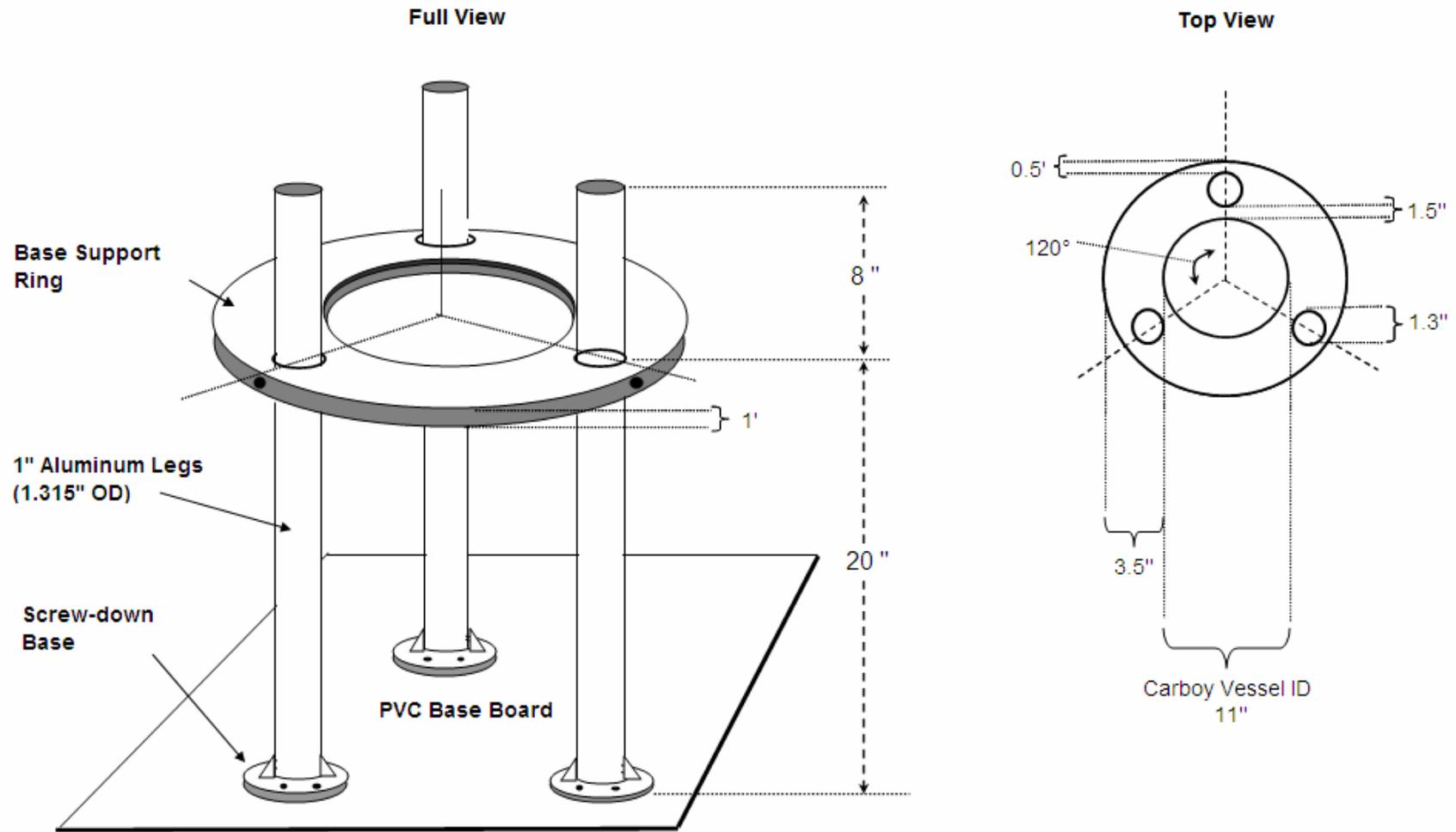


Figure 2-4. Custom-built tripod stand for biogasification vessels

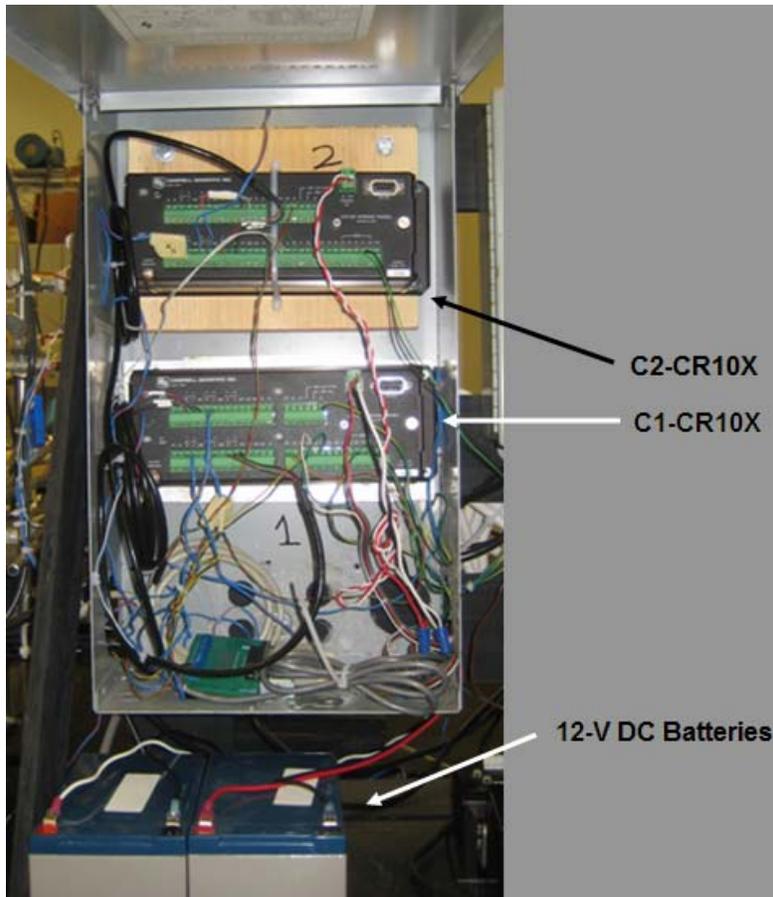


Figure 2-5. Controller panel C1 and C2

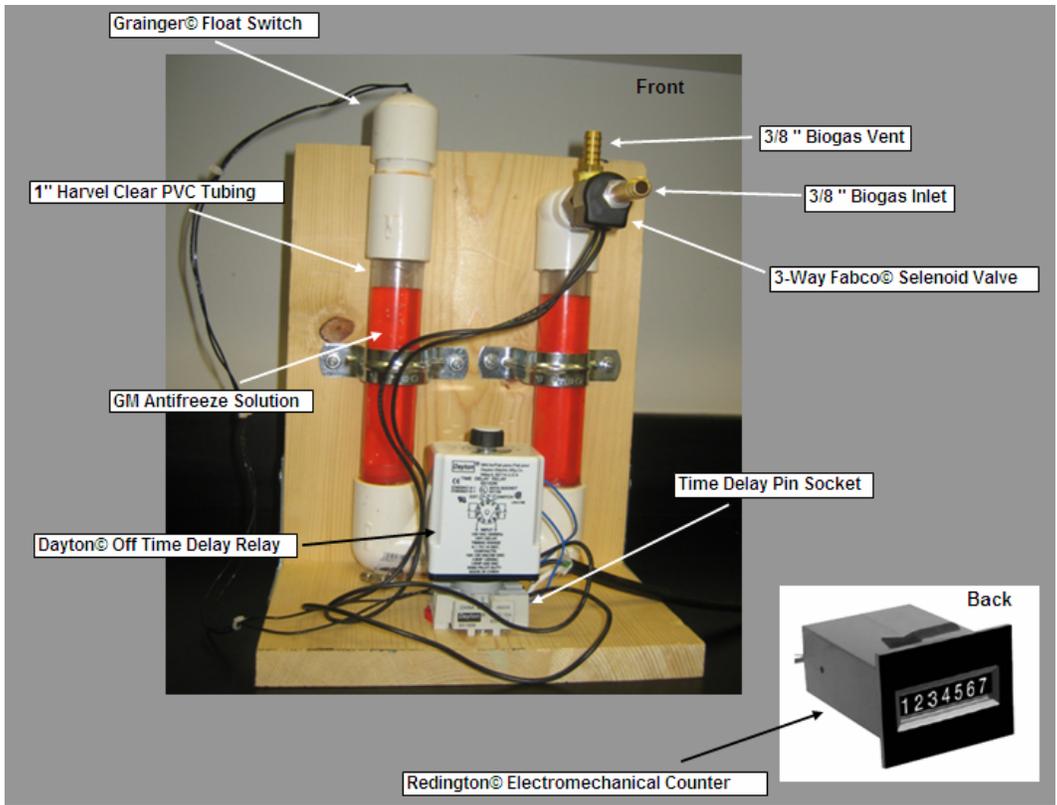


Figure 2-6. Biogas U-tube meter

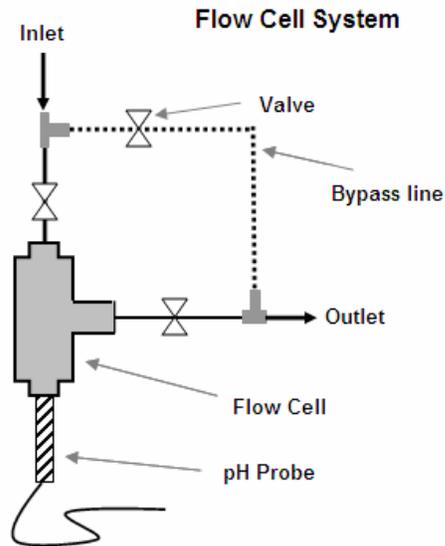
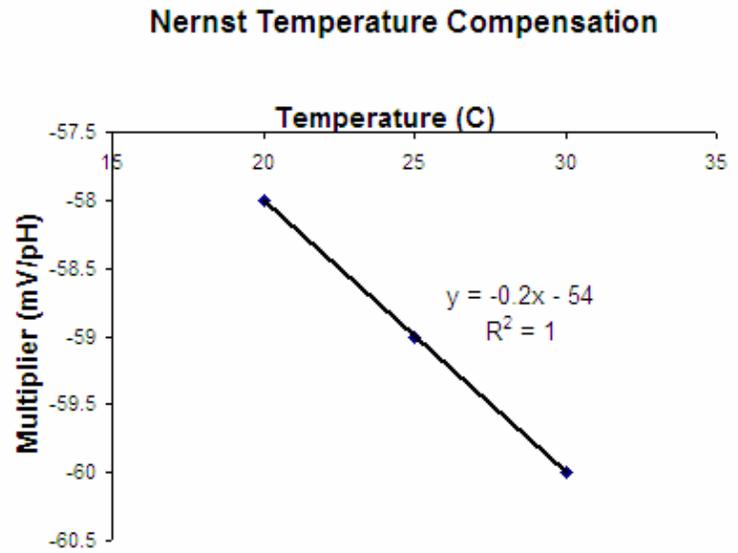


Figure 2-7. pH flow cell system for biogasification system

Temp (Celsius)	Compensation (mV/pH)
20	-58
25	-59
30	-60

Temp (Celsius)	Compensation (mV/pH)
55	-65



$$pH \text{ Multiplier} = \frac{-1}{\left(\frac{[Temp \text{ of Sample} + 273]}{298} \right)} \cdot (Compensation \text{ Factor})$$

$$pH = (pH_{Raw}) \cdot (pH \text{ Multiplier})$$

Figure 2-8. Temperature compensation calibration of pH sensor



Figure 2-9. Heating tape attachment to vessel wall

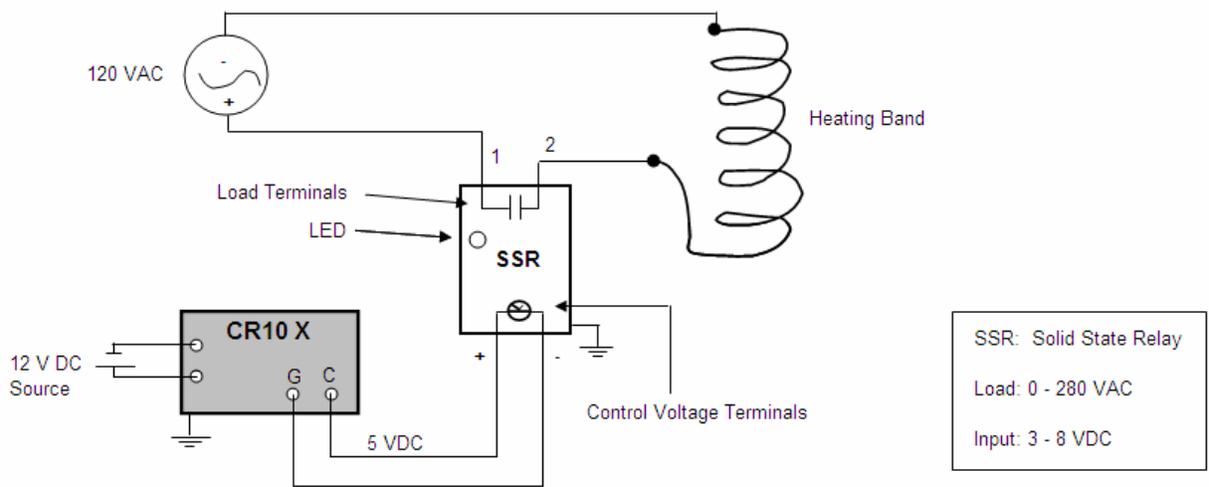


Figure 2-10. Circuit diagram for heating band

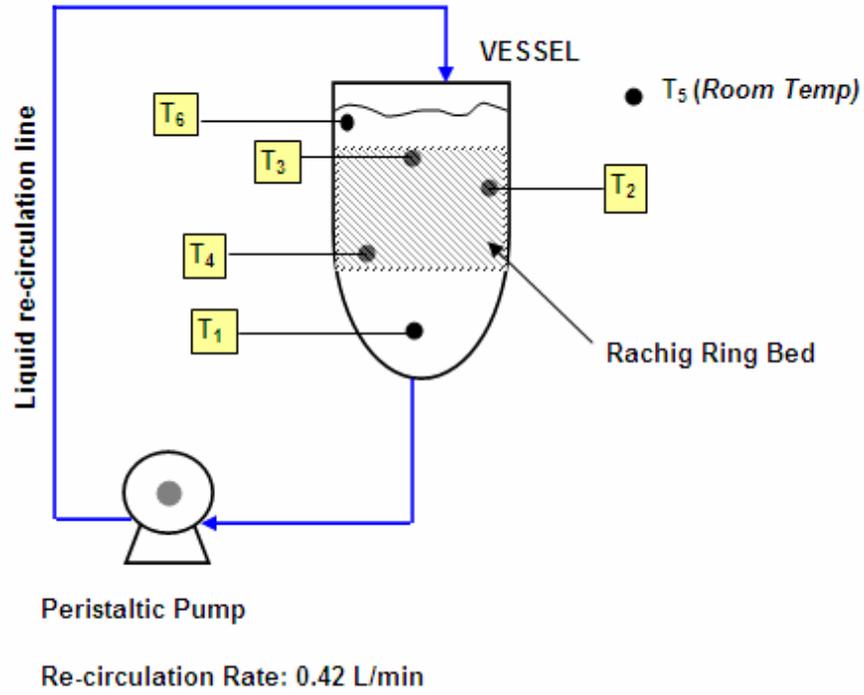


Figure 2-11. Schematic for vessel temperature profiling

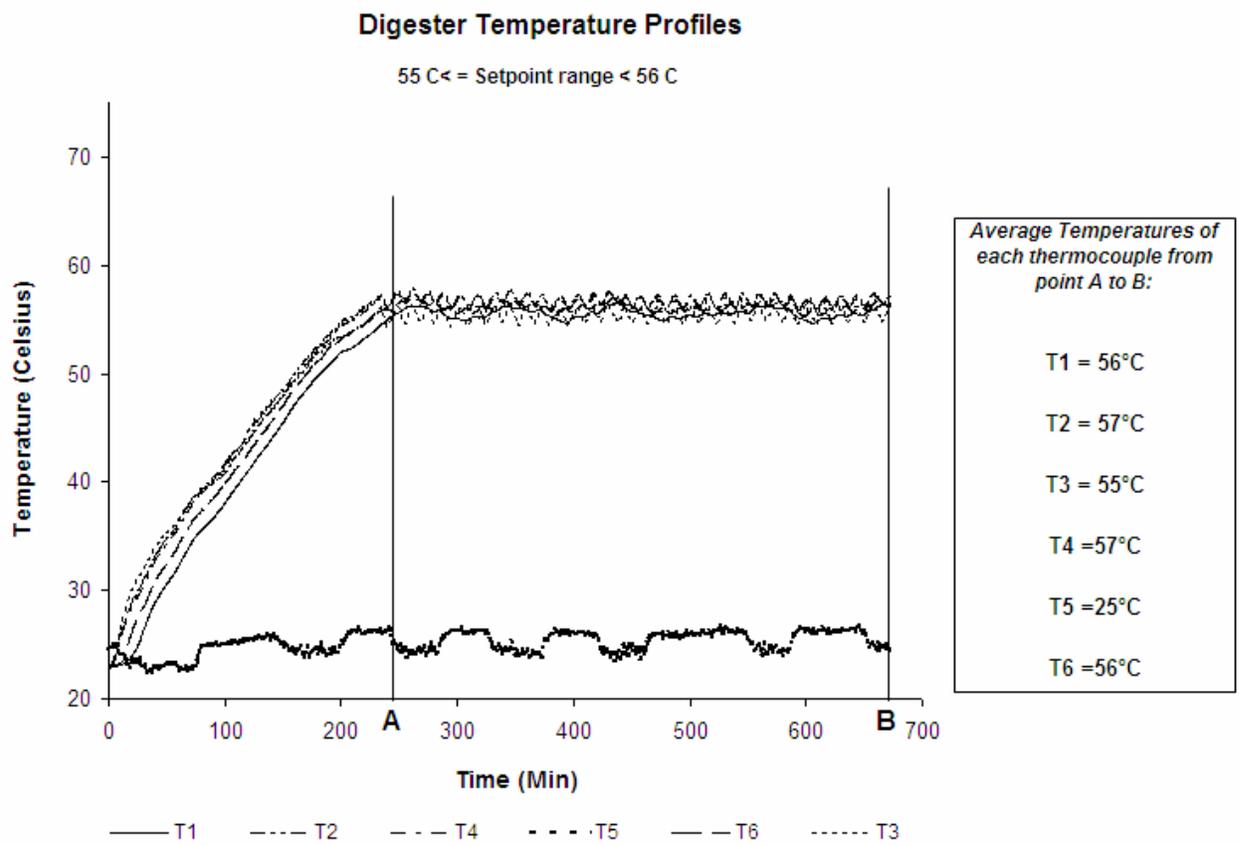


Figure 2-12. Spatial temperature profiles in biogasification vessel

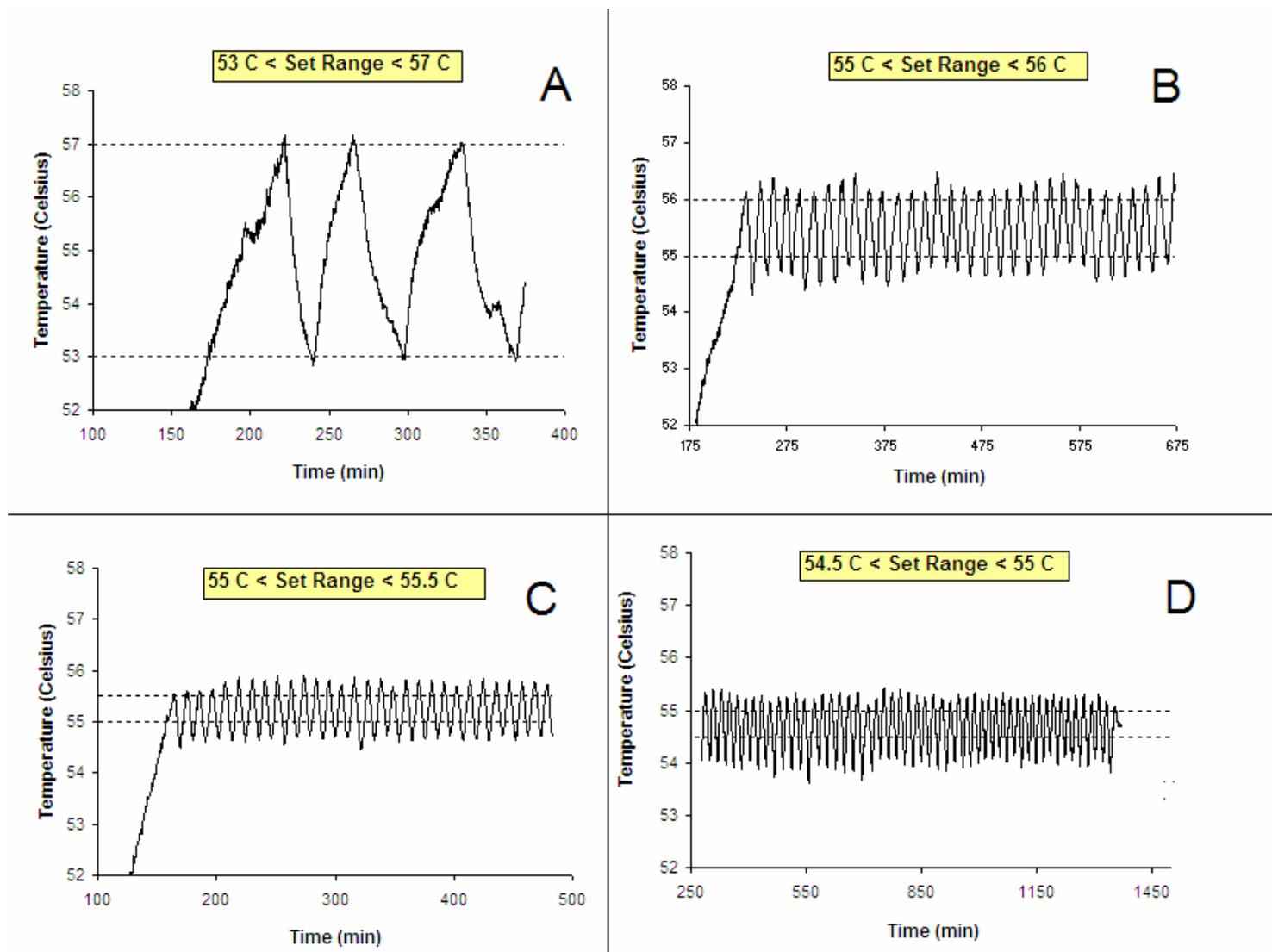


Figure 2-13. On/off controller tuning of heating to biogasification vessel. A) Set-range from 53 to 57 °C. B) Set-range from 55 to 56 °C. C) Set-range from 55 to 55.5 °C and D) Set range from 54.5 to 55 °C

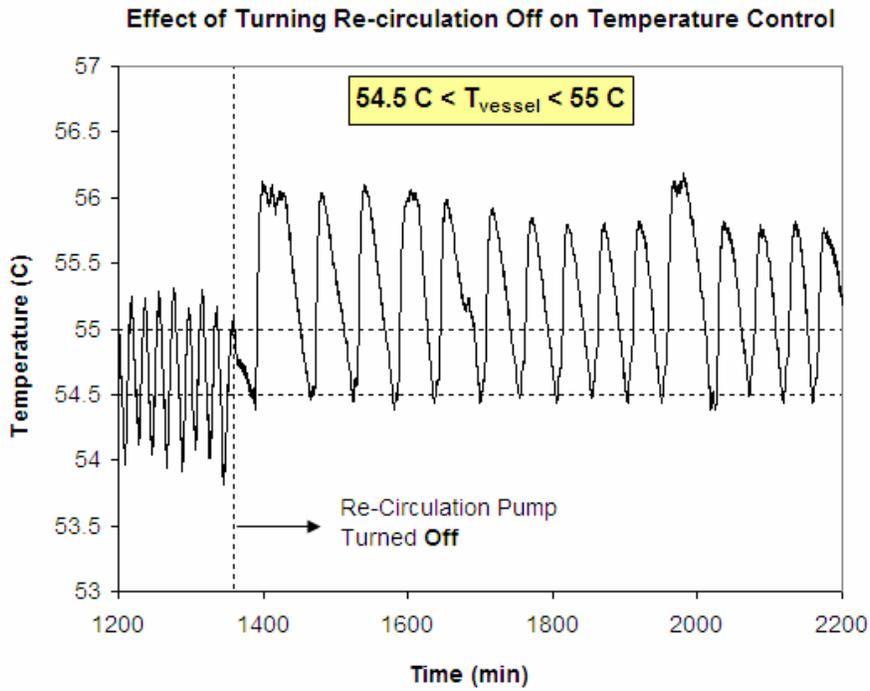


Figure 2-14. Liquid re-circulation effect on temperature control

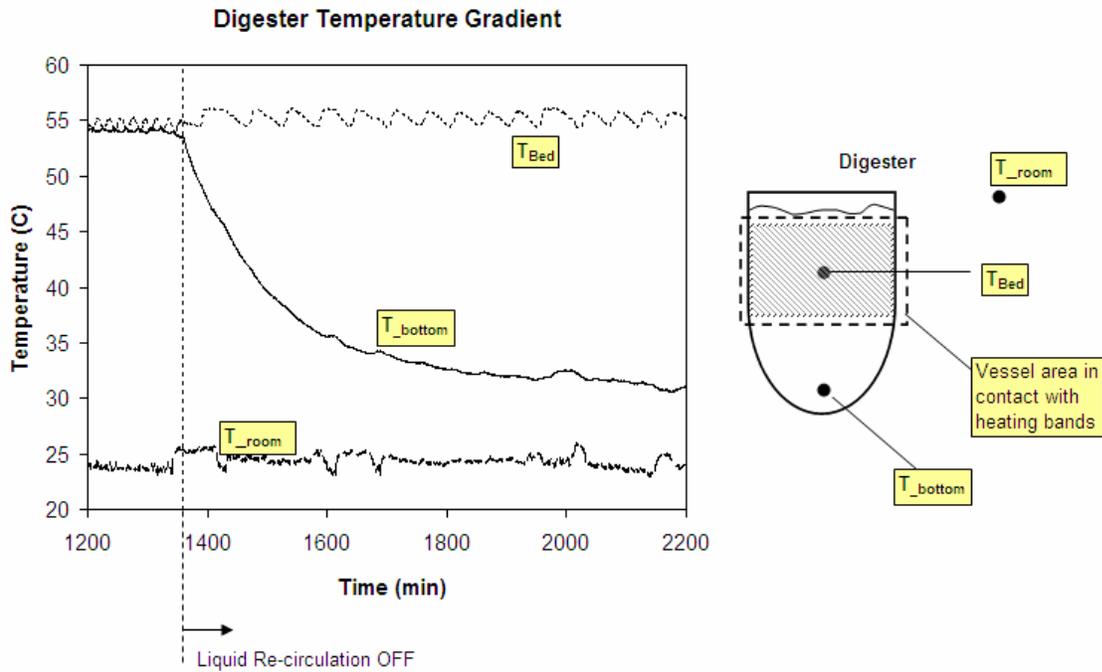


Figure 2-15. Temperature profile within biogasification vessel during on/off re-circulation mode

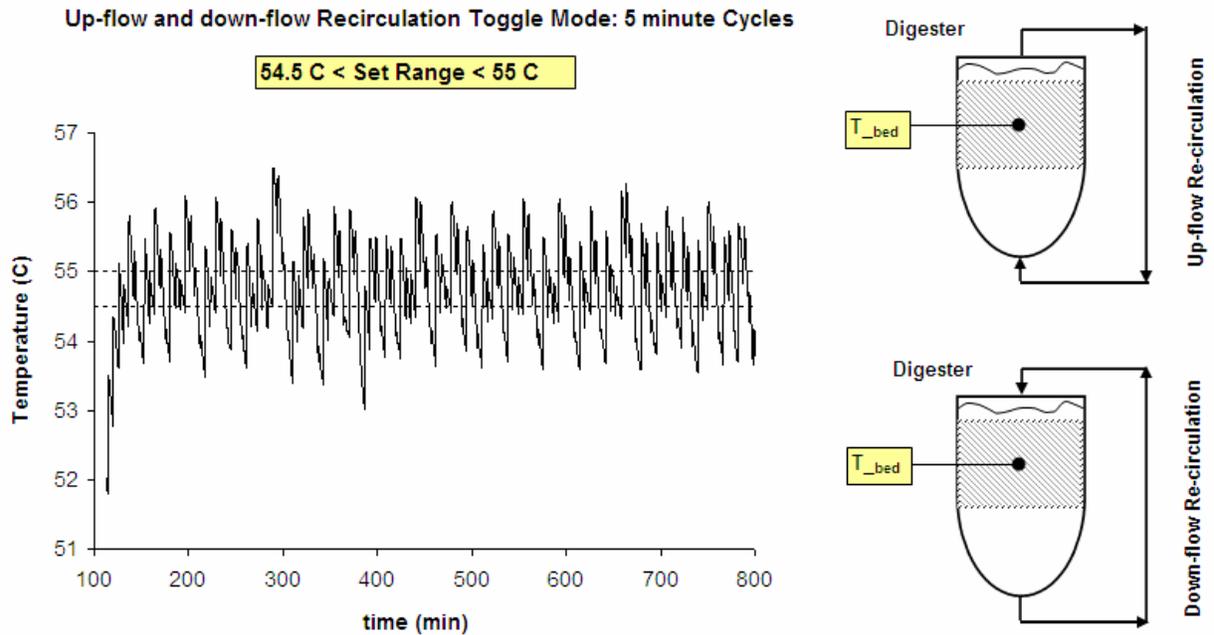


Figure 2-16. Temperature profile within biogasification vessel during up-flow and down-flow re-circulation

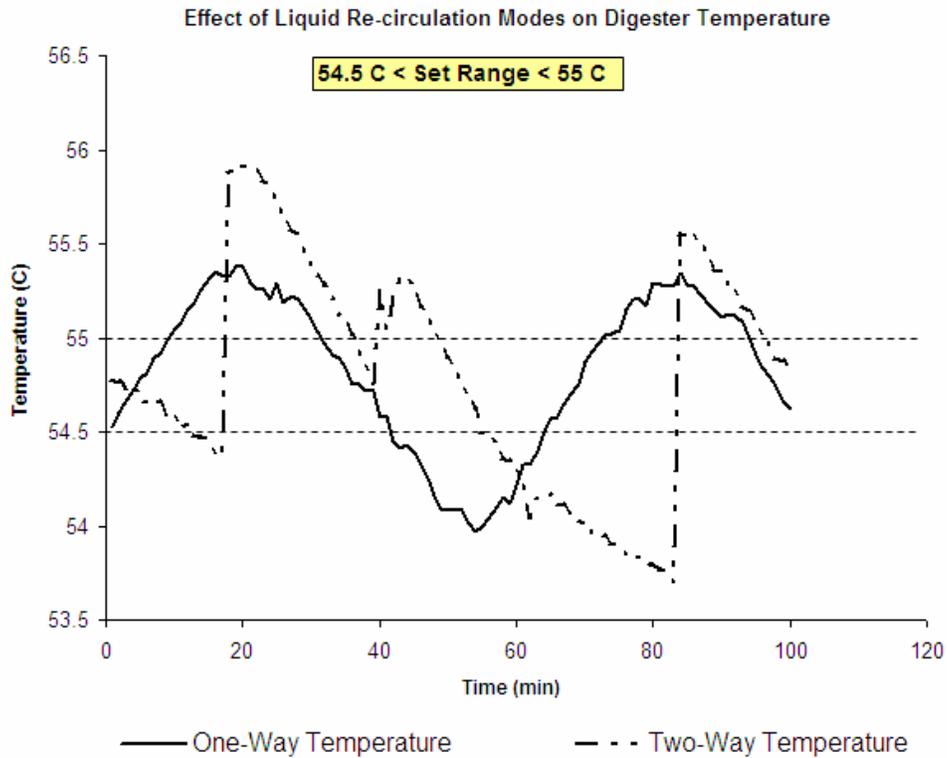


Figure 2-17. Comparison of re-circulation modes on biogasification vessel temperature

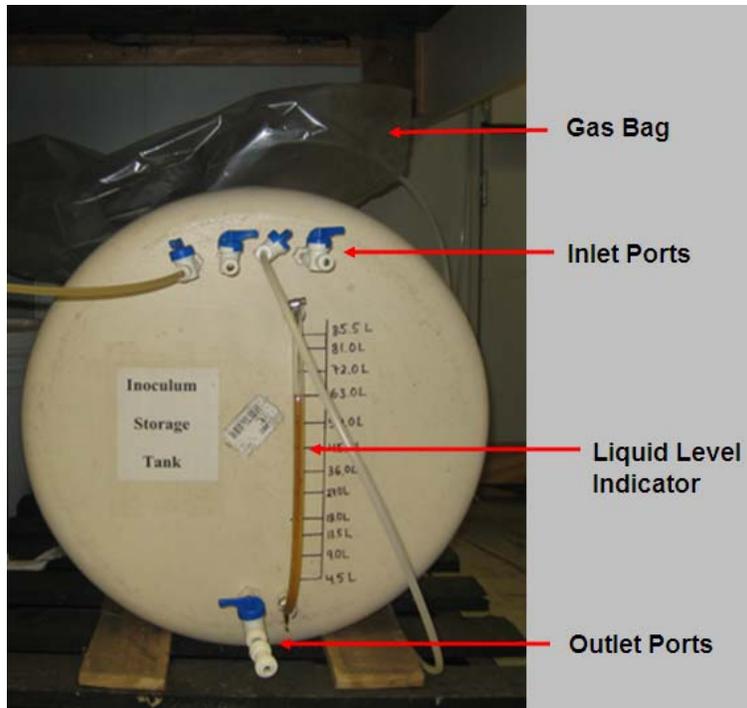


Figure 2-18. Inoculum storage vessel



Figure 2-19. Wash water cold storage bag

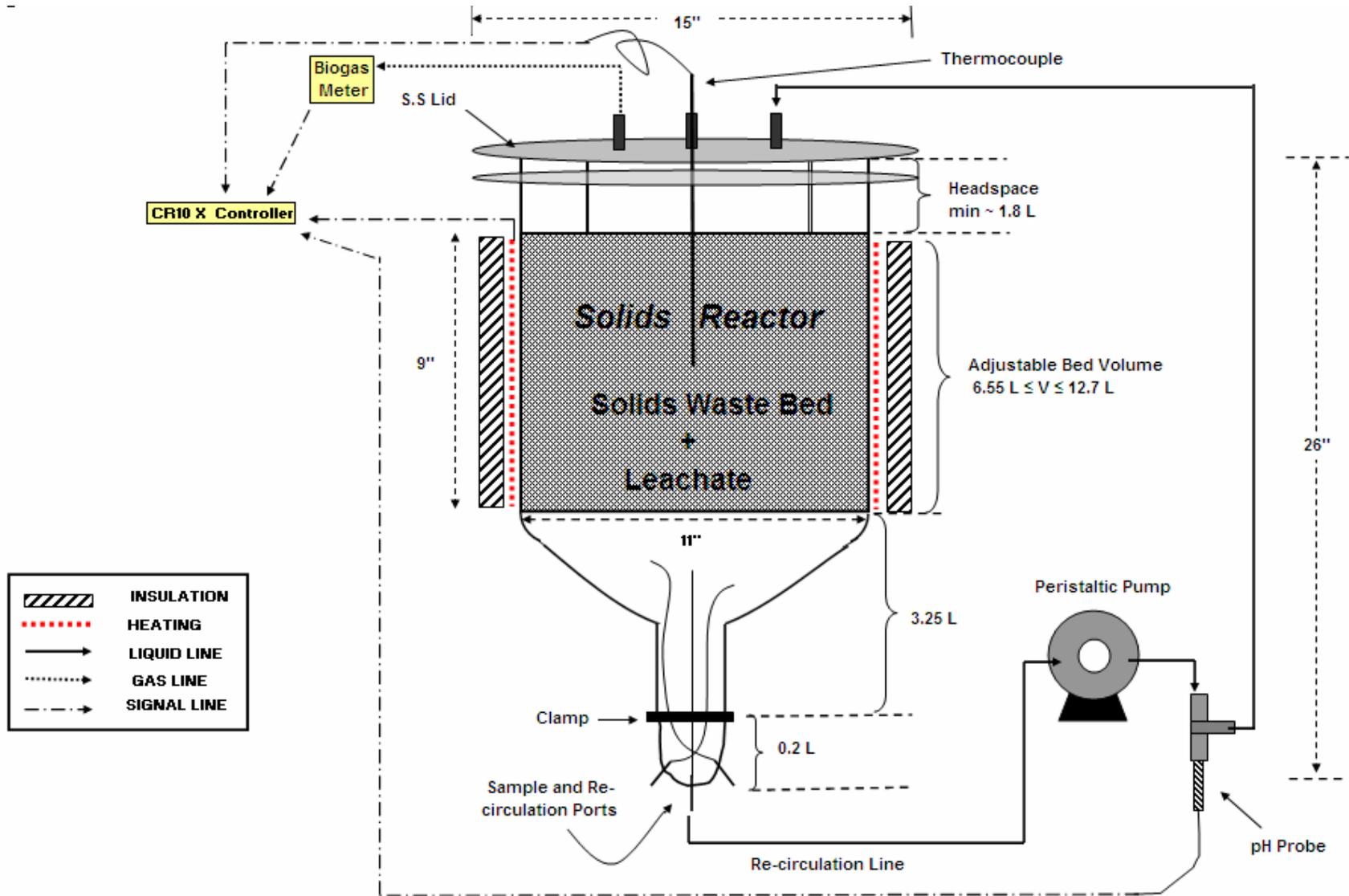


Figure 2-20. Solids biogasification reactor schematic (ABCR)

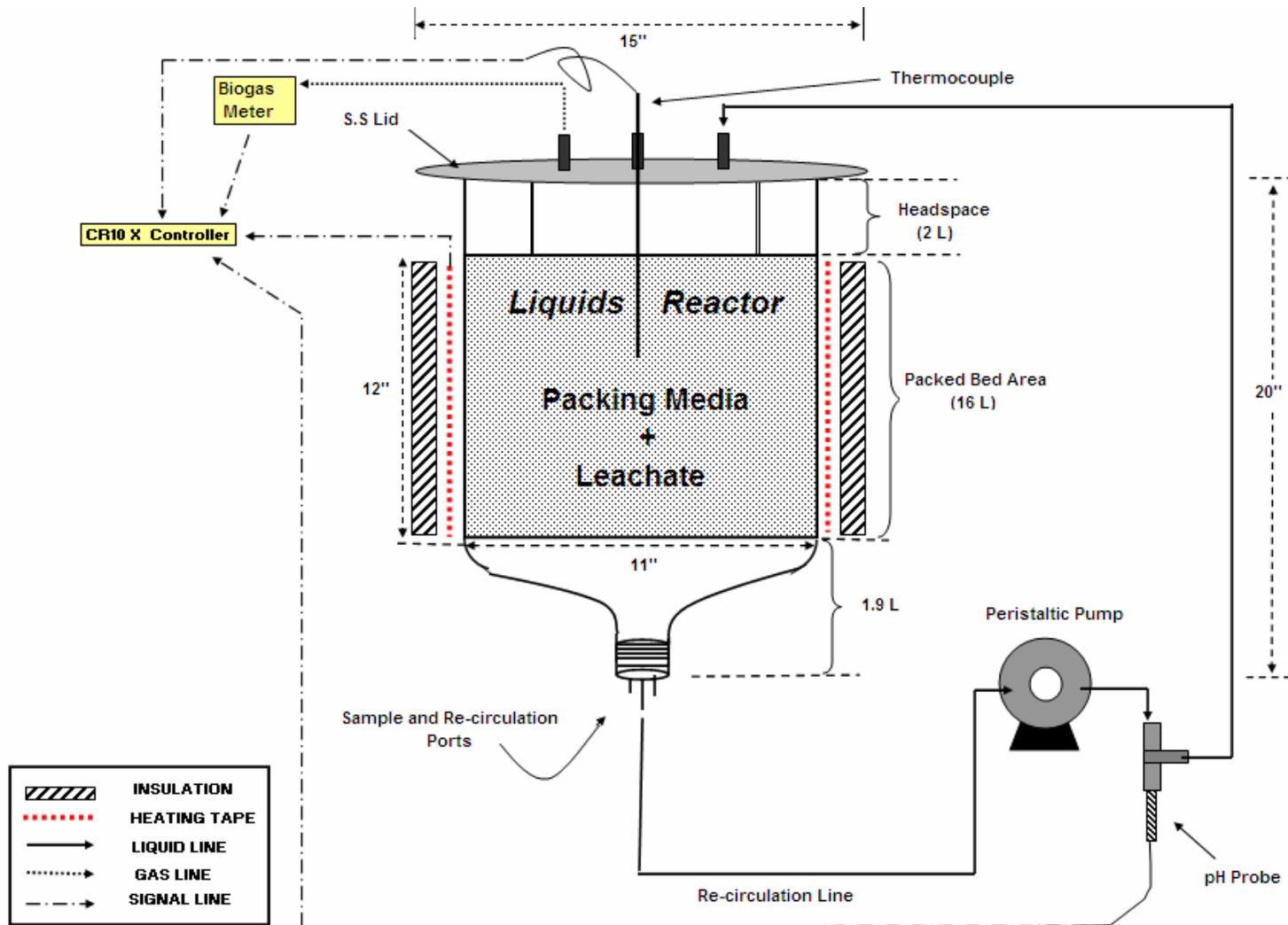


Figure 2-21. Liquids biogasification reactor (AFR) schematic



Figure 2-22. Complete biogasification experiment station



Figure 2-23. Bulking agent layers in sugar beet tailings waste bed

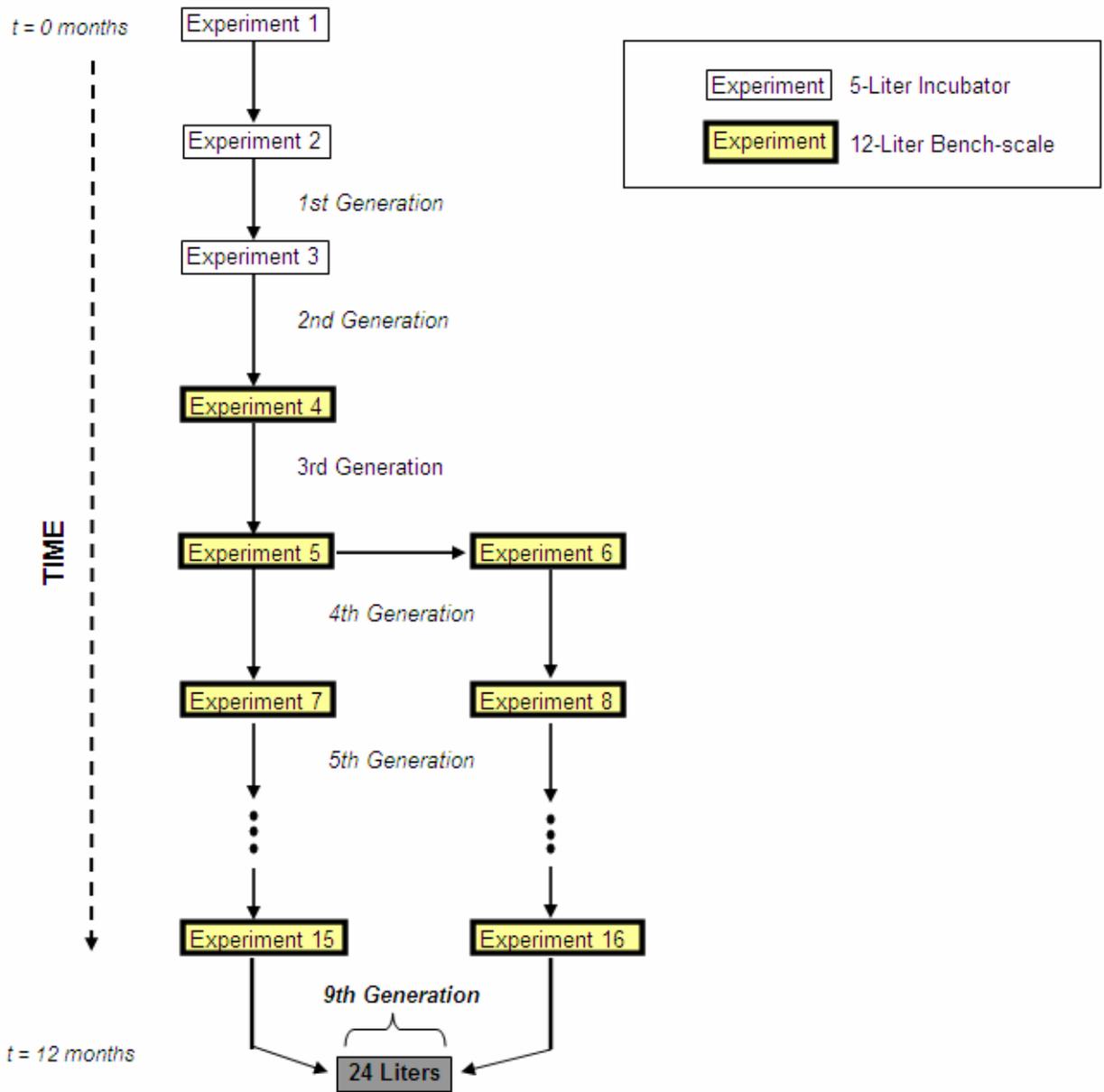


Figure 2-24. Inoculum acclimatization experiments

Title:	Single-Stage Biogasification of Sugar Beet Tailings	Leaching and Treatment of Readily Soluble Fraction of Sugar Beet Tailings	The Effect of Bulking on Biogasification of sugar beet tailings	The Effect of Two-Stage Biogasification		
Chapter:	3	4	5	6		
Feedstock:	As Received Tailings	As Received Tailings	As Received Tailings	As Received Tailings		
Pre-treatment:	None	In-situ Washing	In-situ Washing	Washing/ No Washing		
Reactor:	ABCR 1 & 2	ABCR 1 for solids; AFR for wash water	ABCR 1 & 2 for bulked/un-bulked solids	ABCR + AFR		
	STUDY I	STUDY II	STUDY III	STUDY IV		
	<i>Organic loading Experiments</i>	<i>Washing of Solids Experiments</i>	<i>Bulked Experiments</i>	<i>Un-bulked Experiments</i>	<i>Un-bulked Sequenced Experiments</i>	
	Experiment I.1 ↓ Experiment I.2 ↓ Experiment I.3	Experiment II.1 Experiment II.2 Experiment II.3 Experiment II.4 Experiment II.5	Experiment II.6 ↓ Experiment II.7 ↓ Experiment II.8 ↓ Experiment II.9 ↓ Experiment II.10 ↓ Experiment II.11	Experiment III.1 ↓ Experiment III.2 ↓ Experiment III.3	Experiment III.4 ↓ Experiment III.5 ↓ Experiment III.6	Experiment V.1 ↓ Experiment V.2 ↓ Experiment V.3 ↓ Experiment V.4

Figure 2-25. Design of experiments for sugar beet tailings biogasification

Table 2-1. Constituents tested by Dairy One on solids fraction of sugar beet tailings

<u>Component Measured (% DM)</u>
Moisture
Crude protein
Adjusted crude protein
Soluble protein
Acid detergent fiber (ADF)
Neutral detergent fiber (NDF)
Non-fibrous carbohydrates (NFC)
Lignin
Potassium
Sodium
Sulfur
Calcium
Phosphorus
Magnesium
Iron
Zinc
Copper
Manganese
Molybdenum

CHAPTER 3 STUDY I RESULTS: SINGLE-STAGE BIOGASIFICATION

3.1 Introduction

The first study of the research work involved batch, single-stage thermophilic biogasification of raw sugar beet tailings using a flooded unmixed digester. The aim of this study was to characterize the anaerobic biodegradation potential of sugar beet tailings and its methane potential (measured as methane yield) using different organic loadings. This first iteration of experiments was chosen for its simplistic design and operation; sugar beet tailings were loaded as received from ACSC, flooded with the active thermophilic inoculum and digested in batch mode. The progression of an experiment was measured by the evolution of methane with time. After the tailings were degraded the reactor was opened and the residue removed. There was no agitation of solids during digestion except for re-circulation of the liquid.

3.2 Background

Successful application of anaerobic technology to the treatment of solids is dependent on development of a reactor that can achieve high rates. The evaluation of reactor designs for anaerobic digestion generally depends on biological, technical and economical aspects. Two main parameters considered in making decisions impinging on design includes the number of stages and the concentration of solids in the reactor. About 90% of the full scale plants currently in Europe treating organic fraction of municipal solid waste (OFMSW) rely on a one-stage system (Lissens et al., 2001). Primary modes of operation for one-stage systems are batch, semi-continuous and continuous.

Batch systems have up to now not been successful in taking up a considerable market share. However, specific features such as a simple design and process control, robustness and lower investments make them attractive for developing countries (Bouallagui et al., 2005). For

example in Asia, most of the biogasification plants digesting agricultural and animal wastes are simple, single stage bioreactors without any auxiliary mixing (Ong et. al, 2000). Anaerobic batch digestion has proven to be useful because they can be performed simply, with inexpensive equipment. In addition, batch systems are particularly useful in assessing the rate at which a material can be digested (Parawira, et al., 2004)

Anaerobic digestion systems exhibiting < 20 % TS are usually referred to as “wet” systems whereas 20 to 40 % TS systems are considered as “dry.” Conventional wet systems are performed in a single-stage reactor, where homogeneity is obtained by continuous stirring of a 3 to 8 % TS slurry (Svensson et. al 2006, Hartmann and Ahring, 2006). Slurries rely on high consumption of process water necessary to dilute waste streams, are usually carried out in CSTR-type systems. They are particularly seen advantageous because of their readily easy pumping of solids throughout a system. In dry anaerobic designs, high-solids concentrations are attained with minimal external water necessity; wastes move in a plug flow inside a reactor (Lissens et al., 2001). The advantage of high-solids dry fermentation is that organic loading rates of $10 \text{ kg VS m}^{-3} \text{ d}^{-1}$ and higher can be applied. However, the full contact of biomass and substrate is not guaranteed; individual processes can be observed spatially, which limits an optimal co-operation of the microbial groups involved in anaerobic digestion (Hartmann and Ahring, 2006).

Regardless of solids concentration in digestion systems, reaction rate is also greatly influenced by temperature. All digestion plants were initially operated at mesophilic temperatures (27 to 38°C). However, as of 1992-1993, thermophilic (50 to 58°C) operation has been established as an acceptable mode of fermentation. Using thermophilic temperatures in

preference to mesophilic have been shown to have higher degradation rates and better sanitation effect (Nielse et al., 2003 and L. De Baere, 2000)

A lack of literature on the disposal of sugar beet tailings indicated that not much attention had been devoted towards anaerobic digestion of this organic waste. The unique physical properties of tailings includes having high-solids bulking capabilities but low TS content (13 to 17 %). This unique composition makes a mixed slurry reactor difficult to operate mechanically. Likewise, a dry digestion system would not be efficient with a high-moisture feedstock such as tailings.

A flooded, batch, process seemed the most promising for characterizing biogasification of sugar beet tailings. Conventionally, a high-solids process is a one-stage process that does not require feedstock pre-treatment, mixing, agitation or movement of reactor contents. It also requires minimal water addition and does not require bulky, expensive, high pressure vessels (Hedge and Pullammanappallil, 2007). A flooded operation of a leach-bed process was recently applied to the SEBAC process; it yielded improved kinetics (Luniya et al., 2005). It was speculated that the re-circulation of liquid contents was beneficial for the bacterial distribution in the whole system.

3.3 Results

Experiments: Three experiments (I.1, I.2, and I.3) were conducted consecutively to digest raw sugar beet tailings in a single-stage mode at thermophilic conditions. Organic loading was varied in each case by changing the amount of tailings that was confined in the reactor -low, medium and high total occupied volumes; visually that translated to tailings beds that occupied one-third, half and three-fourths of the total working reactor volume; the active volume of each reactor was maintained between 12 to 13 L. Due to the high moisture content, the amount of tailings loaded in each experiment (1.1, 3.0 and 5.0 kg) translated to 1.3%, 2.9 % and 5.3% of

total solids in the system. Though seemingly low percentage of solids, it was validated that the 5.3% solid slurry of sugar beet tailings could not be mixed with a stir rod.

Varying the organic loading translated to identifying the boundaries of under-loaded and over-loaded reactor in light of volumetric efficiencies. The performance of each experiment was monitored by analysis of biogasification parameters on a daily basis (methane rate, gas composition, methane yield, pH, etc). The duration time for biogasification was held until evidence of stagnation was detected (decreases in methane production, high levels of VFAs, etc.). Starting with experiment I.1, fresh inoculum (pH of 8.1) was doped with 5 g/L of sodium bicarbonate to assure proper buffering during biogasification. Subsequently, Experiments I.2 and I.3 were buffered similarly. The protocol for loading each reactor for each experiment was followed according to 2.8.2.

Characteristics of feed and digested residue: The characteristics of sugar beet tailings (Table 3-2) and loading/unloading parameters (Table 3-3) for experiments conducted were determined experimentally. The total and volatile solids loaded in each experiment were on average 15% total solids and 91 % volatile solids. Therefore, upon loading Experiments I.1 to I.3, the available solids for degradation were 0.16, 0.42 and 0.68 kg, respectively; the subsequent corresponding (compaction-free) dry matter bulk densities loaded were 60, 70, and 75 kg/m³, respectively. Residue samples were collected at the end of each experiment by draining away reactor liquor from the waste bed. It was estimated that the total suspended solids in the drained liquor from the biogasification of sugar beet tailings didn't vary much, ranging from 1 to 3 g/L. After biogasification, the residue appeared as fibrous and homogeneous and visually indicated a 70 to 80% volume decrease from what was loaded (Figure 3-1). In biogasifying sugar beet tailings, the volatile solids reduction for Experiments I.1 and I.2 were 90 and 78 %, respectively;

I.3 was treated as a recovery experiment with AFR and percent volatile solids degradation was not calculated until after post-sequenced time period (Chapter 6, Experiment IV.4).

Physical observations: An increase in liquid height in the headspace of each experiment was observed during the first 2-3 days of biogasification. In I.3 liquid level overwhelmingly increased to beyond the confines of the reactor headspace; approximately 1 liter was captured externally, stored and added back after 3 days. In the case of both I.2 and I.3, compaction was observed on the top-most perforated plate concurrently during the liquid level increases.

Biogasification of sugar beet tailings: The biogasification parameters measured were plotted (Figures 3-2 and 3-3) during each experiment. To eliminate the variations due to differences in wet tailings loaded, cumulative methane production values were normalized on the basis of kg VS loaded in each experiment. The lag periods (Figure 3-2) at the start of biogasification for all three experiments were between 0.1 to 0.3 days, which corresponded to < 1% of digestion time for I.1-2 and ~ 1.5% of biogasification time for I.3. By 0.5 days into biogasification, the rate of methane for I.1 reached $0.3 \text{ L}^{-1}\text{L}^{-1}\text{d}^{-1}$ whereas I.2 and I.3 mimicked each other and peaked at $1.8 \text{ L}^{-1}\text{L}^{-1}\text{d}^{-1}$. The biogas methane compositions at that time were also 25%, 17% and 10% for I.1-3, respectively. Such responses indicated a quick onset of methanogenesis. However, after 2 days, stagnation in I.3 was evident by the lack of increase in methane composition; only a 11% methane composition increase was observed in I.3 from $2.0 < t < 6.7$ days, whereas I.1 and I.2 increased by 31% and 48%, respectively. At 6.7 days, the methane production rates began decreasing steadily; I.2 and I.3 both leveled off to 0.13 and $0.40 \text{ L}^{-1}\text{L}^{-1}\text{d}^{-1}$, respectively; I.1, which was discontinued from digestion at 6.7 days, exhibited a $0.11 \text{ L}^{-1}\text{L}^{-1}\text{d}^{-1}$ final methane production rate. The ultimate methane yields in all three consecutive experiments were 170, 171 and 35 L/kg VS at STP, respectively.

The trends in pH and volatile organic acids (Figure 3-3) revealed stability of anaerobic process in Experiments I.1 to I.3. Experiment I.1 initially started at pH of 8 and decreased to 7.7 in 2.4 days. Notably, acetic acid was the only organic acid that accumulated significantly; with a concentration of 624 mg/L at time 0, acetic acid accumulated to 1220 mg/L within 1.3 days of start up, and subsequently degraded to 500mg/L. Propionic, butyric and valeric acids did not show substantial accumulation, as they all degraded to less than 100 mg/L by end of biogasification.

The pH profile of I.2 was quite similar to I.1, starting a little higher at 8.4 and decreasing to 7.5 by 2.3 days of the start-up. A pH of 8 was observed at the end of biogasification. Unlike I.1, all organic acids accumulated collectively in I.2; acetic acid accumulated up to 3900 mg/L after 3.4 days of start-up and degraded to 1640 mg/L; propionic and butyric acids both accumulated to 400 mg/L and 680 mg/L within the first 4 days before degrading to approximately 350 mg/L and 315 mg/L, respectively; valeric acid concentrations were quite low, evolving within 50 to 100 mg/L during biogasification. In general, a 3.8 fold increase was observed in peak organic acid concentrations for the major VFA acids (acetic and propionic) when comparing I.1 with I.2.

Experiment I.3 indicated the most rapid accumulation of VFA and consecutive pH drops during biogasification. The starting pH of reactor liquor was 7.5 and continually declined to 6.1, where the experiment was stopped at 6.7 days. Acetic and butyric acid concentrations accumulated dramatically during the start-up of I.3. Within 2.4 days of start-up, acetic and butyric acids accumulated to 4000 mg/L and 2500 mg/L, respectively. Thereafter, acetic acid continued to increase to a peak value of 5050 mg/L, whereas butyric negligibly degraded to 2460 mg/L. The concentrations of acetic and butyric acids at the end of experiment (10.5 days)

showed a degradation of 40% and 55% of observed peak values. The remaining acids, propionic and valeric exhibited rapid accumulation reaching peak values of 431 mg/L and 135 mg/L midway through biogasification, before degrading to the final values of 320 mg/l and 55 mg/l within 10.5 days. In all, the total VFA concentrations for I.1 to I.3 at the termination point of each experiment were 650, 2398 and 4514 mg/L, respectively.

Soluble COD (SCOD) profiles (Figure 3-3) were also examined during biogasification for each experiment. In general, as the organic loading in each experiment was increased, an elevated SCOD was observed. In I.1, the SCOD at started at 5 g/L, peaked at 15 g/L and degraded to 8.3 g/L at the end of digestion. I.2 exhibited an increased concentration of SCOD, exhibiting oscillatory concentrations of SCOD during digestion; a start of 12.4 g/L, followed by three consecutive saddle peak points at 23, 25, and 21 g/L. Thereafter, the SCOD proceeded to degrade to 14 g/L, converging to within error ($\pm 0.4\%$ for COD 0 to 20 g/L) of the start value. Finally, I.3 exhibited a first order saturation profile of SCOD in solution. Within 0.5 days, the SCOD value increased from 9 g/l to 34 g/l. By the end of the experiment, the SCOD continued to increase to a value of 41 g/L, where it appeared to remain fixed. At the termination of I.1, I.2 and I.3, the total VFA fractions with respect to total soluble COD were 7%, 17% and 11% percent, respectively.

The modified Gompertz model equation (Eq.1-1) was fit to I.1 and I.2's cumulative methane yield data (continued digestion of I.3 was further investigated after termination at 6.7 days in Study IV) A reasonable fit was established when this model was applied to both experiments. It should be noted that even though experiments in this study were not taken to completion, the cumulative methane yield could be extrapolated by using the Gompertz model equation (Hedge and Pullammanappallil, 2007). The performance parameters (Table 4-3)

between experimentally-determined values and Gompertz model equation was analyzed for Experiments I.1 and I.2.

3.4 Discussion

Employing a single-stage, batch, high-solids biogasification of raw sugar beet tailings as received provided valuable insights into process and performance dynamics. The volumetric efficiency and biogasification performance were scrutinized to ascertain their relationship. Typically, high-solids biogasification systems employ high volumetric efficiencies (i.e. higher bulk densities) for increased throughput. Compaction to higher densities ($\sim 300 \text{ kg/m}^3$) is considered a major parameter influencing the reactor size (Chynoweth and Pullammanappallil, 1996). The best case scenario would be a high volumetric efficiency coupled with rapid mineralization to methane. In the case of tailings, as the organic loading was increased in each batch experiment (i.e. volumetric efficiency increased), the cumulative methane yield decreased; this was especially evident within the first six days of biogasification. This trend appears consistent in the VS reduction as well, decreasing from 90 to 78% for I.1 and I.2, respectively. Additional observations noted during batch operation included a flotation and compaction phenomena of tailings. It was suspected that contact inaccessibility of liquid to solids may have had an impact in the degradation decline from I.1 to I.2. This led to the possibility of trapped gases in the bed during methanogenesis, causing delays in gas evolution and disrupting bed homogeneity.

Preliminary biochemical methane potential (BMP) assays conducted by Teixeira et al., 2005 on sugar beet tailings indicated that a yield of 250 L/kg VS was achievable after about 30 days under mesophilic conditions (38 °C). In general, a bench mark of 20 days or less to attain 95% of biochemical methane potential was used to evaluate if enhancements to previous work by Teixeira et al., 2005 were attained here. The methane yield of all three organic loading

experiments conducted far exceeded the potential of the SEBAC-2 mesophilic experiment in Teixeira et al., 2005, which yielded 40 L CH₄/kg VS after 30 days of biogasification. However, all three experiments did not attain the biochemical methane potential exhibited by BMP studies, when Gompertz model extrapolation was used.

From looking at SCOD profiles (Figure 3-3) it was speculated that sugar beet tailings contain a large fraction of readily soluble organic content. This was seen by rapid SCOD increase within less than half a day, particularly in Experiments I.2 and I.3; SCOD concentrations in both I.2 and I.3 increased two and three-fold during that time. It was suspected that physical solubilization rather than hydrolysis was responsible for this occurrence. First order hydrolysis of biopolymers found in OFMSW suggested k values of 0.5 to 0.63 d⁻¹ (Chynoweth and Pullammanappallil, 1996). The SCOD increases witnessed here would correlate to $k > 1$ d⁻¹. Therefore, it was suggested that this readily soluble fraction became inhibitory (at some SCOD concentration) to hydrolysis of solids and diminished the biochemical methane potential as organic loading was increased. Through modeling, it was shown that that beyond a concentration of 20 g/L SCOD there was (OFMSW biogasification) an on-set of inhibition (Lai, 2001). Previously, it was shown that SEBAC could initiate methanogenesis rapidly in feedstocks such as organic fraction of municipal solid waste (OFMSW), yard waste, mixtures of biosolids and simulated solid waste. For example, soluble COD of reactor liquids from flooded vegetable waste bed was 8 g/L (Hedge and Pullammanappallil, 2007) and that from OFMSW was 12 g/L (Lai, 2001). With the exception of I.1, sugar beet tailings at increased organic loads produced much higher SCOD fractions, ranging 14 to 41 g/L SCOD.

Studies have shown retardation can occur in single-stage anaerobic systems that fail to meet an inoculum-to-substrate ratio (ISR) at start-up. No strategic accommodations were made

in this study to assure that the kg VS loaded to liquid inoculum was maintained constant; rather, the working volume of the reactor was held fixed. As a rule of thumb, the proper choice of ISR will depend on the final objective: methane or intermediate compounds production. In the case of normal single-stage operation, the rate of VFA due to hydrolysis and fermentation of macromolecules (acidogenic stage) should be synchronous with the rate of VFA conversion to methane via methanogenic stage (Sarada and Joseph, 1995). Increased anaerobic degradability usually depends on high ISR value, whereas specific methane productivity maximums depend on small ISR's (Fernandez et al., 2001). This is confirmed with I.2, where higher initial methane rates (with respect to I.1) were observed, but overall anaerobic degradability at the end of the experiment was reduced. Thus, it is speculated that the extensive release of readily soluble COD (substrate), started having a more pronounced effect on synchrony in acetoclastic and methanogenic activities, for loadings > 0.42 kg VS per 12 L of reactor volume.

The VFA accumulation and degradation trends observed in the three experiments bring additional insight to the progression of biogasification. Researchers have found that VFA concentrations are the most important parameters in anaerobic digestion (Babel, et al., 2004; Pind 2002; Kim 2002). Under normal or balanced operation, the rate of production of VFA should be matched by their consumption rates; hence there should be very little accumulation. In a continuous single-stage operation, it has been reported that VFA < 500 mg/L is indicative of stable performance (Chynoweth and Pullammanappallil, 1996). In the present study, trends reveal VFA accumulation levels beyond 500 mg/L, followed by different extents of degradation.

In general, degradation of peak values for VFAs in all the experiments showed improvements by the termination. However, as the organic loading was increased, the final extent of degradation was diminished. With increased values of VFAs, the rate of mineralization

to methane declined. This was especially exhibited in I.3, where the final total VFA concentration represented 25% of the soluble COD. Hence a considerable fraction had the potential of degrading, but was unable to do so due to unfavorable conditions in the reactor. Accumulation and persistence of VFAs is typically inhibitory, if pH of system falls below pH 6.5; at low pH values, un-ionized species of VFAs are formed and have been found to be toxic to methane formers (McCarty 1964; Chugh 1999). This phenomenon was consistent in how the pH and VFA trends behaved in I.3; VFAs accumulating beyond certain peak values (5000 mg/L total VFA) inherently decreased the pH to levels below the 6.5 threshold, producing inhibitory forms of acids and diminishing the potential for conversion.

It is suggested that an adjustment in the amount of inoculum to VS loaded in biogasification of sugar beet tailings need to be considered for enhanced performance. To sustain sufficient volumetric efficiencies and optimal cumulative methane yields, it is therefore proposed that biogasification of sugar beet tailings include a pre-treatment step to remove the readily soluble organic matter. This approach will be considered in Study II. It is hypothesized that pre-treatment removal and separate treatment of readily soluble organic matter would enhance the rate of the current batch operation.

The liquid rise and compaction observed in Experiments I.2 and I.3 gave great insight to some possible physical limitations when employing biogasification at $+400 \text{ kg/m}^3$ (wet) bulking densities. It was speculated that biogas produced in the waste bed in I.2 and I.3 significantly excluded liquid out of the waste bed, causing liquid to rise. Frequent perturbations (vigorous shaking) increased the rate at which biogas was measured by the gas meter. Exclusion of liquid was suspected to have an adverse effect on biogasification performance, as the availability of inoculum to utilize substrate was diminished. Chapter 5 addresses the addition of a bulking

agent to alleviate compaction of the waste bed and promote separation by increased hydraulic porosity.

3.5 Conclusions

- It was possible to anaerobically biogasify sugar beet tailings using a flooded, high solids process at thermophilic temperatures, but with poor efficiency.
- As loading was increased from 0.16 to 0.68 kg VS, a decrease was seen in the % VS reduction and evolution of methane.
- Sugar beet tailings are composed of a high amounts of readily soluble organic components. At increasing solids loading, an increase in SCOD accumulation was observed. Subsequently, overwhelming production of intermediate VFAs imbalanced the synchrony between acidogenesis and methanogenesis, which caused inhibition.
- Flotation and compaction of tailings was observed. It was speculated that this action reduced the contact of liquid to substrate, in addition to percolation of product gases from the waste bed.



Figure 3-1. Sugar beet tailings residue

Table 3-1. Sugar beet tailings characteristics

Tailings characteristics	
Moisture (%)	83 - 87
Total solids (%)	13 - 17
Volatile solids (%)	80 - 92

Table 3-2. Loading and unloading data for Study I experiments

Experiments		I.1	I.2	*I.3
Loading	Wet tailings weight (kg)	1.1	3	5
	Total solids (kg)	0.18	0.45	0.77
	Volatile solids (kg)	0.16	0.42	0.68
	Inoculum added (L)	12	11.5	10.0
	Packing density (kg wet/m ³)	416	465	491
	Packing density (kg dry/m ³)	66	70	75
	Total solids in reactor (%)	1.3	2.9	5.3
Un-loading	Wet residue weight (kg)	0.82	2.30	-
	Total solids (kg)	0.03	0.12	-
	Volatile solids (kg)	0.017	0.090	-
	Total solids reduction (%)	82	74	-
	Volatile solids reduction (%)	74	78	-

* Un-loading of I.3 is conducted after sequencing experiments in Study V

Table 3-3. Summary of biogasification performance in Study I experiments

Experiment	Final cumulative methane yield (experimental)	^a Gompertz parameters (model)			Duration to produce 95% methane yield potential
		^b P	^b R _m	^b λ	
	L CH ₄ kg VS ⁻¹	L CH ₄ kg VS ⁻¹	L kg VS ⁻¹ d ⁻¹	days	days
I.1	170	168	23	0.1	10.7
I.2	171	204	21	0.6	14.9
I.3	36	-	-	-	-

^aGompertz parameters derived by fitting experiment data into Modified Gompertz Model. ^bSymbols have their usual meaning

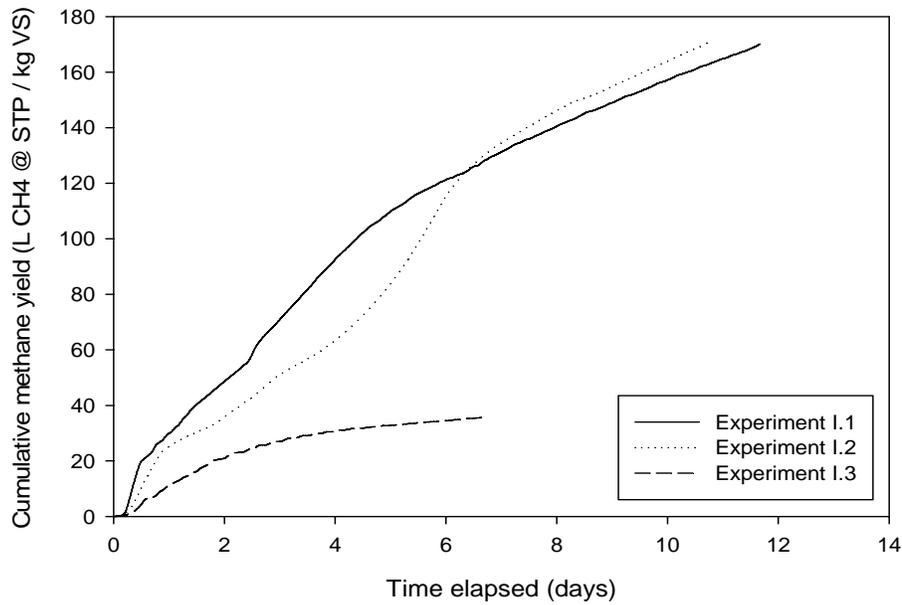


Figure 3-2. Comparison of cumulative methane production from experiments in Study I

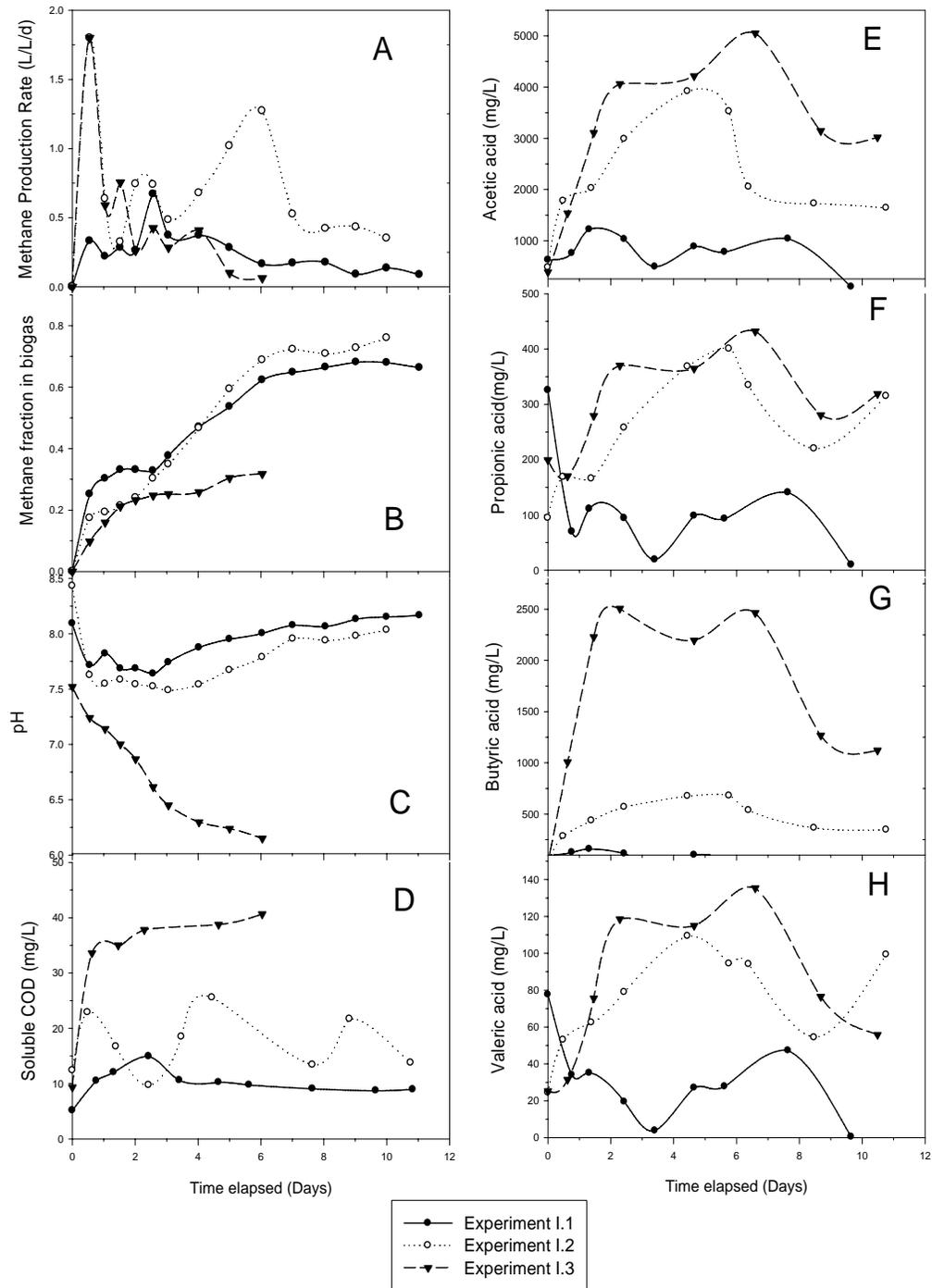


Figure 3-3. Profiles of biogasification parameters from experiments in Study I. A) Methane production rate. B) Methane fraction in biogas. C) The pH profile in reactor. D) Soluble COD in reactor. E) Acetic acid concentration profile. F) Propionic acid concentration profile. G) Butyric acid concentration profile. H) Valeric acid concentration profile.

CHAPTER 4
STUDY II RESULTS: LEACHING AND TREATMENT OF READILY SOLUBLE
FRACTION OF SUGAR BEET TAILINGS

4.1 Introduction

In Study I (Chapter 3), it was speculated that raw sugar beet tailings contained a considerable fraction of readily-soluble organic compounds. Particularly, Experiments I.2 and I.3 showed dramatic increases in the concentration of SCOD accumulating in a short amount of time -0.5 days. It was unclear to what extent this accumulation was due to solids hydrolysis or readily soluble constituents. High levels of soluble chemical oxygen demand (SCOD) in solution that is derived from readily soluble components can be removed by a simple leaching (washing) procedure. It was speculated the pre-treatment of raw sugar beet tailings will enhance the biogasification of solids by minimizing the substrate concentrations in a fixed liquid volume, while attaining a realistic volumetric efficiency. Wastewater effluent (wash water) generated during pre-treatment could contribute significantly to the overall biochemical methane potential of sugar beet tailings. The aims of this study were to:

1. Pre-treat and quantify readily-soluble organic content in raw sugar beet tailings
2. Treat leached tailings' effluent wash water in the AFR to assess the methane contribution of the readily soluble fraction of tailings

4.2 Results

Washing: A set of five washing experiments were conducted to ascertain the amount of readily-soluble organics in raw sugar beet tailings. In-situ washing experiments were carried out in ABCR 1 and 2 at thermophilic temperatures with liquid re-circulation for mixing. Loading of tailings and unloading of wash water were followed according to the loading procedure for bulked experiments (2.9.3) and storage of liquid feeds (2.6), respectively. Bulking agent (pumice stones) was used to avoid flotation and compaction, which was observed in Study I.

Also, to assure adequate removal of readily soluble organics, each experiment was treated to a secondary wash.

Readily soluble COD profiles (Figure 4-1) and experiment parameters (Table 4-1) for in-situ washing of sugar beet tailings. The contact time was held arbitrarily at 10 hours and samples were withdrawn from each unit at fixed intervals and analyzed for their TCOD content. The first wash revealed a first-order rate ($k = 0.99 \text{ hr}^{-1}$) behavior, as concentrations approached $24.5 \pm 3.6 \text{ g COD/L}$; a second pass in washing resulted in a substantially lower soluble COD concentration of $4.0 \pm 1.1 \text{ g COD/L}$. On average, over 85% of the total readily soluble COD fraction in tailings was removed in the first wash. A total of 20 liters of wash water with an average SCOD of $13.9 \pm 1.3 \text{ g/L COD}$ was generated from the combined wash 1 and 2 in each experiment. Physical and chemical constituents of wash water resulted in $< 1 \text{ g/L}$ total suspended solids, total VFA's $< 200 \text{ mg/L}$, and 0.4% simple sugars; analysis for other components, such as crude protein, degradable and soluble proteins were below detection limits for measurement. The readily solubilized organic fraction for sugar beet tailings was approximately $0.54 \pm 0.07 \text{ g COD/g VS}$.

Wash water treatment: Biogasification experiments (II.6 to II.10) were conducted on the wash water effluents incurred from leaching studies. Wash water aliquots containing 11 to 14 g/L COD were processed in a sequencing-batch mode in the AFR to experimentally determine their methane potential. The loading and performance parameters (Table 4-2) for each wash water experiment and the biogasification parameter profiles (Figure 4-2) and soluble COD balances in the AFR (Figure 4-3) were experimentally determined and compared. Feed volumes delivered for experiments II.6 to II.10 corresponded to 1.5, 2, 3, 4 and 2 liters, respectively. This

resulted in displacing 14 to 36 % of reactor liquid contents upon additions at the start of experiment (reactor volume was held constant).

Two initiation experiments were conducted in the AFR to acclimatize the microorganisms to wash water. In general, the progression of experiments show that the AFR was able to biogasify aliquots of wash water generated during leaching. In the case of experiments I.6, I.7 and I.8, a proportional increase in the daily methane rate was observed, while hydraulic retention time (HRT) decreased from 37, 30 and 22 days, respectively. For sequencing batch reactors (SBR), the HRT is defined as the active volume of reactor divided by the feed rate; feed rate was calculated by the volume of feed over the batch-time duration in which it is treated. The cumulative methane yield also increased during the series additions, ranging from 0.23 to 0.28 L CH₄ g COD⁻¹ added. However, upon the addition of 4 L feed volume in II.9, a decrease was observed in the peak methane production rate, falling from 0.64 to 0.44 L L⁻¹d⁻¹. The duration to attain 95% of methane yield also increased most drastically during II.9 addition, increasing on average by 1 day. The pH profiles showed increasingly sharp decreases initially as hydraulic loading was increased, but never fell below 6.8; the total VFA concentration was sustained below 200 mg/L, but increased to 325 mg/L after II.9 addition into the AFR.

It was observed that the SCOD concentration fell with each addition of wash water; starting at 2.4 g/L COD, a mostly linear drop relationship was seen as wash water was pushed through the AFR. Dotted marks on the SCOD profile plot on Figure 4-2 (B) indicate the initial concentration of SCOD in the AFR upon addition of wash water; it was unclear whether the degradation to the final SCOD value was linear or non-linear. Soluble COD balances (Figure 4-3) for each batch-fed experiment were conducted for validation of experimentally-determined quantities. Calculations were conducted according to commonly-accepted stoichiometric

relationships in anaerobic digestion. For a given batch experiment, a COD balance was performed at the start and end of a run; start-values presented the residual and feed fraction of COD; end-values presented the fractions for measured COD mineralized to methane, COD discarded as effluent, COD consumed for biomass growth and the final residual remaining in reactor. The COD going towards biomass was shown to be 9% of the COD added as feed; biomass COD is usually considered a negligible term, and usually not considered in COD balances. The effluent exhausted after each feed addition accounted for only 9% of methane COD. In general, the sum of components making up COD at the start of a batch balanced with the measurement error with end value; II.6 fell short by 2.6 g COD or 9% of total COD added. The relative reproducibility in closing the COD balance (within error) fortified the analytical techniques used for measuring critical parameters.

The modified Gompertz model equation (Eq. 1-1) was fit to all five experiments to determine the critical biogasification parameters. In general, each fit was very precise and indicated remarkable reproducibility of a typical batch growth rate curve. Final experimental cumulative methane values were within each other when the biogas measurement error was attributed; values were averaged since the degree of sensitivity dismissed any detectable differences in yields in lieu of differences in organic loading. Both Gompertz and experimental values revealed that the cumulative methane yield of sugar beet tailings wash water was $0.25 \pm 0.02 \text{ L CH}_4 \text{ g}^{-1} \text{ COD added}$. In addition, the lag phase in all experiments was < 0.1 days and with the exception to II.9, the duration to produce 95% of the methane yield potential was approximately 1.5 days.

4.3 Discussion

It was concluded through experimentation that sugar beet tailings contain a significant amount of readily soluble fractions that can be degraded by anaerobic digestion in an anaerobic

filter reactor. The readily-soluble organic matter derived from in-situ washing experiments was 0.54 g COD/g VS; 86% of solubilized organic matter was achieved within 5 hours of the first wash. Therefore, the readily solubilized COD amounts suspected of inhibitory affects in I.2 and I.3 of Study I were 86, 227 and 367 g, respectively. The corresponding total increase in COD concentrations experienced in I.1 to I.3 were 6.5, 17.4 and 36.7 g/L COD, respectively. It was quite evident from these findings that the removal of readily soluble components on sugar beet tailings was a critical step in mitigating COD levels for batch operation.

Volumetric efficiency can be defined as a ratio loaded material to available reactor volume. Qualitatively speaking, this parameter can be used to assess how efficiently reactor volume is used. In experiment I.1, it was shown that 1.1 kg of sugar beet tailings were loaded in 12 L working volume; un-compacted tailings occupied only 23% of the working volume (low volumetric efficiency). A pre-treatment washing step would therefore improve volumetric efficiencies in batch reactors by increasing volume occupied by sugar beet tailings

From stoichiometry, the readily soluble content per kg VS loaded of tailings translated to a 118 L CH₄ kg VS⁻¹ (assuming 75% degradation of readily soluble COD). Biochemical methane potential (BMP) values for sugar beet tailings were reported as 250 L CH₄ kg VS⁻¹ (Teixeira et al., 2005), which implied that readily soluble fraction accounted for 47% of total biochemical methane potential; Methanogenesis from the solid fraction of tailings should account for the remaining 53% of methane potential, or approximately 132 L CH₄ kg VS⁻¹. Therefore, a two-fold increase in total solids loaded in a single batch reactor could be accommodated if pre-treatment was employed. At a bulking density of 465 kg/m³ for sugar beet tailings inside a reactor, approximately 2.2 L or 15% of the working volume would be additionally occupied with tailings subjected to washing. For example, in looking at experiment I.1, the corresponding

equivalent soluble COD would be produced in biogasifying 2 kg of washed tailings, rather than 1.1 kg of raw tailings. In general, experiment I.1 ($ISR = 0.04 \text{ L g SCOD}^{-1}$) provided adequate biogasification start-up and minimal accumulation of intermediates; pre-treatment in such case would not only increase total solids loaded, but maintain a ISR value sufficient for acceptable biogasification outcomes. It is speculated that removing readily soluble organic substrate could even enhance the rate of solids' degradation to methane (Chapter 5).

The production of an additional waste stream (tailings wash water) was not optimized to minimize quantities generated; two washes provided adequate removal of readily soluble COD. During the process, the total VFA of $< 200 \text{ mg/L}$ indicated that acidogenesis did not occur naturally under the wash conditions; any presence of indigenous microorganisms on tailings did not promote biogasification at detectable levels. Furthermore, the washing process produced very low concentrations of suspended solids ($< 1 \text{ g/L}$) and did not require any clarification before treatment in the AFR. The time reserved for pre-treatment was regarded a crucial parameter. For a complete biogasification cycle of 20 days, pre-treatment employed here accounted for 4% of the cycle time. Therefore, pre-treatment of sugar beet tailings via in-situ washing could be afforded given that time spent for washing would be outweighed by increased degradation rates.

Assessment of the biochemical methane potential of wash water containing readily soluble organic compounds from tailings was conducted in the AFR reactor in batch mode. The simple start-up and operation of this unit provided a sensible outlook operating combined suspended and attached growth rate system on the lab scale. The treatment of wastewater is a conventional practice and is not disputed or researched extensively in this work. In general, wash water from pre-treated tailings had a solubilized organic content of 13.9 g/L COD ; by convention, this is considered a moderate-strength wastewater and can be treated in high-rate AF (anaerobic filter)

or Upflow Anaerobic Sludge Blanket systems (UASB), at 5 to 40 g COD L⁻¹ d⁻¹. In experiments II.6 to II.10, low rate process (< 5 g COD L⁻¹ d⁻¹) was adapted to determine the potential generated by wash water. It was shown that wash water had a biogasification potential of 0.25 ± 0.02 L CH₄ g COD⁻¹ added. Therefore, 71% efficiency in the mineralization of readily soluble COD to methane was experimentally determined.

Biogasification of wash water provided insight to the operational characteristics of the AFR. It was speculated that SCOD residuals present in AFR reactor were driven to further degradation once plug additions of wash water were added (Figure 4.2 (C)). The initial start of experiments in AFR was a result of priming the unit for about 15 days with mild wastewater (~ .25 g COD L⁻¹ d⁻¹). Thereafter, the COD leveled around 2 g/L COD and it was assumed that this would be a non-degradable residual (where total VFA's were < 0.03 g/L COD). Conventional practices typically use aerobic cultures to treat wastewater strength between 0.05 to 1.5 g/L COD and anaerobic if wastewater is between 1.5 to 50 g/L COD. From initiation experiments to the end of II.9, it was shown that additions of wash water COD facilitated the decrease of residual concentration of solubilized organic content in the reactor. The AFR system operated as low as 0.57 ± 0.02 g/L COD before SCOD started accumulating.

Characterization of the process during the batch feedings of wash water also revealed that increasing the hydraulic and organic loading rate caused an increase in the duration to produce 95% of the methane yield potential. In particular, the extreme case was seen when the liquid addition of 4 L or 36% of the working liquid volume in the AFR was displaced with wash water (experiment II.9). The duration to produce 95% of the methane yield was increased by one day. This suggested that a significant part of the microbial growth in the reactor was suspended, rather than attached on the bulking media. Therefore, considerable removal in the percentage of active

microorganisms diminished the methane rate in II.9 and washout of microorganisms was becoming apparent. But by reducing hydraulic loading to 3L in II.10, kinetics of methane production was improved.

Visual inspection of bulking media (after Study II experiments) confirmed that no biofilms were present. This was logical considering that the AFR system was only operated for 35 days and was initiated with suspended growth inoculum (generated in a re-circulated system) and trace amount of sugar beet tailings. Moreover, it was reasoned that the mode of operation in the AFR most likely didn't promote the formation of biofilms. At a 0.42 L/min re-circulation rate, the working liquid volume was turned over every 26 minutes; this was necessary to assure proper temperature control in the vessel. Therefore, it was suspected that the vessel during Study II experimentation acted as a Stirred Tank Reactor with bulking media, rather than an ideal AFR reactor; bulking media seemed to mainly facilitate liquid – gas separation, which was indicated by continuity in methane production rates.

From such experiments, it was projected that the AFR would operate satisfactorily up to a hydraulic loading rate of 3 L d⁻¹ (HRT = 21 days) for the wash water concentrations presented in Chapter 4. Further maturation of this unit could sufficiently bring down the HRT to lower values, increasing the throughput of wash water. However, this exploration was beyond the scope of this work, as anaerobic processes operating at HRT of 5 days are conventionally and commercially used for moderate-strength, low suspended solids, wastewaters.

4.4 Conclusions

- Sugar beet tailings can be leached of their readily soluble COD content by in-situ solid-bed leaching. The readily soluble fraction was calculated as 0.54 ± 0.07 g COD/g VS
- 85% of the readily solubilized fraction of sugar beet tailings leached within 5 hours of the first wash

- With a BMP value of 250 L/kg VS, it was estimated that 53% of the methane yield would come from solid fraction of sugar beet tailings; the remaining 47% would be contributed from biogasification of wash water
- Wash water generated yielded 0.25 L CH₄ at STP g COD⁻¹ added in the AFR; the COD-to-methane mineralization efficiency was estimated as 71%
- The lab-scale AFR behaved more as a batch STR; it was suspected that very little attached growth was present during the 20-day study and the mode of operation promoted suspended growth

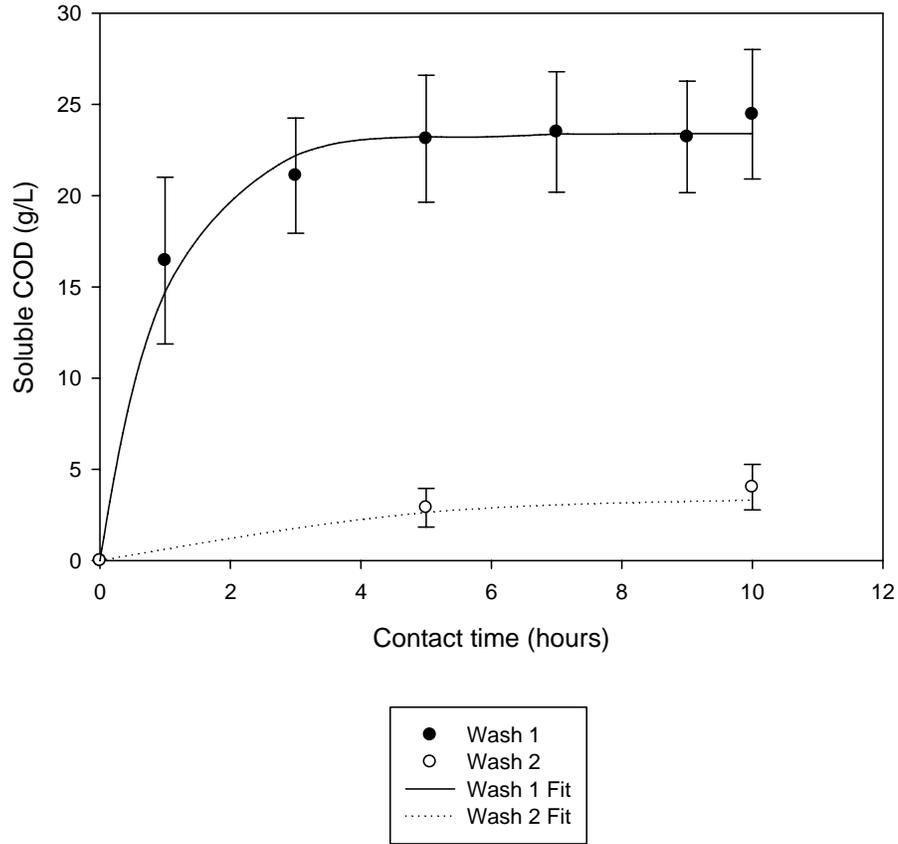


Figure 4-1. In-situ leaching of sugar beet tailings

Table 4-1. Leaching experiments for sugar beet tailings

Experiments		II.1 to II.5
Loading	Wet tailings weight (kg)	3.0
	Total solids (kg)	0.52 ± 0.05
	Volatile solids (kg)	0.48 ± 0.05
	Packing density (kg wet/m ³)	650
	Bulking agent (kg)	2.5
Wash 1	H ₂ O added (L)	10
	Contact time (hr)	10
	Temperature (°C)	55 ± 2
	Saturated concentration (g/L COD)	24.5 ± 3.6
	Rate constant, <i>k</i> (hr ⁻¹)	0.99
Wash 2	H ₂ O added (L)	10
	Contact time (hr)	10
	Temperature (°C)	55 ± 2
	Saturated concentration (g/L COD)	4.0 ± 1.1
	Rate constant, <i>k</i> (hr ⁻¹)	0.20
Wash total	Total wash water (L)	18.6 ± 0.34
	Total suspended solids (g/L)	1.0
	Wash water concentration (g/L COD)	13.9 ± 1.3
	Readily-solubilized fraction (g COD/ g VS)	0.54 ± 0.07

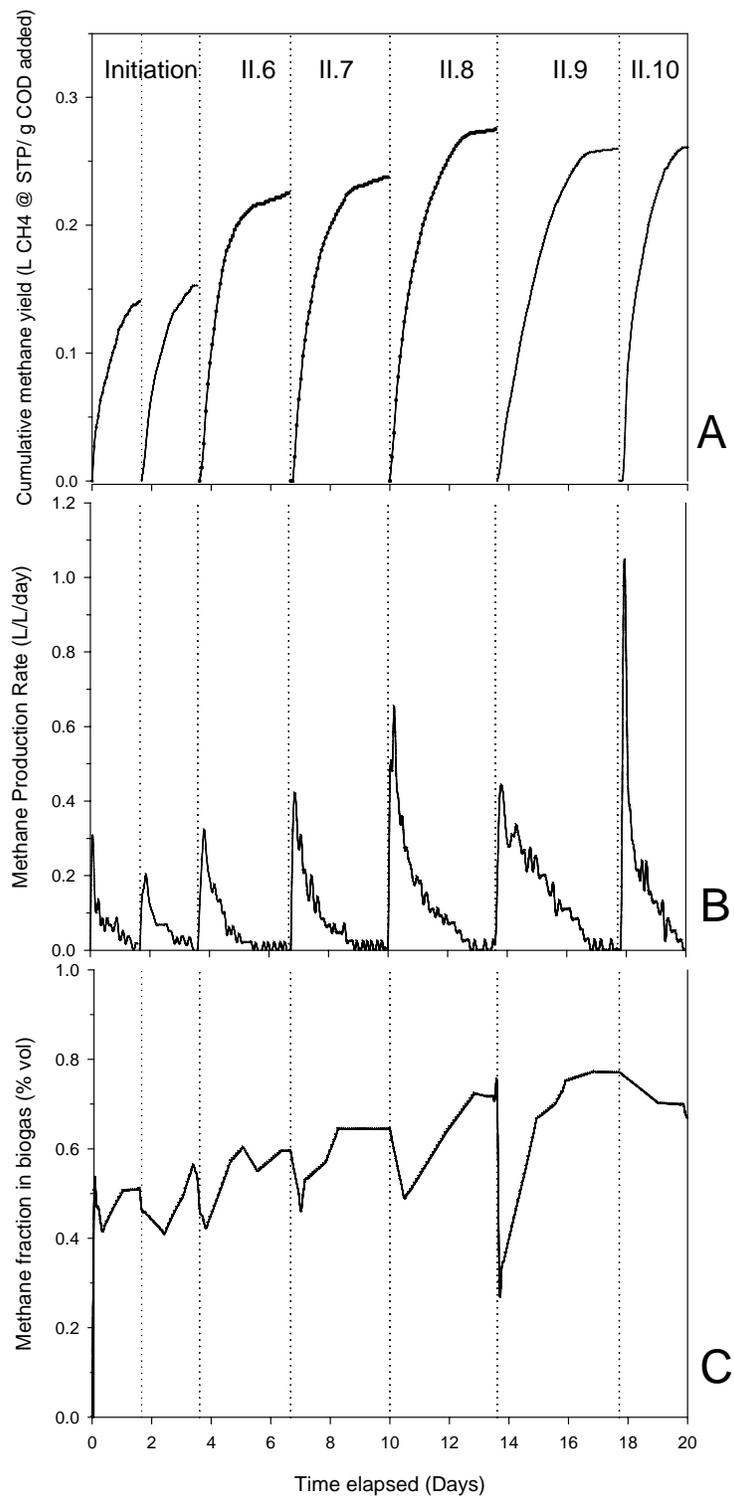


Figure 4-2. Performance profiles from wash water biogasification. A) Cumulative methane yield. B) Methane production rate. C) Methane production rate. D) Profile of pH. E) SCOD profile. F) Total VFA profile.

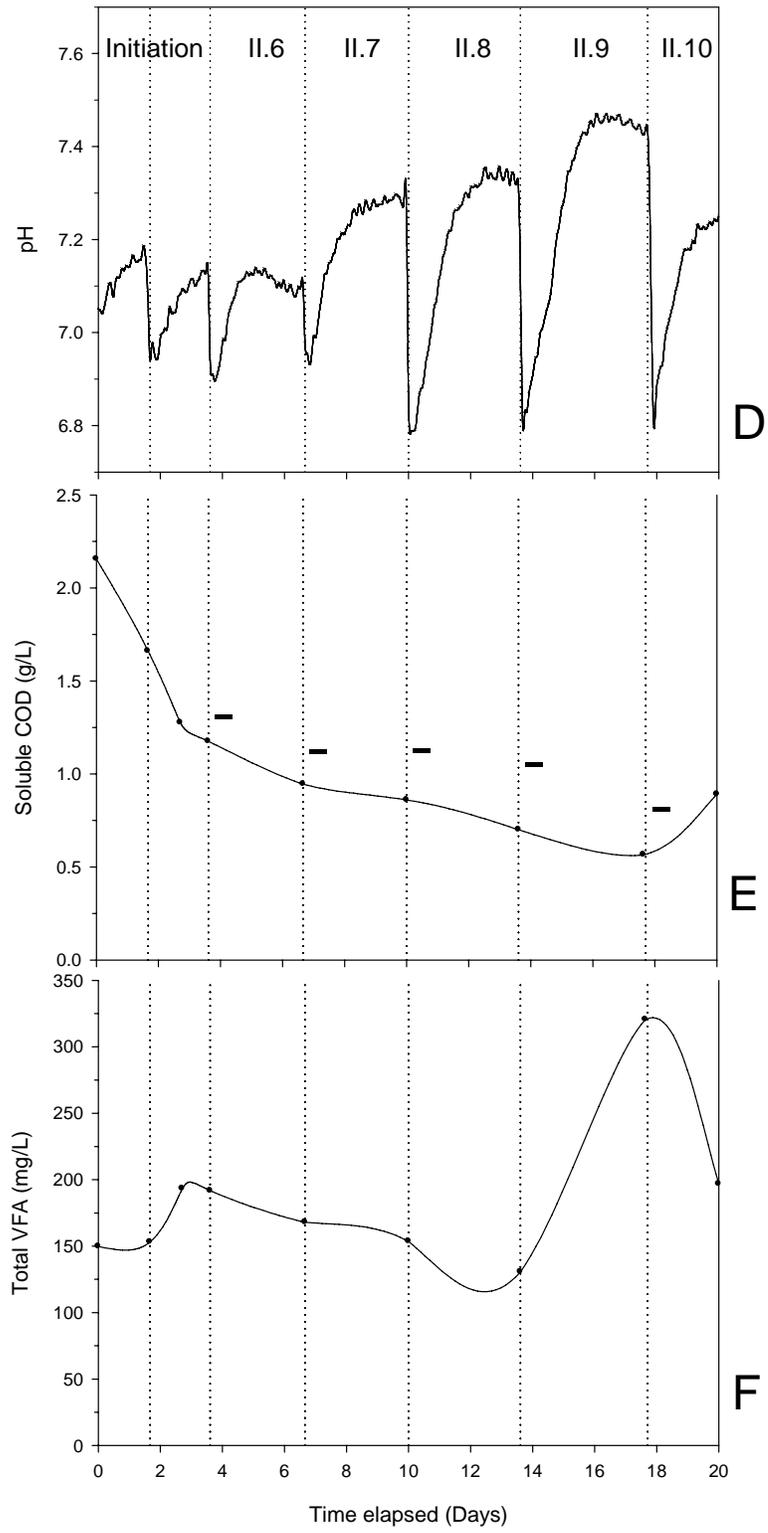


Figure 4-2. Continued

Wash Water (Batch) Soluble COD Balances in AFR

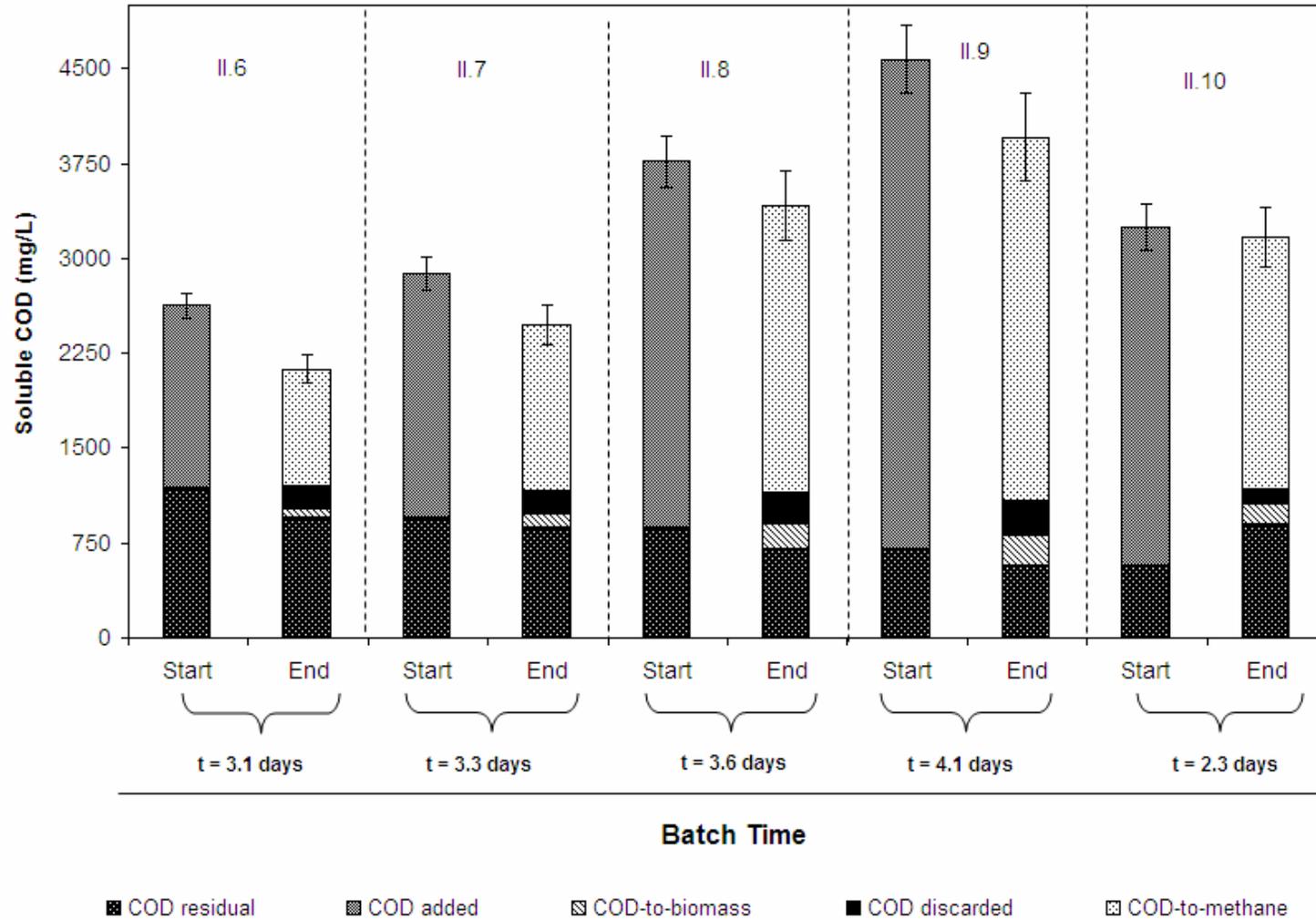


Figure 4-3. COD balance from wash water biogasification in the AFR

Table 4-2. Summary of parameters from biogasification of wash water in the AFR

Experiment	Loading rate	HRT	Final cumulative methane yield (experimental)	^a Gompertz parameters (model)			Duration to produce 95% of methane yield potential
				^b P	^b R _m	^b λ	
	g COD L ⁻¹ d ⁻¹	days	L CH ₄ g COD ⁻¹	L CH ₄ g COD ⁻¹	L g COD ⁻¹ d ⁻¹	days	days
II.6	0.5 ± 0.02	37	0.23 ± 0.02	0.23	0.24	0.1	1.4
II.7	0.6 ± 0.03	30	0.24 ± 0.03	0.27	0.24	0.1	1.5
II.8	0.6 ± 0.03	22	0.28 ± 0.03	0.27	0.24	0.1	1.7
II.9	1.6 ± 0.08	19	0.26 ± 0.02	0.25	0.30	0.1	2.7
II.10	1.2 ± 0.06	21	0.26 ± 0.02	0.22	0.29	0.1	1.5
				^c 0.25 ± 0.02			

^a Gompertz parameters derived by fitting experiment data into Modified Gompertz Model. ^b Symbols have their usual meaning. ^c Average and standard deviation of Gompertz P-values.

CHAPTER 5
STUDY III RESULTS: THE EFFECT OF BULKING ON THE BIOGASIFICATION OF
SUGAR BEET TAILINGS

5.1 Introduction

In study I, experiments revealed that single-stage batch biogasification of raw sugar beet tailings may require pre-treatment to mutually sustain high concentration of solids and balanced biogasification. Moreover, certain physical phenomena that were observed to occur, like compaction and flotation, were regarded as possible kinetic-limiting culprits. It was observed that once the reactor was loaded with tailings and liquid added; the liquid level rises by 15 to 20% during the first 1 to 3 days of biogasification. It was speculated that this rise in liquid level was due to compaction of bed with concomitant expulsion of liquid from the bed. In addition, gas builds up within the bed as the wetted substrate undergoes fermentation; localized VFA accumulation and pH drops would become imminent. When the reactors were subjected to frequent physical perturbations (like vigorous shaking) a sudden release of overwhelming amounts of biogas (> 0.11 L/min) was observed and liquid level fell as a result of such perturbations.

The goal of this study was to examine the effect of bulking the tailings on the biogasification performance of sugar beet tailings. It was important to overcome the above physical limitations for the development of a biogasification strategy that promoted faster degradation of solids and maximized ultimate methane potential. The strategy tested in this study involved addition of an inert bulking agent to the tailings bed that would prevent compaction and allow movement of gas from the bed and liquid in and out of the bed; liquid movement would bring buffer and methanogenic inoculum to more areas and buffer against pH changes and mediate degradation of VFA. Further understanding was also needed in characterizing feedstock

transformation. The extent of degradation or solubilization of chemical components (lignin, cellulose, hemicellulose, etc) during biogasification was also analyzed in this study.

5.2 Background

The addition of a bulking agent in a batch, single-stage biogasification of sugar beet tailings was believed to alleviate the flotation and compaction of the tailings and facilitate the percolation of trapped biogas. Limited literature was available on the use of bulking agents to remedy these physical limitations. Notably, the addition of a bulking agent to enhance anaerobic digestion in vessels system has been reported in very few studies. In Hegde and Pullammanappallil (2007), a feedstock comprising of vegetable waste and woodchips was anaerobically digested at mesophilic and thermophilic temperatures in a single-stage, batch, high-solids system. The addition of wood chips was suggested to improve the structural strength of the waste bed and imparted bulking properties. A similar approach was also taken with the anaerobic digestion of organic fraction of municipal solid waste (OFMSW) by Adhikari, 2003. In that work, shredded OFMSW was loaded with bamboo cutlets to a bulking density of 600 kg/m^3 in a flooded reactor. However, neither work mentioned the effect of bulking on the biogasification performance. Typically, since high-solids anaerobic digestion is carried out on feedstocks that are naturally bulked (for example unsorted municipal solid waste or un-shredded organic fraction of municipal solid waste, yard waste, and mixtures of manure and straw), not much attention has been paid to understand the effect of bulking in these digesters.

Based on physical observations in Study I, it was proposed that the exclusion of liquid inoculum by trapped biogas and subsequent compaction could be addressed by constructing a structured matrix within the bed using landscaping rocks as a bulking agent. As the onset of methanogenesis would produce biogas, gas-liquid/solid separation would be facilitated by a more porous structure; biogas bubbles would overcome cohesive forces from the surfaces of tailings or

other boundaries impeding gas separation. Efficient biogas expulsion (upon generation) in waste beds was hypothesized to minimize compaction/flotation caused by trapped bubbles and maximize the intimate liquid-solid contact. Therefore, the biogasification progression would not be limited by physical boundaries between active organisms and substrate surfaces.

The concept behind this reasoning was taken somewhat analogously from mechanisms inherent in aerobic composting. It has been shown that adjusting the ratio of organic waste: bulking agent has had beneficial effects in developing high rates of respiration (Boen et al., 2003; Aasen et al., 2003; Pagans et al., 2005). Studies there have demonstrated the importance of the interaction of compaction and moisture in lieu of porosity and permeability of composting matrices. In general, the rate-limiting parameter for respiration – oxygen uptake – was enhanced by having optimized pile configurations (Malinska and Richard, 2003). Bulking agents provide certain waste bed structure to encourage porosity for efficient permeation of oxygen to surfaces, whereupon aerobic degradation can occur. The lack of sufficient bulking in aerobic systems has been widely accepted to cause compaction. A downstream implication of this phenomenon included increased concentrations of organic acids as a result of poor aerobic respiration rates (Aasen 2003). Furthermore, it has been suggested that metabolically active organisms could be located on the surface of a bulking agent, where they might be less exposed to high concentrations of acids on substrate surfaces during a process (Boen et al., 2003).

Using this as an analogy to anaerobic digestion of flooded waste beds, it can be concluded that, sufficient porosity is needed to expel biogas formed and allow liquid to percolate into the bed. Chen and Chynoweth (1994) addressed hydraulic conductivity of municipal solid waste (MSW) under various degrees of compaction for leachate re-circulation improvements in landfill applications. Hydraulic conductivity is defined as a measure of the ability of porous media to

conduct liquid. In such work, MSW waste beds underwent changing degrees of moisture content as a result of metabolic gas production. It was observed that gas continued to exclude water from the pore spaces within the matrix, which caused a decline in hydraulic conductivity. Once easily fermentable substrates of MSW were depleted, gas formation diminished and the hydraulic conductivity increased and eventually leveled off. Due to degradation, it was reasoned that hydraulic conductivity becomes a time-dependent parameter, as structure constantly degrades.

It was reasonable based on Study I observations to investigate the effect of bulking on biogasification performance be investigated. Extensive experimentation regarding the changes in hydraulic conductivity or efficiency in gas-liquid/solid separation is beyond the scope of this work. However, quantifying possible improvements offered by bulking tailings in flooded operation could have design implications on the larger scale.

5.3 Results

Experiments: A total of six experiments were conducted consecutively to digest 3 kg aliquot of sugar beet tailings. Experiments III.1 to III.3 were un-bulked trials, whereas Experiments III.4 to III.6 were bulked trials. The decision to conduct experiments with 3kg batch samples was decided by two factors:

1. Bulking agent and 3 kg of raw tailings was the maximum (un-compacted) volumetric load that could be confined to a 12-L working volume and
2. The 3-kg load in Study I (Chapter 3) did not breach headspace tolerance during liquid exclusion from the waste bed.

The protocol for loading un-bulked and bulked experiments was followed according to 2.9.2 and 2.9.3, respectively. To extract the readily soluble organic fraction from sugar beet tailings, each experiment was subjected to in-situ pre-treatment described in Study II.

The performance of each experiment was monitored by analysis of biogasification parameters on a daily basis. Observations were focused during start-up to characterize liquid-level increases (or decreases). The biogasification experiments were carried out until evidence of a stagnation or slow-down in the methane production rate was observed. Experiment III.1 and III.4 were inoculated with fresh stock inoculum, followed by re-use within their respected sets. Bicarbonate buffering was provided similar to Study I.

Characteristics of feed and digested residue: The loading and unloading data of Study III (Table 5-1) were experimentally determined and recorded. As seen, the un-compacted packing density (dry basis) from bulked to un-bulked experiments was almost tripled; the volume fraction taken up by landscaping rocks was considerable, therefore increasing demand for volume usage. Moreover, it was observed that feedstock used for experiments in Study III were on the low end of the range of total solids at 13%. Any sampling procedures for collecting sugar beet tailings at EGF was conducted externally and therefore not controlled or scrutinized. Pre-cautions were taken to always homogenize samples received (by thorough mixing), but variations were present from shipment to shipment.

Residue samples from each experiment were unloaded and measured for TS and VS reduction. Upon opening bulked reactors, it was clearly visible that rocks and residue were intermittently mixed with each other. External washing of residue fixed on rocks was conducted followed by filtration. On average, it was shown that the TS reduction for bulked runs was 86 ± 4 % whereas un-bulked runs yielded 76 ± 3 % TS reduction; a narrower margin was seen in VS reduction, where bulked and un-bulked runs showed $85 \pm 2\%$ and $85 \pm 1\%$ reductions, respectively (It is suspected that the VS measured was actually VSS). Additionally, chemical characteristics of tailings and residue were analyzed by Dairy One Forage Lab (2.14.3.4)

Physical observations: The rise of liquid level inside the reactor for both sets of experiments was observed during the duration of biogasification. As expected, the rise in the liquid level for un-bulked was higher than that of bulked runs. From the headspace viewing window, the average maximum excluded volumes observed for bulked and un-bulked trials were 1 to 1.5 L and 2.5 to 3 L, respectively. The level in both sets began to fall during progression of digestion, notably faster in the bulked reactor.

Biogasification of sugar beet tailings: The biogasification parameters measured during each experiment (Figures 5-1 to 5-3) were plotted side-by-side to highlight differences in magnitude. In general, all the profiles within a set exhibited reproducibility. From the cumulative methane yield plots, it is evident that bulked experiments resembled more closely the shape of a typical growth curve; plots of un-bulked experiments exhibited an irregular inflection point, occurring between days 4-6. Scrutiny of inflection points revealed that methane composition increased only 7% during the two-day spans. On average, the experimentally-determined cumulative methane yields of bulked and un-bulked runs were 137 ± 9 and 127 ± 6 L kg VS⁻¹, respectively.

Considerable differences were exhibited in the methane production rates between bulked and un-bulked schemes. In general, un-bulked plots exhibited oscillatory behavior; initial increases to $0.5 \text{ l l}^{-1} \text{ day}^{-1}$ by the first day, fell to 0.2 to 0.35 between days 4 to 6. Thereafter, the methane production rate increased again to levels 0.4 to $0.5 \text{ L L}^{-1} \text{ d}^{-1}$; finally, the rates fell to below $0.1 \text{ L L}^{-1} \text{ d}^{-1}$ after 15 days. In the bulked experiments, rates were seen to increase up to $1 \text{ L L}^{-1} \text{ d}^{-1}$ after 2 days (except for III.6, where the rate reached this value after 3.5 days) and thereafter decreased and approached $0.25 \text{ L L}^{-1} \text{ d}^{-1}$ after 6 to 7 days. Differences were also seen in the duration by when each experiment attained a particular methane composition. In general,

bulk experiments rapidly attained a 60% methane composition after 4 days whereas un-bulked experiment took twice as long. Un-bulked trials experienced stagnation early on, as methane compositions hovered between 20 to 30 % for a two-day duration. On average, the highest methane compositions attained in bulked and un-bulked experiments were 68% and 80%, respectively.

The pH profiles for both sets of experiments display a similar trend; at the start of experiments, the pH drops to a minimum value, before making an eventual rise. Bulk experiments decreased on average up to 0.5 pH units with the first two days, and steadily increased thereafter, leveling off at approximately 7.3. Un-bulked trials showed similar behavior, but maintained the low-end values (~ pH of 7.5) for duration of 3 to 4 days before making the climb. The final pH level-off for un-bulked experiments occurred between 7.8 and 8.4, and was speculated due to higher concentrations of carbon dioxide gas in the liquid phase.

The contrast in SCOD profiles between bulked and un-bulked runs was not as distinct as the aforementioned parameters. Both sets of experiments started at SCOD values below 5 g/L COD and accumulated to values less than 12 g/L; bulk experiments accumulated a to their maximum values of 5 to 8 g/L COD within 2 to 3 days, before leveling off; un-bulked experiments attained increased max values within 6 days of biogasification. At the termination of the experiment, neither set decayed back to the starting SCOD levels.

The VFA profiles (Figure 5-3) for both sets of experiments were examined and plotted during biogasification. In general it can be seen that all four VFA acids accumulated to higher levels in un-bulked experiments as compared to bulked experiments. The most notable difference is in acetic acid concentrations; bulk concentrations accumulated only as high as 800 mg/L in two days before degrading below 100 mg/L in 7 days; un-bulked experiments

reached as high as 2000 mg/L and sustained acetic levels between 900 and 1600 mg/L for 3 days before degrading below 300 mg/L. With the exception of acetic acid in both sets of experiments, no other VFA's accumulated to values > 500 mg/L

The summary of performance for bulked and un-bulked experiments (Table 5-2) was used to make notable comparisons between the two modes of operation. The modified Gompertz model equation (Eq 1-1) was applied to bulked experiments to determine critical model parameters. Un-bulked experiments were shown to deviate from a classical growth curve, and were not reasonably ideal for Gompertz fitting. The duration to produce 95% of methane yield potentials for bulked and un-bulked experiments was 6.7 ± 1 and 14.5 ± 1.6 days, respectively. Gompertz P and R_m values for bulked experiments yielded 148 ± 5 L CH₄ kg VS⁻¹ and 27 ± 7 kg VS L⁻¹ d⁻¹.

The methane potential distribution between wash water and solids biogasification (Table 5-3) combined the effects of both solid and liquid fractions in biogasification. Wash water generated from in-situ solubilization produced concentrations between 0.52 and 0.58 g COD g VS⁻¹; the average reported in Study II was 0.54 ± 0.07 g COD g VS⁻¹. Using the experimentally-determined yield coefficient for wash water (0.25 ± 0.02 L CH₄ g COD⁻¹ added), wash water methane potentials were calculated for bulked and un-bulked experiments as 145 ± 32 and 131 ± 23 L CH₄ g COD⁻¹, respectively. Thus, the combined solids and wash water contributions to cumulative methane yields for bulked and un-bulked experiments were 282 ± 22 and 258 ± 27 L CH₄ kg VS⁻¹, respectively.

The % VS of major components (Table 5-4) considered in degradation of plant-based organic matter measured by Dairy One were also examined. Clearly, % NFC (non-fibrous carbohydrates) was the largest VS fraction of tailings, at 44.9%. Other critical component

fractions included: cellulose at 21.8 %; hemi cellulose at 14.3%; lignin at 5.1 %; crude protein at 7.3 %; and soluble protein at 1.2%. Residue taken from Experiment III.6 was also measured for the same components. The % degradation (VS basis) of NFC was the highest, at 92%.

Degradation of other components included: cellulose at 87%; hemi cellulose at 84%; lignin at 42%; and crude protein at 52%. Experimentally, solids unloading analysis indicated that the % VS of total dry matter of sugar beet tailings and residue was 93% and 60%, respectively. The mineral components (considered non-volatile solids) of sugar beet tailings and residue were measured (Table 5-5); results showed that minerals account for 3.1 and 6.8% of the total sugar beet tailings and residue dry matter content, respectively. The experimentally-determined ash content of III.6 residue was 40% of the dry-matter unloaded from the reactor. The discussion describes discrepancies between component-derived balances and experimental observations.

5.4 Discussion

By implementing a second iteration (pre-treatment and bulking) in process methodology, clear improvements in biogasification performance were attained. In general, batch experiments in Study III resulted in lower accumulation of SCOD and VFA's and higher degradation rates, as compared to Study I and mesophilic SEBAC-2 work, (Teixeira et al., 2005). A biochemical methane potential of $> 250 \text{ L kg VS}^{-1}$ was achieved in 15 (un-bulked runs) or 10 (bulked runs) days, provided that a high-rate wastewater reactor could concurrently treat wash water generated in the pre-treatment stage. Enhancing the waste bed structure by adding a bulking agent minimized the overall residence time for the biogasification of sugar beet tailings (bulked vs. un-bulked experiments).

The theory that bulking would diminish the liquid exclusion and compaction phenomena and enhance biogasification was confirmed visually in Study II. Within the first few days of biogasification, bulked experiments showed less than half of the excluded fluid in un-bulked

experiments. Therefore, more liquid was available for interaction with tailings, and biogas generated had improved passage through the solid bed. It was speculated that increased levels of VFA accumulation in un-bulked experiments occurred from localized isolation of tailings from bulk fluid, encapsulated in trapped biogas. As acidification occurred, insufficient methanogens were present locally to convert VFA's or inhibitory concentrations of the VFA's restricted methanogenic growth. The stagnation in % methane between day 2 and 3 can be used as further evidence to this claim. However, as biogasification progressed, the volume of excluded liquid minimized and improvements in methane composition, VFA concentrations and pH were seen after the sixth day. As of late, no literature references in anaerobic digestion have been found to support or refute the postulated mechanism aforementioned.

The % VS reduction for bulked and un-bulked runs was experimentally determined to be 85 ± 2 and 81 ± 2 %, respectively. Discrepancies however exist between measured cumulative methane yields and %VS reduction recorded. From stoichiometry, a 100 % VS reduction (i.e. all of material digests) should yield $350 \text{ L CH}_4 \text{ kg VS}^{-1}$. Along that basis, an 85 and 81% VS reduction in sugar beet tailings would correlate to 284 and 298 L kg VS^{-1} . Differences between the measured and stoichiometric yields were 5 and 9%, and suggested that not all of the VS was degraded or accounted by solids analysis and methane measured.

As a case study, experiment III.6 was used in lieu of components analysis to help explain discrepancies between measured cumulative methane yields and % VS reduction values. From analysis, 279 g of VS was lost in the biogasification process; experimental methane yield of 247 L kg VS^{-1} corresponded to 218 g VS, therefore 61 g of VS remained un-accounted for. At the end of experiment III.6, a positive 1.86g/L SCOD difference was measured from start and finish liquid samples. If the end solids concentration in the liquid is assumed to be 1% (close to what

was measured in Study I), then 54 g VS would be additionally accounted for by both soluble and suspended volatile solids. By scrutinizing the effluent solid recovery, the balance on missing VS was accounted to within 12%. If suspended solids (SS) and volatile suspended solids (VSS) were accounted for, then the VS reduction reported for bulked and un-bulked would have been close to what experimental values correspond to.

Typically, VS reductions above 85% were seen in feedstocks such as sorghum halapense, or a mixture of wheat straw and dairy manure (Jerger et al, 1987). Such feedstocks were typically operated in reactors with HRT's of 50 days, whereas tailings were shown to be successfully degraded at HRT < 10 days (bulked experiments only). Degradation rates normalized across the entire batch duration indicated improved volume usage efficiency. On average, bulked experiments degraded tailings at 3.1 kg VS m⁻³ d⁻¹ and un-bulked experiments were measured to 1.4 kg VS m⁻³ d⁻¹. In experiments I.1 and I.2 of Study I, degradation rates across a batch study averaged to 1.1 and 2.5 kg VS m⁻³ d⁻¹, respectively. Therefore, pre-treatment and bulking effect produced 2-fold increase in degradation efficiency per m³ of reactor volume.

The extent of degradation of individual components also provided insight to composition and biodegradability of sugar beet tailings. In general, the retardant component for biodegradation – lignin – was only 4.7% (DM) of tailings. Increased amounts of lignin are usually retardant to biodegradation by sheathing cellulose from microbial attack (Chynoweth and Pullammanappallil, 1996). In Jerger et al 1987, the lignin concentration ranged from 5 to 10% (dry matter), which suggested that most of the cellulose, hemi cellulose and non-structural carbohydrates (NFC) fractions were converted to methane and carbon dioxide. In the case of sugar beet tailings, it was shown that NFC's (starch, sugar, pectin and fermentation acids) had

the greatest degradation at 92%. The NFC's are composed of non-cell wall carbohydrates and are readily biodegradable (Dairy One). The fibrous bulk of the forage of sugar beet tailings was the measure of hemi cellulose, cellulose and lignin; these components made up the cell wall or structural carbohydrates. Through analysis, over 87% of the cellulose and 84% of hemi cellulose were found to be degraded; hemi cellulose is usually more readily biodegradable than cellulose by anaerobic microbes (Chynoweth and Pullammanappallil, 1996; Tsao 1984) Lignin was thought to only solubilize by 42%, as digestibility to methane was considered limited (Odiar and Artaud, 1992). Any residual un-degraded carbohydrates were assumed to have been intertwined with lignin, which prevented their degradation.

The mineral compositions presented (Table 5-5) suggest that sugar beet tailings harnessed many of the nutrients required for microbial growth. Apart from carbon, nitrogen and phosphorus are the major nutrients required for anaerobic digestion. Approximately 1.2% and 0.024% of biodegradable volatile matter is required for cell biomass nitrogen and phosphorus requirement, respectively (Chynoweth and Pullammanappallil, 1996). From analysis, this crucial requirement was met in excess from a batch of tailings; nitrogen was assumed to be in sufficient ratio by observing that the extent of degradation of crude protein (various essential amino acids) was 41.3%. The recycle of inoculum from experiment to experiment was also suspected to contribute to the overall nitrogen and phosphorus concentration. Nutrients needed in intermediate concentrations (sodium, potassium, calcium, magnesium, sulfur, etc) were also met by natural concentrations of sugar beet tailings themselves.

In Experiment III.6, an ash balance was conducted for all the non-volatile components (i.e. minerals). Analysis determined that only 6.8% of the residue dry matter was composed of non-volatiles; VS calculations confirmed that 60% of the dry matter loaded was volatile, therefore an

unknown was suspected. Sugar beet tailings contain a considerable portion of sand, which typically is characterized as SiO₂. Therefore, it was speculated that 83% of ash measured experimentally accounted for sand contained on sugar beet tailings; this component was not picked up by Dairy One,

Study III further established that sugar beet tailings can be operated in a robust mode, requiring minimal supplements. Biomethanogenesis is known to be sensitive to several groups of inhibitors, namely to sulfides, heavy metals, halogen, hydrocarbons, VFA's, ammonia and cations (Chynoweth and Pullammanappallil 1996; Speece 1987b). The parameters that influence digester performance (VFA's and pH) were shown to be within the acceptable ranges (pH > 6.8, total VFA < 500 mg/L). The presence of inhibitors or overloading was not suspected as experiments in series within each set did not show significant deviation in trends as a result of accumulation or toxicity.

The preliminary approach to Study III as a means to classify the extent of biodegradation and improve on rate of conversion was sufficiently met as seen by the results. A more detailed analysis on parameters not mentioned but considered important in anaerobic biogasification (alkalinity, C/N ratio, total and free ammonia) should be addressed in the future. From the aforementioned findings, implications to design, operation and material handling for large scale applications in sugar beet processing should also be addressed (Chapter 7).

5.5 Conclusions

- The effect of pre-treatment was shown to decrease the SCOD accumulation levels during biogasification of a 3-kg un-bulked waste bed of sugar beet tailings.
- The effect of bulking on pre-treated sugar beet tailings was shown to increase the degradation rate 3-fold; the duration to achieve 95% of the methane potential in bulked experiments was less than 7 days whereas un-bulked experiments took nearly 15 days.

- The addition of a bulking agent decreased the volume of excluded liquid inside a reactor by more than 50% during the start-up phase; no appreciable compaction, as observed in Study I was detected in Study III.
- Based on the VS reduction after digestion (86 ± 2 when bulked; 81 ± 2 when un-bulked) sugar beet tailings were considered to be a highly degradable feedstock
- Over 90% of the NFC's in sugar beet tailings were readily degradable. The % degradation for cellulose and hemi cellulose was 87 and 84%.
- Robust operation of biogasification on sugar beet tailings was attained with minimal addition of supplements or minerals. Accumulation of toxins or inhibitors was not detected at sensitivity levels that would indicate diminished biogasification performance.

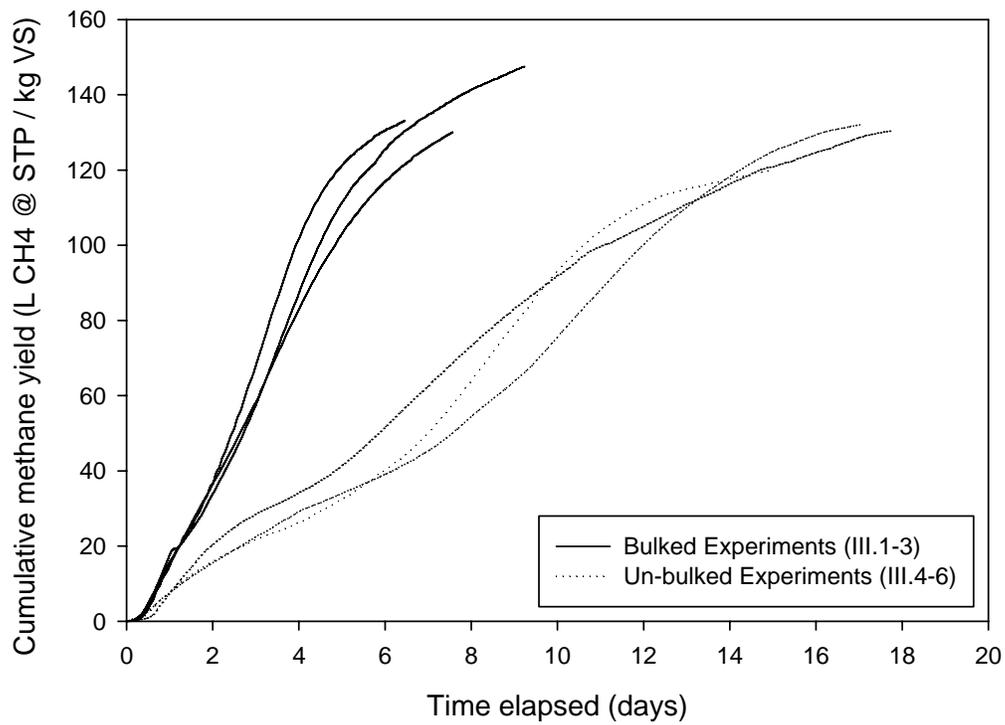


Figure 5-1. Comparison of cumulative methane production from bulked and un-bulked experiments

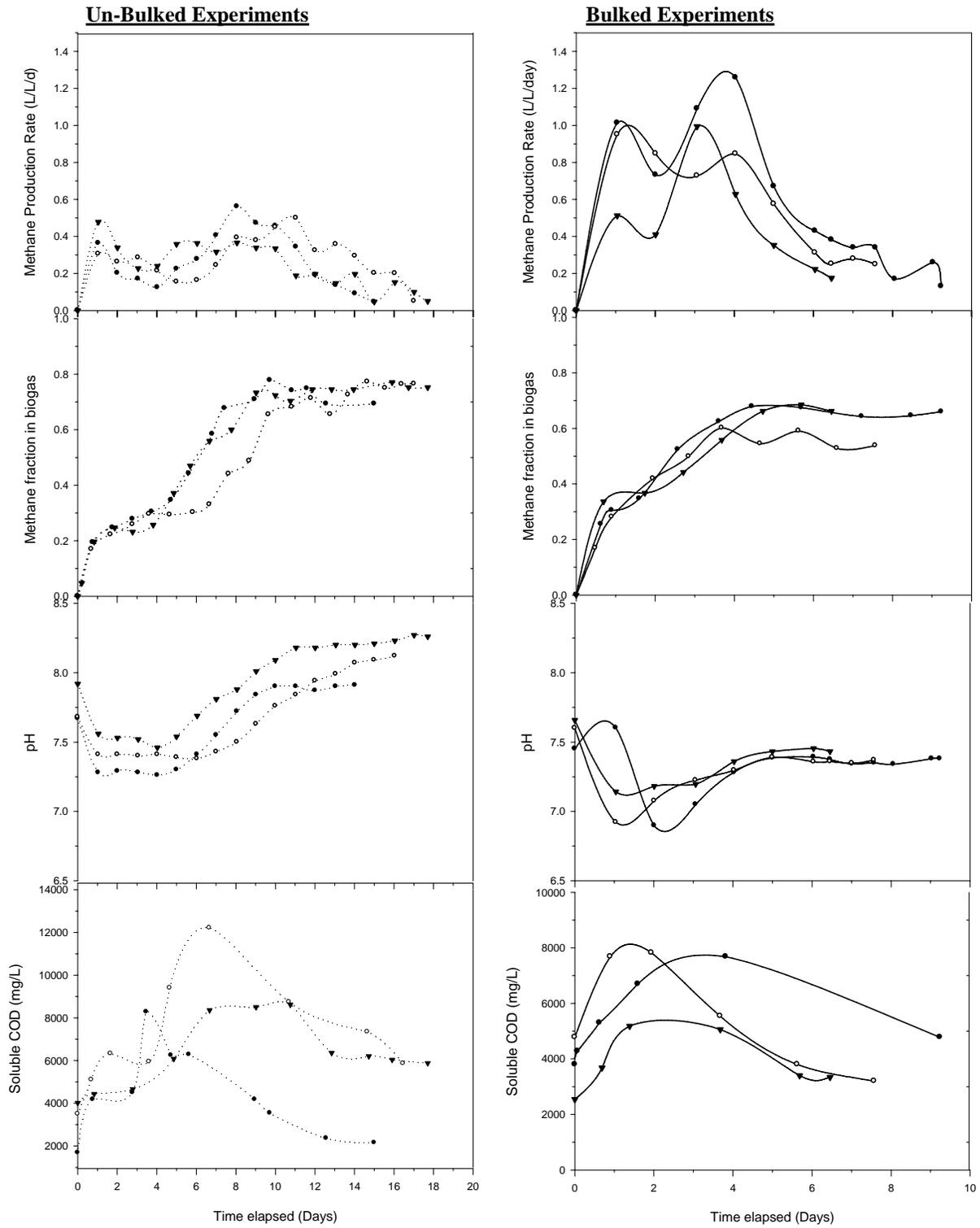


Figure 5-2. Comparison of biogasification parameter profiles for bulked and un-bulked experiments

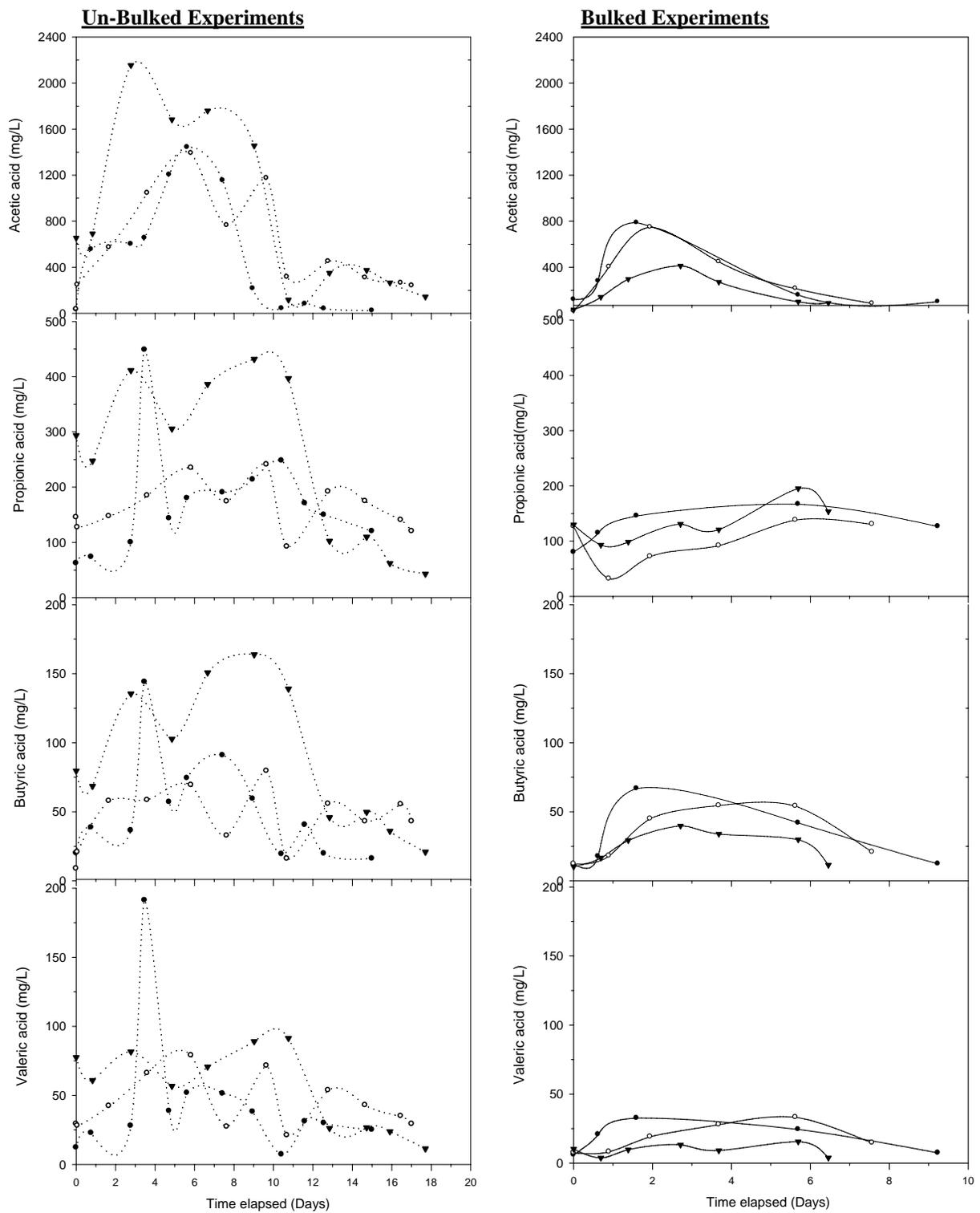


Figure 5-3. Comparison of VFA profiles for bulked and un-bulked experiments

Table 5-1. Loading and unloading data for bulked and un-bulked experiments

Experiments		III.1 to III.3 (Bulked)	III.4 to III.6 (Un-bulked)
Loading	Wet tailings weight (kg)	3	3
	Total solids (kg)	0.38 ± 0.02	0.38 ± 0.02
	Volatile solids (kg)	0.33 ± 0.06	0.34 ± 0.02
	Inoculum added (L)	9.0 ± 0.5	11.8 ± 1.2
	Packing density (kg wet/m ³)	250	650
	Packing density (kg dry/m ³)	32 ± 2	81 ± 4
	Total solids in reactor (%)	3.3 ± 0.2	2.6 ± 0.4
Unloading	Wet residue weight (kg)	0.67 ± 0.05	0.88 ± 0.3
	Total solids (kg)	0.050 ± 0.01	0.09 ± 0.02
	Volatile solids (kg)	0.047 ± 0.01	0.06 ± 0.01
	Total solids reduction (%)	86 ± 4	76 ± 3
	Volatile solids reduction (%)	86 ± 2	81 ± 2

Table 5-2. Summary of performance in Study III experiments

Experiment	Final cumulative methane (experimental)	^a Gompertz parameters (model)			Duration to produce 95% methane yield potential (days)
		^b p	^b R _m	^b λ	
	(L CH ₄ kg VS ⁻¹)	(L CH ₄ kg VS ⁻¹)	(L kg VS ⁻¹ d ⁻¹)	(days)	(days)
Bulked					
III.1	148	153	28	0.8	7.8
III.2	130	143	20	0.7	6.7
III.3	133	149	33	0.9	5.6
	^c 137 ± 9	148 ± 5	27 ± 7	0.8 ± 0.1	6.7 ± 1
Un-bulked					
III.4	120	-	-	-	12.7
III.5	132	-	-	-	15.0
III.6	130	-	-	-	15.8
	127 ± 6				14.5 ± 1.6

^a Gompertz parameters derived by fitting experiment data into Modified Gompertz Model. ^b Symbols have their usual meaning. ^c Mean ± standard deviation of three experiments.

Table 5-3. Summary of methane potential distribution in Study III

Experiment	Readily-solubilized fraction (g COD/g VS)	^a Wash water methane yield (L CH ₄ kg VS ⁻¹)	^b Total cumulative methane yield (L CH ₄ kg VS ⁻¹)
Bulked			
III.1	0.44	109	257
III.2	0.67	167	297
III.3	0.64	160	293
	^c 0.58 ± 0.12	145 ± 32	282 ± 22
Un-bulked			
III.4	0.48	120	240
III.5	0.63	158	290
III.6	0.47	117	247
	0.52 ± 0.09	131 ± 23	258 ± 27

^a Wash water biogasification potential determined from experimental efficiency in Study II. ^b Sum of methane potential from readily soluble fraction and solids degradation. ^c Mean ± standard deviation of three experiments

Table 5-4. Chemical characteristics of tailings and digested residue

Chemical component	Tailings (% VS)	Residue (% VS)	Extend of degradation or solubilization (% VS)
Crude protein	7.3	22.8	52
Soluble protein	1.2	3.9	0
NFC	44.9	22.9	92
Lignin	5.1	19.1	42
Hemi cellulose	14.3	14.7	84
Cellulose	21.8	18.0	87

Table 5-5. Mineral compositions in sugar beet tailings and residue

Minerals	Tailings (% DM)	Residue (% DM)
Calcium	1.23	2.82
Phosphorus	0.12	0.23
Magnesium	0.41	0.51
Potassium	0.92	0.60
Sodium	0.229	2.277
Sulfur	0.09	0.36
Iron	6.0×10^{-4}	7.0×10^{-3}
Zinc	5.9×10^{-4}	5.4×10^{-4}
Copper	2.7×10^{-4}	2.0×10^{-4}
Manganese	2.7×10^{-4}	2.9×10^{-4}
Molybdenum	2.7×10^{-4}	7.9×10^{-4}

CHAPTER 6
STUDY IV RESULTS: THE EFFECT OF TWO-STAGE OPERATION ON THE
BIOGASIFICATION OF SUGAR BEET TAILINGS

6.1 Introduction

In Study III, it was shown that performance of single-stage biogasification of sugar beet tailings can be enhanced by washing and bulking the solid-bed. Notably, a three-fold increase in degradation kinetics was obtained and the duration to produce 95% of the cumulative methane potential was reduced to less than 7 days (bulked experiments only). Such kinetics were significant outcomes when compared to Study I results. The implication of accelerated biogasification was estimated to translate directly into reducing the number of reactors by more than one half in commercial applications

However, the application of a bulking agent to in-vessel biogasification technologies was regarded unconventional and efficiency of material handling operations during loading/unloading and separation of residue and bulking agent (if recycled) were challenged. Furthermore, the higher volume occupancy of a bulking agent would increase volume requirements to accommodate critical throughputs. For example, in Study III, the dry matter packing density was halved from un-bulked to bulked experiments. Therefore, any kinetic improvements offered by bulking would have to supercede practical design and economic tolerances.

Study IV implemented a two-stage approach to biogasifying sugar beet tailings by incorporating a sequence operation between the solids containing reactors and the anaerobic filter reactor (AFR) used to treat wash water. It was speculated that a separate second stage would have a considerable impact in alleviating certain limitations of single-stage batch operation (VFA accumulation, high SCOD levels, un-synchronized cooperation of microbial groups) that were observed in Study I and Study III (un-bulked runs). The goals of Study IV

were to conduct two-stage experiments on un-bulked tailings (with and without pre-treatment), with the exclusion of a bulking agent. It was believed that improvements in biogasification would justify the utilization of a two-stage system (with attached film or high rate reactor) as an additional option for biogasifying of sugar beet tailings.

6.2 Background

The designs and strategies employed to enhance biogasification of organic feedstocks has been thoroughly researched in the last two decades. Among design options, each has its own set of benefits and constraints and the selection process is usually dependent upon feedstock characterizations and/or personal preference. Designs usually depend on factors such as reactor solids concentration, mixing strategy, temperature and number of stages (Pullammanappallil and Chynoweth, 1996; Gunaseelan 1997; Mata-Alvarez and Llabres, 2000). Single-stage biogasification quite commonly is limited in organic loading (especially when $TS > 20\%$); the rate of volatile acid formation due to hydrolysis and fermentation of macromolecules (acidogenic stage) is often not synchronous with the rate of volatile acid conversion to methane (methanogenic phase). When the acidogenic and methanogenic processes are not synchronized, the maximal methane gas yield is only achieved after longer retention times (Sarada and Joseph, 1995).

Two-phase and two-stage systems permit much higher loads and have been proven to run at lower retention times than single-stage (combined) systems. Figure 6-1 shows the block-flow diagrams comparing two-phase and two-stage systems (Azbar and Speece, 2001). In literature, these terms tend to be used interchangeably. For the purposes of this research, the two-phase and two-stage will be treated as separate processes.

Two-phase system usually refers to the development of unique biomasses in separate reactors. In this process, fermentation and methanogenesis are separated by using different

retention times; usually, only acidogens are found in the first phase, while primarily methanogens are found in the longer SRT of the second phase (Azbar and Speece, 2001; Gunaseelan 1997; Yang et al., 2002). Phased systems, which produce substrate gradients and in turn metabolic intermediates (VFA's), have been found to enhance the methanogenic conversion in the second reactor. Therefore, phase separation promotes biogas formation in the second reactor for the most part; attached film reactors are typically employed as second reactors for their ability to digest high quantities of wastewater at low HRT's (< 10 days) without the fear of washout (Mata-Alvarez and Llabres, 2000).

In a two-stage system, acidogenic and methanogenic reactions occur in both reactors but are operated at a different retention time. For rapidly fermentable wastes, it has been shown that a two stage reactor can lower the overall retention time compared to a single stage system (Gunaseelan, 1997). The initial approach to biogasifying sugar beet tailings (Teixeira et al., 2005) was to use a two-stage mesophilic system in flooded mode referred to as SEBAC-2. The original SEBAC process was a dry-digestion concept developed at the University of Florida for bioconversion of OFMSW. The process used a leachate management strategy that provided microorganisms, moisture and nutrients for rapid conversion of OFMSW and the removal of inhibitory fermentative products during start-up. A mature bioreactor would take the leachate containing inhibitory fermentative products (such as VFA's) from the freshly-started bioreactor and convert them to methane (Chynoweth et al., 1992; Chugh et al., 1995). This operation was called sequencing. The treated leachate was then fed back to the bioreactor containing fresh waste. The freshly-started waste reactor achieving pH > 6.5 and a methane composition of > 30% after a certain duration of sequencing would be considered balanced and self-sustaining and sequencing would be disengaged.

Implementing SEBAC for the biogasification of raw sugar beet tailings was suspected to be limiting due to feedstock characteristics. Success of SEBAC depends on the availability of a mature reactor containing a bed of degraded solids. As leachate passes through the bed, VFA's are degraded and microorganisms, buffer and other nutrients are picked up. However, Study III showed degradation greater than 80% for sugar beet tailings and hardly any residue was left at the end of the run, Residue settling at the bottom was suspected to diminish the contact between microorganisms and fresh incoming leachate. Furthermore, the highly soluble COD component of tailings was assumed to exceed the assimilation capacity of stabilized waste bed in Teixeira et al., 2005. Previously, SEBAC was shown to initiate methanogenesis rapidly in feedstocks such as organic fraction of municipal solid waste, yard waste, mixtures of biosolids and yard wastes, where COD values are typically < 20 g/L (Chynoweth et al 2002).

Biogasification of sugar beet tailings was speculated to be enhanced using a two-stage concept, by implementing the AFR previously used for wash water treatment (Study II). It should be noted that other high-rate wastewater anaerobic systems could have been used as well instead of AFR. The system considered (Figure 6-2) for two-stage biogasification of sugar beet tailings was constructed without previous sizing of vessels with respect to each other. The solids reactor (ABCR) and liquid reactor (AFR) were operated at 12 and 18 L working volumes, corresponding to 5 and 7.5 day HRT, respectively. Bulking media in the AFR was speculated to harness sufficient attached growth for rapid conversion of incoming streams for the solids reactor; both reactors were contributors to biogas formation.

6.3 Results

Experiments: A total of four experiments were conducted consecutively in a sequenced mode with the AFR. Sugar beet tailings in Experiments IV.1 and IV.2 were loaded in ABCR's

and pre-treated exactly as un-bulked experiments in Study III. The AFR was used intermittently to process wash water generated from pre-treatment or sequenced with ABCR during the early stages of biogasification. Similarly, Experiment IV.3 was also loaded with 3-kg of raw sugar beet tailings, but in-situ pre-treatment to remove the readily soluble fraction was bypassed; biogasification and sequencing with the AFR were initiated immediately upon start-up. Lastly, experiment IV.4 was conducted to demonstrate the utility of having an AFR when single-stage systems are overloaded; Experiment I.3 in Study I (5-kg raw tailings) was sequenced with the AFR after the termination point reported in Study I.

As reported in Study I and III, the performance of each experiment in Study IV was monitored by analysis of biogasification parameters. Treatment of wash water in the AFR and sequencing between AFR and ABCR for the aforementioned experiments is described in sections 2.10 and 2.11, respectively. Sequencing between the AFR and ABCR was carried out until process performance (methane yield, % CH₄ composition, pH, decline if VFA concentration) in first stage (ABCR) showed improvements. Bicarbonate buffering was provided similar to Study I and III.

Characteristics of feed and digested residue: Table 6-1 lists the loading and unloading data for the experiments in Study IV. The un-compacted packing density (dry basis) for all Experiments (IV.1 to IV.4) ranged between 75 to 100 kg/m³. The visible volume usage for loading 3 and 5 kg of tailings in experiments was approximately half and three-quarters of the working volume (12 L), respectively. Similar procedures addressed in Study III were used to collect and homogenize sugar beet tailings samples before loading each reactor. Upon loading raw tailings to digesters and flooding the TS concentration inside the 3 and 5 kg experiments were approximately 3.3 and 5.3 % TS, respectively.

Residue samples from each experiment were unloaded and measured for TS and VS reduction. In opening reactors, it was observed that Experiment IV.4 had the highest visible volume reduction, approximately 80 to 90%; Experiments IV.1 to IV.3 were visually observed to have reduced between 70 to 80%. On average, TS and VS reduction for Experiments IV.1 to IV.3 were 82 ± 2 and 88 ± 2 %, respectively; Experiment IV.4 yielded a TS reduction of 86% and VS reduction of 93%.

Physical observations: The rise of liquid in all four experiments due to the mechanism proposed in Study III was observed during Study IV as well. However, during sequencing with the AFR, the excluded liquid level in the ABCR reduced at a rate much faster rate than excluded liquid level in the un-bulked runs of Study III. It was suspected that additional hydraulic injections and withdrawals due to sequencing promoted separation of accumulated biogas from the waste bed.

Biogasification of sugar beet tailings: The cumulative methane yield profiles for the AFR and ABCR in Experiments IV.1 to IV.4 (Figures 6-3 to 6-6) were plotted together to highlight progression with respect to one another. The plots are also sectioned off to illustrate regions where AFR was either sequenced with an ABCR or used to treat wash water generated from pre-treatment. The abbreviations “ww” and “seq” (Figures 6-3 to 6-6) symbolize regions where wash water was being treated by the AFR and sequencing between the AFR and ABCR commenced, respectively. All un-marked regions indicated that both the AFR and ABCR were operating in a solo mode. The complete summary of operation times (Table 6-2), and experimental cumulative methane distributions (Table 6-3) was constructed as a basis for comparison between experiments.

In Experiments IV.1 and IV.2, sugar beet tailings generated approximately 0.5 g COD/gVS when pre-treated with in-situ method (Study II). Only one pass of washing was implemented, generating 12 L of 15 to 17 g/L SCOD strength wash water. The availability of the AFR to process the wash water was dependent the biogasification progression in the ABCR; precedence was put on AFR sequencing with ABCR during the start-up stages of biogasification to alleviate accumulation of intermediates. In Experiment IV.1, wash water was processed at the beginning of biogasification (0.7 to 2 days) and after sequencing duties (6.1 to 10.9 days). Wash water treatment in experiment IV.2 was implemented only after AFR sequenced operation with ABCR was halted. The processing of wash water in the packed bed was conducted at an HRT of 7.5 days in both experiments.

The implementation of sequenced operation in Experiments IV.1 and IV.2 was dictated by what was observed in Study III; un-bulked experiments exhibited poor increases in methane rate and composition between days 4 to 6. Both Experiments IV.1 and IV.2 were operated in a two-stage sequenced operation for 4.1 and 5.1 days, respectively. The on-set of sequencing on the performance parameters of both the ABCR and AFR (Figures 6-7 and 6-10) was considered an important response factor. In general, methane production rate in the ABCR reactor was shown to improve by 0.4 to 0.6 L L⁻¹ d⁻¹ after a lag time (~ 2 days). The methane fraction in biogas showed dramatic increases, spanning from 25% to 55% within three days in both experiments. Similarly, the pH profiles exhibited in both ABCR and AFR showed increases at varying degrees; sequenced operation caused an increase from pH 7.8 to 8.1 in IV.1 and 7.2 to 8.1 in IV.2. The pH trends observed during the treatment of wash water in the AFR decreased to from 8.1 down to 7.4, before leveling off in to mid-range pH values (7.4 to 7.8) after four days.

Soluble COD and VFA concentrations in Experiments IV.1 and IV.2 exhibited similar trend behaviors. The SCOD concentrations in the ABCR increased as high as 10 to 14 g/L during the first three days of biogasification. Upon sequencing, a short lag time (1 to 3 days) was followed by a rapid decay of SCOD; concentrations reduced by 6 g/L SCOD in 3 days, before leveling off to values < 8 g/L SCOD. The SCOD levels in the AFR showed an increase only when effluent from ABCR was treated; concentrations reached as high as 7 g/L SCOD before gradually falling to concentrations as low as 1.3 g/L SCOD within 8 days. Wash water treatment did not contribute to any increases to the SCOD concentration in the AFR. The total VFA concentration in the ABCR reached as high 2260 and 1600 mg/L within 1 to 3 days in both Experiments IV.1 and IV.2, respectively. Next, the rapid decay of VFA's was observed after a 2-day lag in the sequencing stage, where concentrations fell on average by 1000 to 1500 mg/L within 4 days and leveling off under 500 mg/L at the end of biogasification. The total VFA concentrations in the AFR during sequencing and wash water treatment were maintained below 500 mg/L during the complete duration.

Experiments IV.1 and IV.2 yielded a total cumulative yield of 293 and 315 L CH₄ kg VS⁻¹, respectively. Approximately 66% of the total cumulative yield in both stages evolved in the AFR and the remaining 34% from the ABCR; the duration to produced 95% of the total methane potential in both units was in the range of 9.2 to 9.8 days. The two-stage concept of operating at different retention times was exercised; ABCR and AFR operated at 7.5 and 5 day HRT's, respectively.

In Experiment IV.3, pre-treatment was bypassed on the 3 kg sample of sugar beet tailings. The AFR was sequenced with the ABCR (at HRT's mentioned in Experiments IV.2 and IV.3) immediately at the start of the run. Unlike Experiments IV.1 and IV.2, the duration to produce

95% of the cumulative methane potential was lower at 7.4 days; the total cumulative methane produced, 303 L CH₄ kg VS⁻¹. More equal distribution of methane was observed, as 54% of the total cumulative yield evolved from the AFR and 46% from the ABCR.

From start-up, Experiment IV.3 showed rapid increases in methane production rate and methane fraction in the biogas. In the ABCR, methane production increased to 1.6 L L⁻¹ d⁻¹ within 0.5 days and methane composition reached 50% after only 3.5 days of operation. The AFR similarly achieved a max rate of 0.9 L L⁻¹ d⁻¹ after 1 day and reached 60% methane after 1.75 days. As biogasification progressed, the methane production rate in both units declined daily by 0.4 L L⁻¹ d⁻¹ and the methane composition increased, leveling off at 70% methane. At 4.5 days, 90% of the liquid contents in the ABCR were sequenced out and replenished by AFR liquid contents; the pH values at this point were both at 8.05. Sequencing was terminated at 6.7 days, as methane production rate in the AFR fell to 0.1 L L⁻¹ d⁻¹.

Experiment IV.3 SCOD profile increased to 19 g/L SCOD by the first day; the daily ABCR decay of SCOD in the sequenced stage occurred was 3.1 g/L SCOD. After 6.7 days, the SCOD level in the leveled off just below 5 g/l SCOD. The AFR SCOD concentrations also never exceeded 5 g/L and hovered at 4.5 g/L by end of sequencing. Total VFA concentrations in the ABCR reached as high as 2200 mg/L in 2.5 days; rapid decay observed in IV.1 and IV.2 was consistent in IV.3 as well, where the total VFA concentration fell below 500 mg/L after 7 days of biogasification. The AFR total VFA concentrations were also below 500 mg/L throughout sequencing duration.

Figures 6-6 and 6-10 show the biogasification parameter profiles for Experiment IV.4. The start-up of this experiment was originally established in Chapter 3, as Experiment I.3. The accumulation SCOD and VFA intermediates diminished the progression of cumulative methane

yield after 6.6 days in single-stage biogasification. In Study IV sequencing with the AFR was conducted between 6.6 days and 10.5 days to revive and activate the pickled reactor. Following a 1.5-day lag, biogasification parameters rapidly increased from day 8 to day 10.5: the methane production rates in the ABCR increased from 0.5 to 2.5 L L⁻¹ d⁻¹; the methane composition increased from 35% to 64%; and the pH increased from 6.6 to 7.3. Moreover, the SCOD and VFA profiles during the sequencing duration decreased significantly by 16 g/L and 3000 mg/L, respectively. After the 10.5-day mark, single stage biogasification was re-instated; SCOD and VFA fell to final values of 11 g/L and 1,500 mg/L after 7 days.

The total cumulative methane yield for experiment IV.4 was experimentally determined as 319 L CH₄ kg VS⁻¹. Approximately 57% of the total cumulative yield in both stages evolved in the ABCR and the remaining 43% from the AFR; the duration to produced 95% of the total methane potential in both units was 15.2 days. A sequencing duration of only 3.8 days was applied towards reviving the inhibited single-stage experiment aforementioned.

6.4 Discussion

The problems associated with volatile fatty acids and high levels of soluble COD were shown to impede the rates of degradation in Experiments I.3, III.4 to III.6 (Studies I and III). Implementing a two-stage operation for the biogasification of sugar beet tailings translated to enhancing the rate at which accumulated constituents (SCOD and VFA) were removed and degraded; the AFR provided the necessary replenishment of micro-organisms, and buffer necessary for methanogenic start-up support in the ABCR reactor; it did not rely on a certain % of digested residue

Increases in the TS and VS reduction in Study IV confirmed that a substantial portion of degradable matter residing in the liquid was capable of being degraded further. From un-bulked experiments in Study III, a VS reduction of 85 ± 1% did not coincide with the total measured

cumulative methane yield, $258 \pm 27 \text{ L CH}_4 \text{ kg VS}^{-1}$; effluent solid recovery was shown to unaccount for 12% of un-degraded VS. In un-bulked sequenced Experiments IV.1 to IV.3, the discrepancy between the total experimentally measured yield and % VS reduction was greatly reduced. The average experimental cumulative methane yield measured was $304 \pm 11 \text{ L CH}_4 \text{ kg VS}^{-1}$, which theoretically corresponded to $88 \pm 4\%$ VS reduction; residue VS analysis for Experiments IV.1 to IV.3 yielded $88 \pm 2\%$ VS reduction. It is speculated that sequencing increased the retention of contributing constituents within the AFR that would otherwise not break down as rapidly in a single-stage solids reactor; total suspended solids in wash water and VS locked-up in reactor liquor were mineralized to methane more readily. Further evidence of increased degradation was indicated by the SCOD profiles in both ABCR and AFR, where accumulated concentrations returned or fell below the typical starting values (5 g/L).

The effect of sequencing in Experiments IV.1 and IV.2 circumvented the sluggish behavior observed in Experiments III.4 to III.6 between the second and the fourth day. Methane production rate was increased by $0.2 \text{ L L}^{-1} \text{ d}^{-1}$ and yield was improved by $10 \text{ L kg VS}^{-1} \text{ d}^{-1}$ when sequenced. It is suspected that the balance between acidogenic and methanogenic groups in the ABCR during that time was improved addition of microorganisms and removal of VFA's and SCOD. Experiment IV.3 showed that pre-treatment was not a necessary step implementing two-stage operation with the AFR used in the research work. At a peak organic loading rate of $2.5 \text{ g COD L}^{-1} \text{ d}^{-1}$ on the first day of sequencing, the AFR's methane production rate increased to $0.9 \text{ L L}^{-1} \text{ d}^{-1}$ with no signs of sluggish behavior. In Experiment IV.4, the organic loading rate delivered varied between 5.3 and $3.3 \text{ g COD L}^{-1} \text{ d}^{-1}$ for the first two days of sequencing. The AFR sustained a methane production rate of $0.9 \text{ L L}^{-1} \text{ d}^{-1}$ and VFA concentrations climbed to 670 mg/L before falling below 500 mg/L . Thus, the AFR demonstrated its potential to effectively

treat effluents between 5 to 40 g/L at an HRT of 7.5 days without major complications during sequencing.

On the contrary, the spent digester in the two-stage flooded mesophilic SEBAC-2 reported Teixeira et al., 2005 showed poor performance because of the process' inability to treat the high amount of readily soluble organic compounds that formed initially. In a SEBAC process, the leachate re-circulation strategy ensures that readily soluble COD generated in a fresh waste bed (1st stage) would be converted to methane in the second stage and that microorganisms, buffer and nutrients would be recycle back; this was contingent on the basis that a significant amount of residue remains in the mature reactor, harboring the necessary microorganisms to carry-out degradation of incoming intermediates (Chynoweth et al, 2002). The AFR used in Study IV was independent of feedstock residue; it provided a consistent centralized treatment option that can handle high SCOD liquor from a solids reactor. However, it should be noted that thermophilic operation was a critical factor that improved the rates of degradation in the two-stage implemented in this work; the mesophilic kinetic rates of SEBAC-2 are therefore expected to be lower than thermophilic operation. The effects of sizing the ABCR and AFR accordingly to attain optimum loading and characterize boundaries should be addressed in the future.

The concept of running two-stage sequential batch biogasification on sugar beet tailings with a high-rate anaerobic wastewater reactor suggests that pre-treatment could be avoided and that higher bulking densities may be afforded in the first stage. The physical limitations of trapped biogas however may limit the latter. Experiment IV. 3, which had an in-vessel bulking density of 75 kg/m³ (dry basis), occupied 83% of the working volume. Therefore, the savings in pre-treatment on account of incorporating the AFR as a supporting unit process to the treatment of raw sugar beet tailings was a considerable accomplishment. High rate systems such as

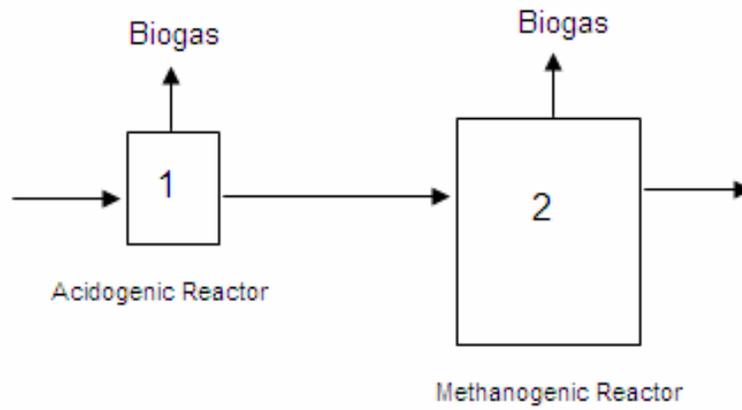
anaerobic filter (AF) or Hybrid UASB/AF are known to treat wastewaters $> 5 \text{ g COD L}^{-1} \text{ d}^{-1}$.

Thus, practical outlooks of increasing the compaction density and attaining high degradation of sugar beet tailings seem promising.

6.5 Conclusions

- The cumulative methane potential and VS reduction in the combined two-stage ABCR/AFR system for the biogasification of sugar beet tailings were found to be 304 L kg VS^{-1} and $88 \pm 2\%$.
- On average, the overall methane yield contributions of the ABCR and AFR during two-stage operation were $116 \text{ L CH}_4 \text{ kg VS}^{-1}$ (38%) and $188 \text{ L CH}_4 \text{ kg VS}^{-1}$ (62%), respectively.
- The recovery of a single-stage inhibited reactor was fulfilled by sequencing with the AFR at an HRT of 7.5 days; cumulative methane yield and VS reduction for 5 kg of un-washed sugar beet tailings were 319 L kg VS^{-1} and 93%
- Expulsion of a pre-treatment step to remove readily soluble fraction of tailings was justified by the AFR's ability to process organic loading rates between 2.5 and $5.3 \text{ g COD L}^{-1} \text{ d}^{-1}$. This resulted in reducing the total process time by 0.5 – 1 days
- The two-stage system concept of using sequencing between a solid and liquid reactor was shown decrease the duration to produce 95% of the methane yield less than 10 days consistently.

Two-phase



Two-stage

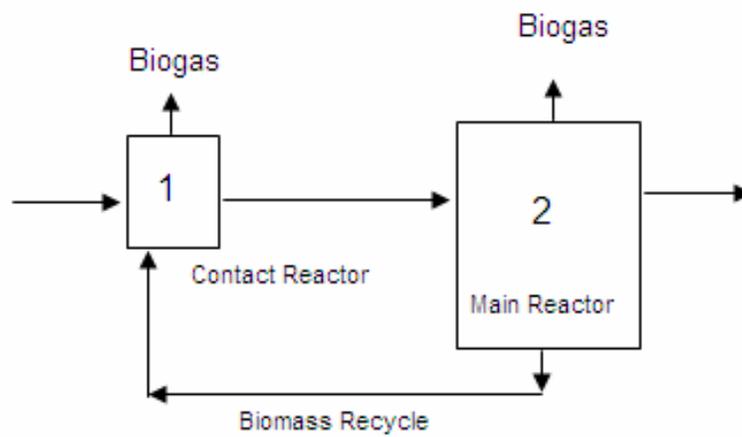


Figure 6-1. Two-phase/stage block flow diagrams

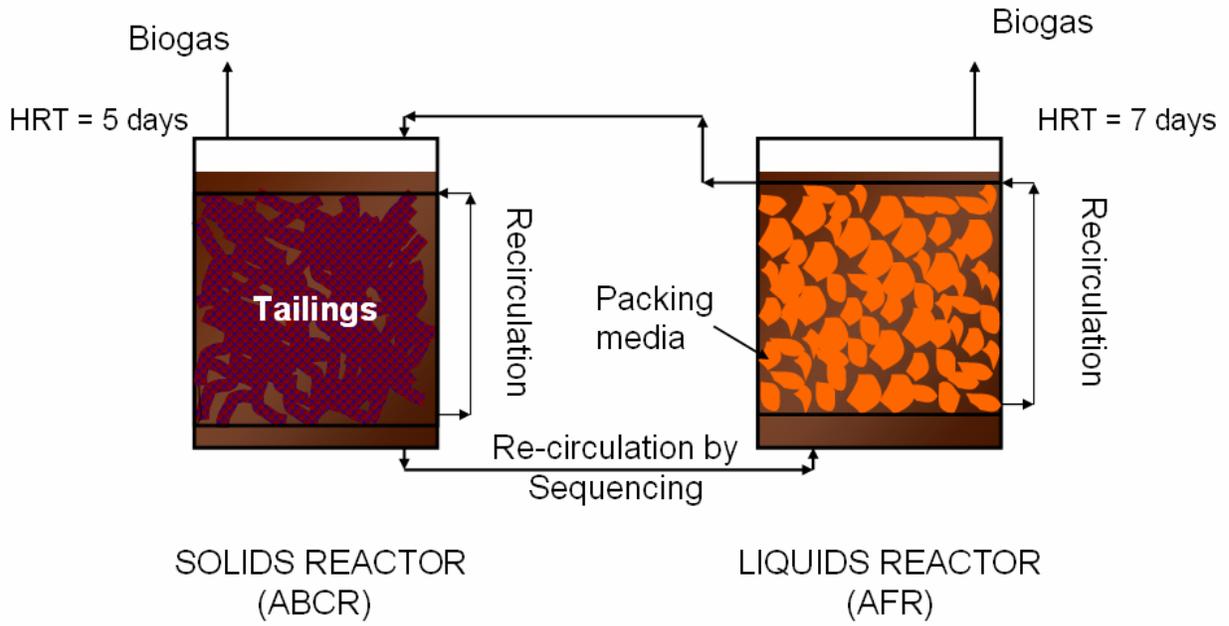


Figure 6-2. Two-stage system for the biogasification of sugar beet tailings

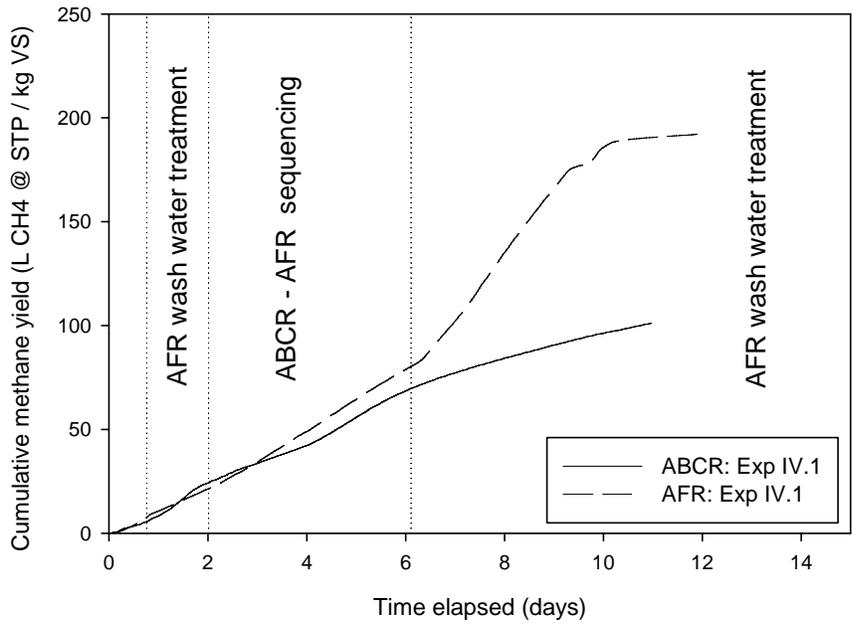


Figure 6-3. Cumulative methane yields from ABCR and AFR in Experiment IV.1

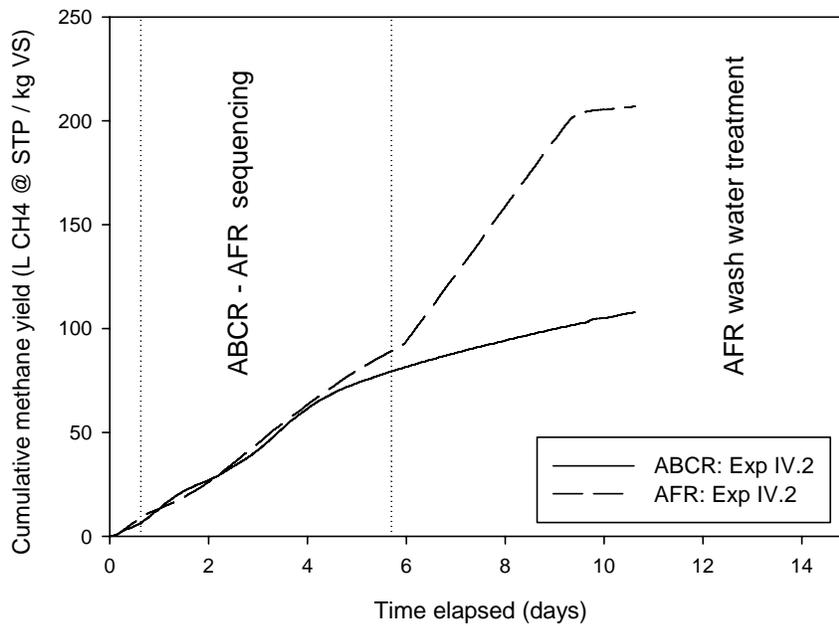


Figure 6-4. Cumulative methane yields from ABCR and AFR in Experiment IV.2

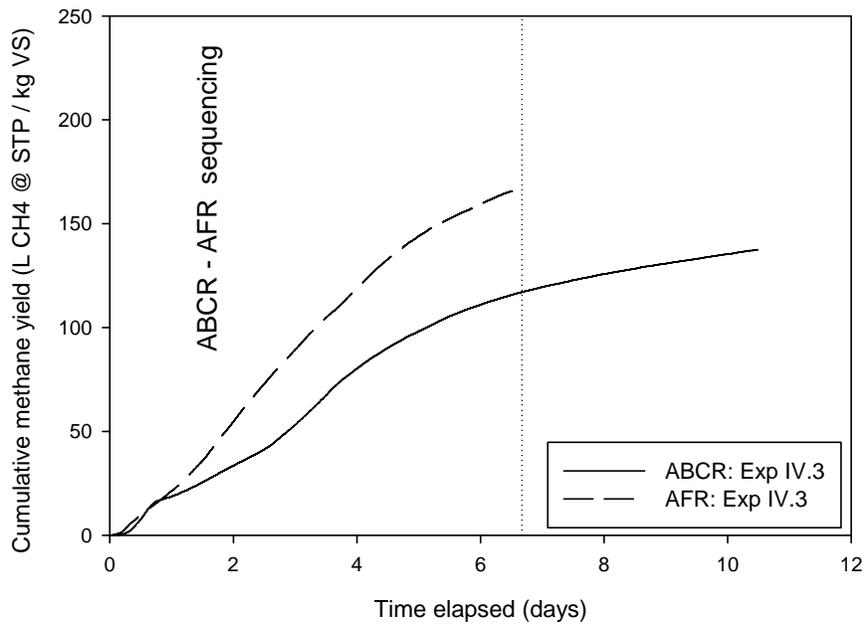


Figure 6-5. Cumulative methane yields from ABCR and AFR in Experiment IV.3

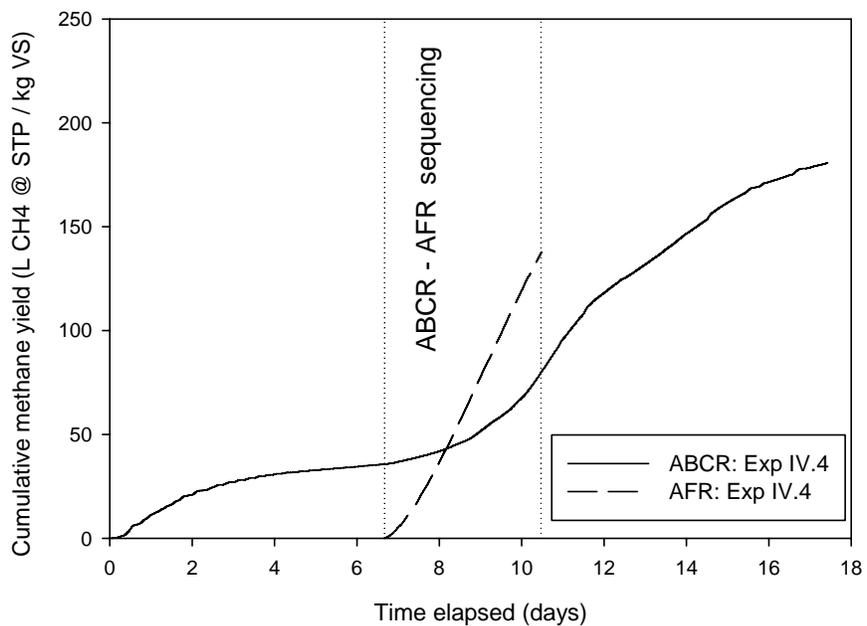


Figure 6-6. Cumulative methane yields from ABCR and AFR in Experiment IV.4

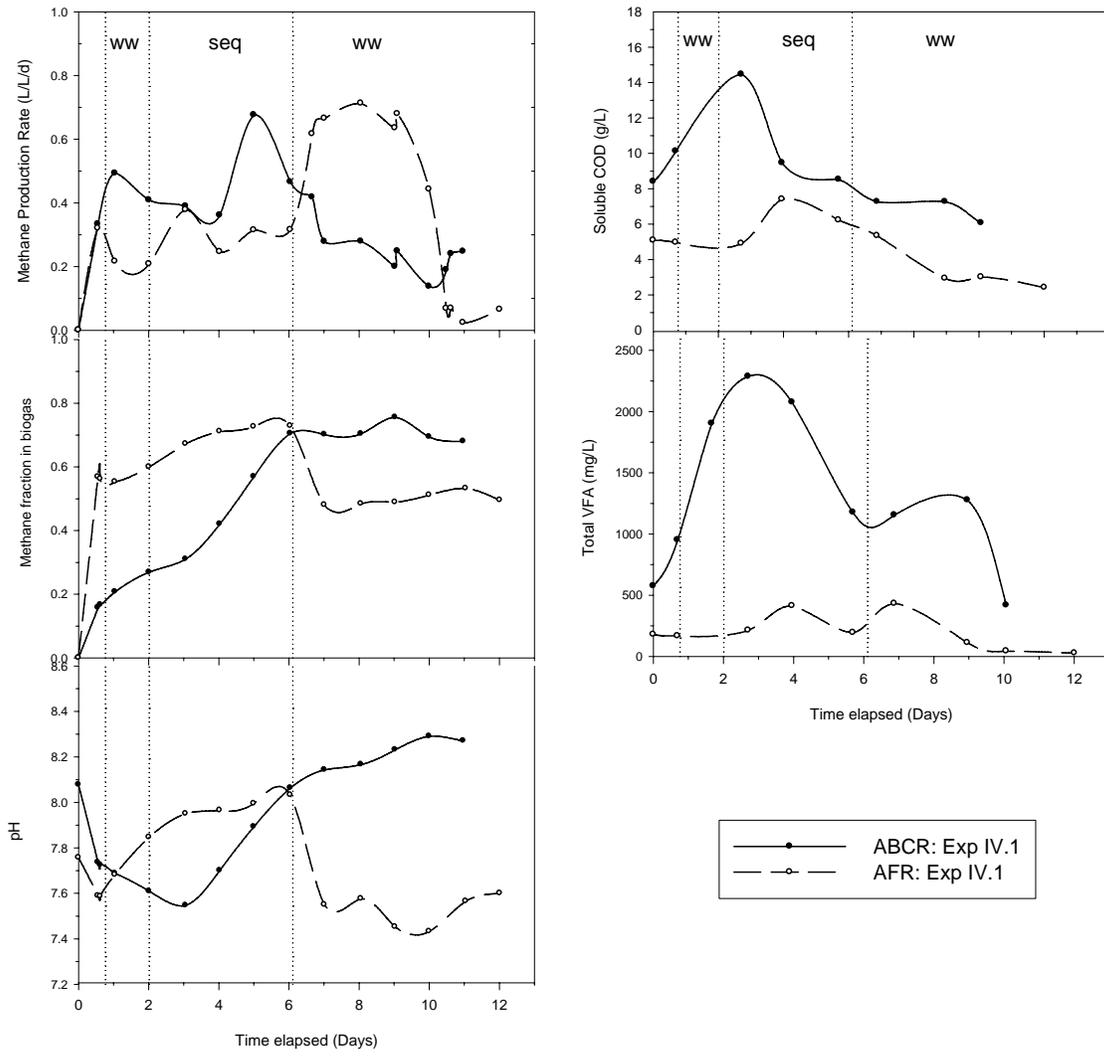


Figure 6-7. Biogasification parameter profiles from ABCR and AFR in Experiment IV.1

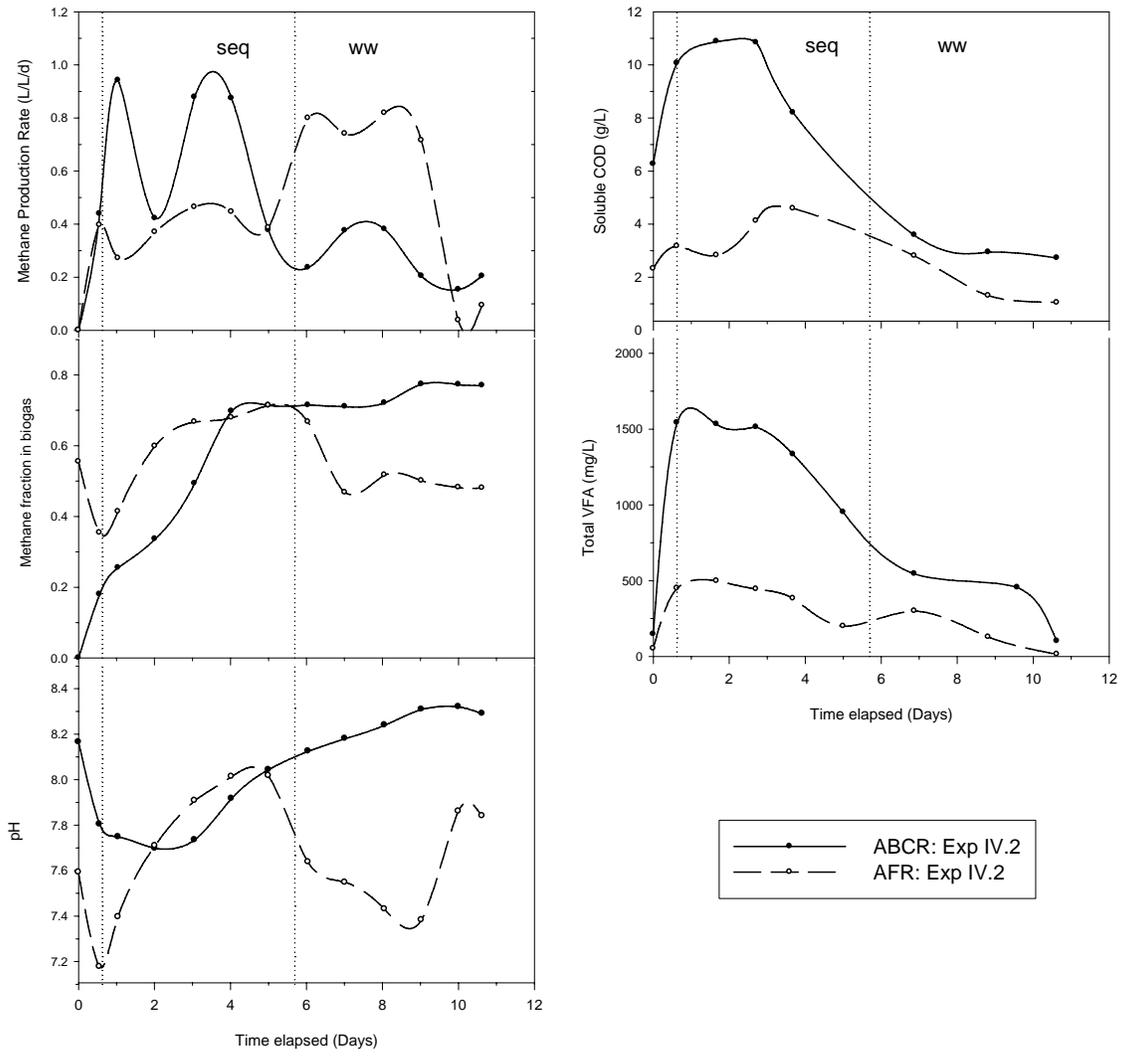


Figure 6-8. Biogasification parameter profiles from ABCR and AFR in Experiment IV.2

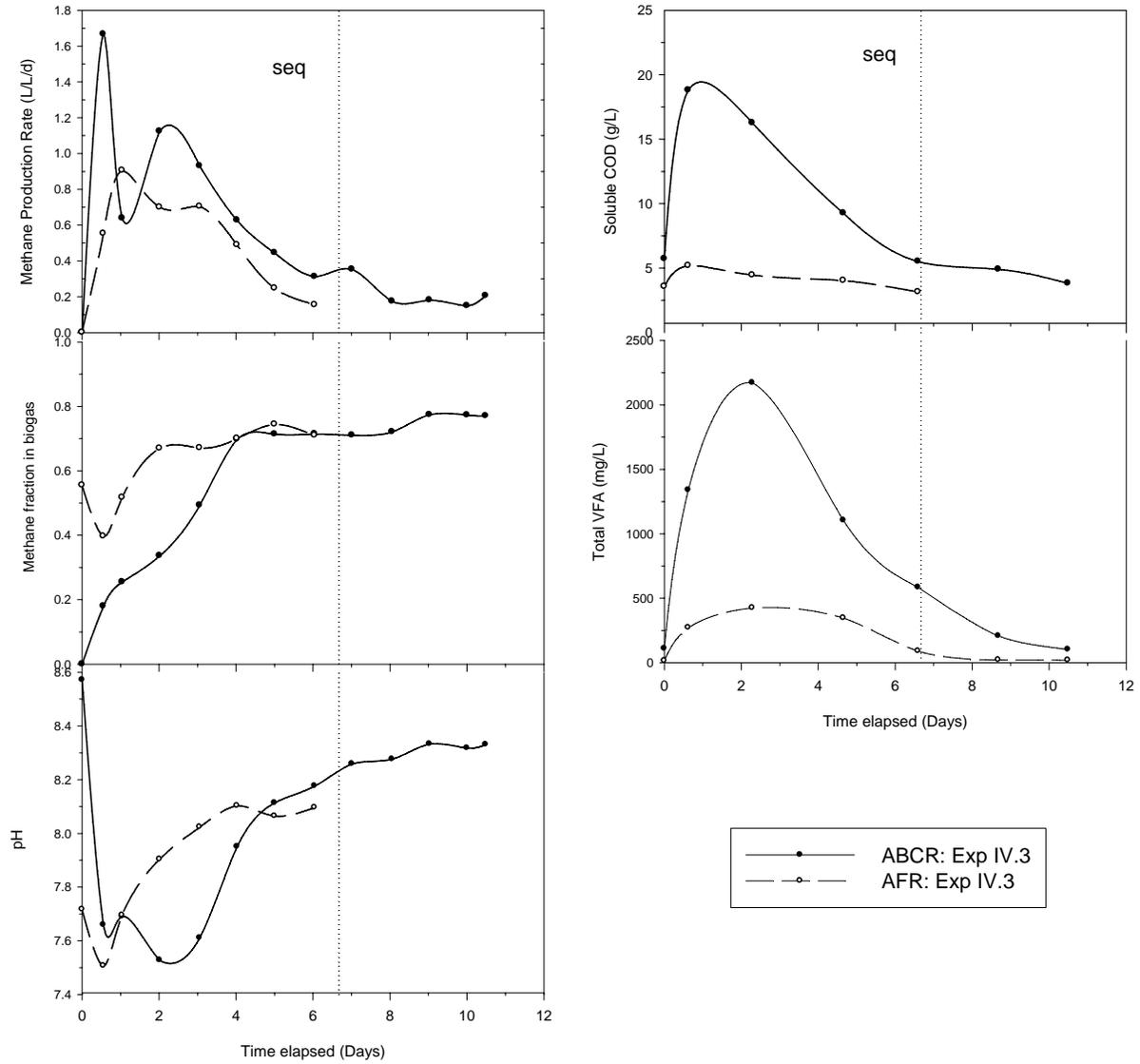


Figure 6-9. Biogasification parameter profiles from ABCR and AFR in Experiment IV.3

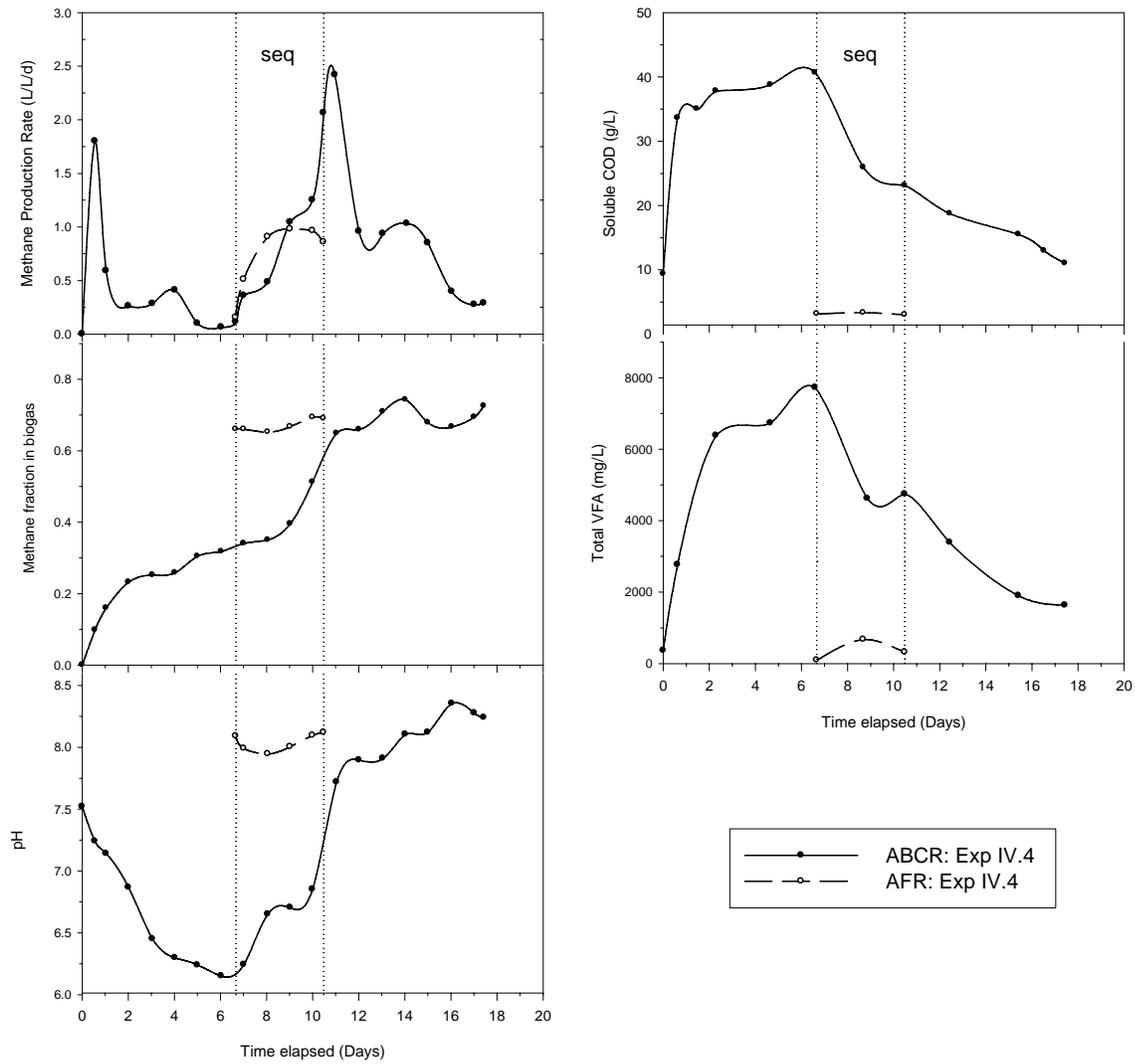


Figure 6-10. Biogasification parameter profiles from ABCR and AFR in Experiment IV.4

Table 6-1. Loading and unloading data for Experiments IV.1 to IV.4

Experiments	IV.1 to IV.3	IV.4	
Loading	Wet tailings weight (kg)	3	5
	Total solids (kg)	0.48 ± 0.02	0.77
	Volatile solids (kg)	0.43 ± 0.02	0.68
	Inoculum added (L)	12	10
	Packing density (kg wet/m ³)	470	490
	Packing density (kg dry/m ³)	97 ± 11	75
	Total solids in reactor (%)	3.3 ± 0.1	5.3
Unloading	Wet residue weight (kg)	0.93 ± 0.2	2.25
	Total solids (kg)	0.050 ± 0.01	0.088
	Volatile solids (kg)	0.05 ± 0.05	0.047
	Total solids reduction (%)	82 ± 2	86
	Volatile solids reduction (%)	88 ± 2	93

Table 6-2. Summary of operation times for two-stage experiments

Experiment	Readily-solubilized fraction (g COD/g VS)	Wash time (Days)	Sequencing duration (Days)	Biogasification duration in ABCR (Days)	Biogasification duration in AFR (Days)	Sequencing HRT in ABCR (Days)	Sequencing HRT in AFR (Days)	Total process time (Days)
Two-stage								
IV.1	0.51	0.5	4.1	10.9	12.0	5	7.5	12.5
IV.2	0.50	0.5	5.1	10.6	10.6	5	7.5	11.1
IV.3	-		6.7	10.5	6.7	5	7.5	10.4
^a Single/Two-stage								
IV.4	-	-	3.8	17.4	4.1	5	7.5	17.4

^a Refers to recovery operation of a single-stage unit sequenced with the AFR

Table 6-3. Summary of cumulative methane yield distribution in two-stage biogasification

Experiment	ABCR Cumulative Methane Yield (L CH ₄ kg VS ⁻¹)	AFR Cumulative Methane Yield (L CH ₄ kg VS ⁻¹)	Total Cumulative Methane Yield (L CH ₄ kg VS ⁻¹)	Duration to produce 95% methane yield potential (Days)
<i>Two-stage</i>				
IV.1	101	192	293	9.8
IV.2	108	207	315	9.2
IV.3	138	165	303	7.4
<i>Single/Two-stage</i>				
IV.4	181	138	319	15.2

CHAPTER 7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The conclusions to this research work were all based on the findings from experimental studies on the biogasification of sugar beet tailings. The objective to carry out bench-scale studies in an effort to identify critical factors and performance measures during batch operation was fulfilled. Design of experiments established that feedstock characteristics and mode of operation were critical factors that influenced the rate and extent of biogasification. The implications of improved biogasification will ultimately lead to the development of a scalable process for application to the sugar beet industry.

At the start of this research, sugar beet tailings biogasification was implemented only on mesophilic SEBAC-2 and rates of methane generation were poorer to that of other organic residues; cumulative methane yield and daily methane production from mesophilic SEBAC-2 did not meet expectations. To progress previous accomplishments, this research tailored design and operation in flooded mode to the unique requirements of sugar beet tailings in thermophilic conditions.

Table 7.1 and Figure 7.1 depict a final summary of data from different modes of biogasification and the corresponding cumulative methane yield plots, respectively. Each mode was represented by the best experimental trial obtained on bench-scale. Single-stage experiments that implemented in-situ solubilization were subjected to separate wash water treatment (SWWT) in an AFR; a lag was added to justify the time for washing. Two additional experiments not mentioned in this thesis that were conducted included investigating the effect of maceration and long-term storage of inoculum on the start-up and biogasification of sugar beet tailings. Such studies provided valuable insight as to potential benefits of additional pre-

treatment (maceration) or inoculum viability after long storage time (6 months). Appendices B and C show the biogasification performance profiles of the aforementioned additional studies, respectively.

Critical findings on the characteristics of sugar beet tailings and performance of high-solids, batch, thermophilic biogasification experiments were:

- Performance and efficiency of single-stage biogasification was limited by organic loading.
- Sugar beet tailings contain a significant fraction of readily solubilizable organic matter (~ 0.54 g COD/g VS). Wash water generated from leaching of this organic matter yielded 0.25 L CH₄ @ STP g COD⁻¹ in a lab-scale wastewater digester (AFR) and was estimated to contribute 47% of the total methane available from tailings.
- Compaction of sugar beet tailings and exclusion of liquid from the waste bed retarded the biogasification rate during single-stage operation.
- The addition of a bulking agent overcame compaction, decreased liquid exclusion from the waste bed and tripled the biogasification kinetics.
- Particle-size reduction by maceration did not significantly improve the reactor performance or efficiency
- Robust operation was attained with the re-use of inoculum without any addition of nutrients or supplements. Storage of inoculum at room temperature for up to six months did not significantly affect the biogasification activity
- Two-stage biogasification using a wastewater reactor was shown to improve breakdown of VS matter locked-up in liquid phase; cumulative methane yield was increased by 17% as compared to single-stage achievements and residual volatile organic acids were low.
- Biogasification of tailings in both single and two-stage systems showed a volume reduction between 70 to 90%.

Based on the findings presented, two different design options can be considered for scale-up applications on the biogasification of sugar beet tailings:

1. Single-stage biogasification process which would take up both the duties of biogasifying sugar beet tailings and processing any wash water generated from pre-treatment. System analysis would have to evaluate whether the improved kinetics versus efficient volume usage would justify adding a bulking agent

2. Two-stage biogasification process consisting of a solids reactor and a high-rate wastewater reactor. Sequencing between the two vessels would bypass pre-treatment altogether and encourage increased loading rates. This process established a 3-fold increase in the rate of conversion; solids retention time was improved from 20 days to 7.4 days.

The accelerated degradation observed with the two-stage system presents significant implications for scale-up system for the sugar beet industry. Tripling the kinetics of degradation would translate to almost a 2/3 reduction in volume needed for the solids vessel. Therefore, economic and technological incentives of implementing mesophilic SEBAC-2 addressed in Teixeira et al, 2005 are speculated to have improved by incorporation a modified thermophilic two-stage system tailored to the needs of sugar beet tailings. Investigations into economic improvements however are beyond the scope of this thesis.

7.2 Future Work

This research work was the jump-off point in establishing a basis for understanding biogasification of sugar beet tailings. Considerable efforts went into fabrication and design of an experiment station to carry out batch experiments for operating well-controlled experiments.

The studies presented here open some areas of expansion for this research. The following topics of interest can be addressed:

- Recognizing that further improvements in kinetics are possible, more iterations of process and design changes can be investigated. For example, bulked and sequenced experiments could improve the rate of degradation even further.
- Investigating how continuous versus batch feed operation affects the throughput and biogasification rate of sugar beet tailings. Continuous feeding could decrease the required solids reactor volume by 50% and improve solids handling issues faced in batch systems
- Designing gas-liquid/solid separation system inside the waste bed of a reactor as to circumvent biogas entrapment during the start-up of biogasification
- Formulate dynamic modeling and simulation on sugar beet tailings biogasification. Modeling single and two-stage system for sugar beet tailings as a validation process for experiments conducted here.

Mode	Units	Thermophilic					Mesophilic
		1	2	3	4	5	6
Temperature	°C	55	55	55	55	55	35
Initial Feedstock Weight	(kg)	3	3	3	3	3	2.4
Packing Density (wet)	(kg/m ³)	465	400	250	250	427	407
TS Reduction	%	74	79	82	-	81	-
VS Reducton	%	78	81	88	-	87	-
Volume Reduction	%	70 - 80	70 - 80	70 - 80	90	85 - 90	-
Methane Yield	L CH ₄ @ STP kg VS ⁻¹	170	259	285	267	305	47
Final Biogas Methane	vol %	76	70	63	76	65	59
Maximum CH ₄ Production Rate	L L ⁻¹ d ⁻¹	1.8	0.5	1.1	1.2	1.3	0.15
Maximum CH ₄ Production Rate	L CH ₄ kg VS ⁻¹ d ⁻¹	7.4	1.9	4.1	2.2	6.4	2.1
Final VFA in reactor liquid	mg/L	2400	220	195	1386	101	4000
Minimum pH	-	7.5	7.4	6.9	6.2	7.5	6.2
Final pH	-	8.1	8.2	7.3	7.8	8.3	6.8
Duration to achieve 95% of Methane Potential	Days	10 - 20	14.6	7.9	15	7.4	> 30

Figure 7-1. Summary of different modes investigated in biogasifying sugar beet tailings. Mode 1: Single-stage (no washing; no bulking; no maceration). Mode 2: Single-stage with SWWT (washing; no bulking; no maceration). Mode 3: Single-stage with SWWT (washing; bulking; no maceration). Mode 4: Single-stage with SWWT (washing; bulking; maceration). Mode 5: Two-stage (no washing; no bulking; no maceration). Mode 6: Mesophilic SEBAC-2 (no washing; no bulking, no maceration)

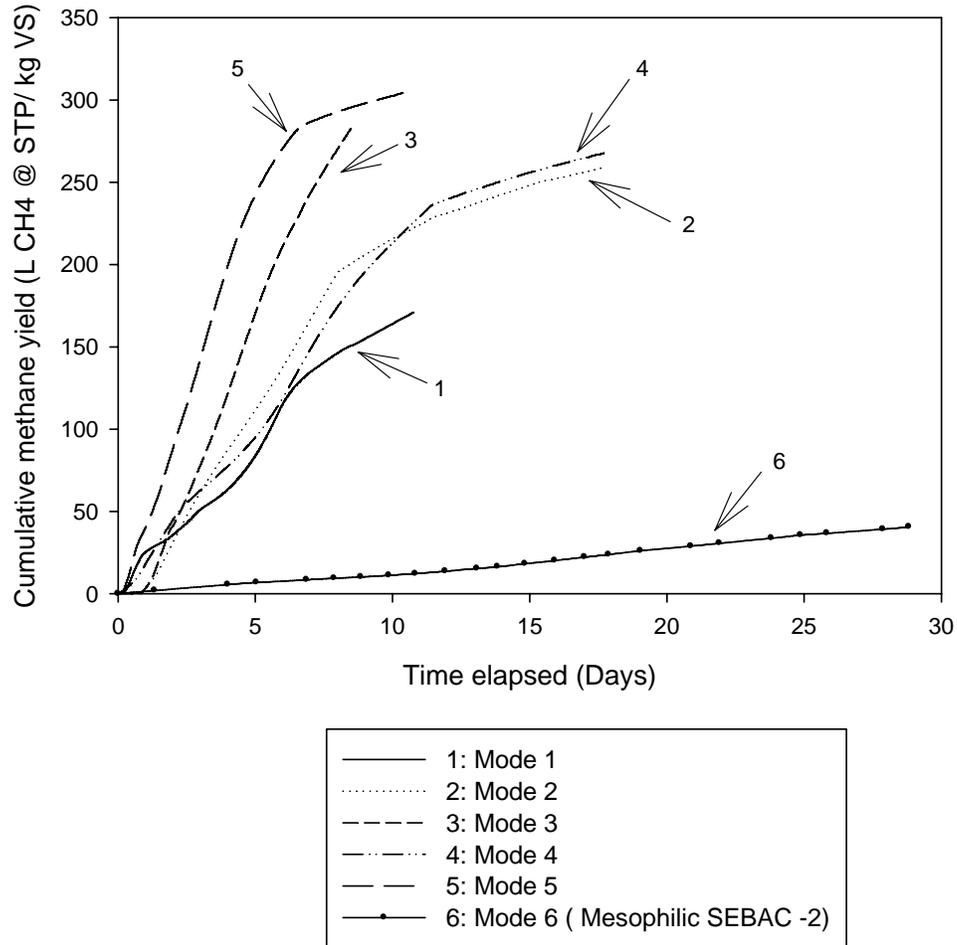


Figure 7-2. Performance comparison for mode of operation on the biogasification of sugar beet tailings. Mode 1: Single-stage (no washing; no bulking; no maceration). Mode 2: Single-stage with SWWT (washing; no bulking; no maceration). Mode 3: Single-stage with SWWT (washing; bulking; no maceration). Mode 4: Single-stage with SWWT (washing; bulking; maceration). Mode 5: Two-stage (no washing; no bulking; no maceration). Mode 6: Mesophilic SEBAC-2 (no washing; no bulking, no maceration)

APPENDIX A
PROGRAM CODE FOR CR10X

```

;{CR10X}
;ABCR 2 + AFR Progam
;Version 1
;Date: February 16, 2007
;Programmer: Ioannis M. Polematidis
;Comments:
;    1) Temperature Monitoring (Type-T Thermocouple Probe)
;    2) pH Monitoring (Campbell Sci CSIM11 pH Sensor)
;    3) Heating System (Thermolyne Briskheat Heating Tape)
;    4) Biogas Rate
;-----
;Flag/Port/Channel Usage

;Port 1:          Used to Control Heating Coil in AFR
;Port 2:          Used to Control Heation Coil in ABCR_2
;Pulse Port 1:    Used to Monitor Gas Meter 3 (AFR)
;Pulse Port 2:    Used to Montior Gas Meter 2 (ABCR_2)
;Diff Channel 1:  Used to Monitor Temperature in AFR
;Diff Channel 2:  Used to Monitor Temperature in ABCR_2
;Diff Channel 3:  Used to Monitor pH Sensor in AFR
;Diff Channel 4:  Used to Monitor pH Sensor in ABCR_2
;Flags:          Set Output Flags High => Final Monitored Values are Calculated Externally
;-----
;=====
;*****PROGRAM START*****
;=====
;-----

;{CR10X}

;-----
; Execution Intervals, Sampling and Flag Status
;-----

1: Batt Voltage (P10)
1: 1    Loc [ Voltage ]

2: Internal Temperature (P17)
1: 2    Loc [ CR10XTemp ]

;-----
; Fail-Safe

```

;-----

3: If (X<=>F) (P89)

1: 1 X Loc [Voltage]

2: 4 <

3: 11.5 F

4: 51 Set Port 1 Low

4: If (X<=>F) (P89)

1: 1 X Loc [Voltage]

2: 4 <

3: 11.5 F

4: 51 Set Port 1 Low

5: If (X<=>F) (P89)

1: 1 X Loc [Voltage]

2: 4 <

3: 11.5 F

4: 57 Set Port 7 Low

6: If (X<=>F) (P89)

1: 1 X Loc [Voltage]

2: 4 <

3: 11.5 F

4: 57 Set Port 7 Low

;-----

;Temperature Control

;-----

7: Thermocouple Temp (DIFF) (P14)

1: 2 Repts

2: 1 2.5 mV Slow Range

3: 1 DIFF Channel

4: 1 Type T (Copper-Constantan)

5: 2 Ref Temp (Deg. C) Loc [CR10XTemp]

6: 3 Loc [T_1]

7: 1.0 Mult
8: 0.0 Offset

8: If (X<=>F) (P89)

1: 3 X Loc [T_1]
2: 3 >=
3: 56 F
4: 51 Set Port 1 Low

9: If (X<=>F) (P89)

1: 3 X Loc [T_1]
2: 4 <
3: 54 F
4: 41 Set Port 1 High

10: If (X<=>F) (P89)

1: 4 X Loc [T_2]
2: 4 <
3: 54 F
4: 42 Set Port 2 High

11: If (X<=>F) (P89)

1: 4 X Loc [T_2]
2: 3 >=
3: 56 F
4: 52 Set Port 2 Low

; Feeding Schedule (AFR)

12: Thermocouple Temp (DIFF) (P14)

1: 1 Repts
2: 1 2.5 mV Slow Range
3: 5 DIFF Channel
4: 1 Type T (Copper-Constantan)
5: 2 Ref Temp (Deg. C) Loc [CR10XTemp]
6: 20 Loc [Tfeed]
7: 1.0 Mult
8: 0.0 Offset

13: If time is (P92)

1: 59 Minutes (Seconds --) into a
2: 60 Interval (same units as above)
3: 47 Set Port 7 High

14: If time is (P92)

1: 0 Minutes (Seconds --) into a
2: 60 Interval (same units as above)
3: 57 Set Port 7 Low

; pH Monitor Protocol (AFR + ABCR_2)

$$\text{pHMult}_1 = -1/(((T_1+273)/298)*58.7)$$

$$\text{pHMult}_2 = -1/(((T_2 + 273)/298)*58.7)$$

15: Volt (Diff) (P2)

1: 2 Repts
2: 5 2500 mV Slow Range
3: 3 DIFF Channel
4: 5 Loc [pH_1]
5: 1.0 Mult
6: 0.0 Offset

$$\text{pH}_1 = \text{pH}_1 * \text{pHMult}_1$$

$$\text{pH}_2 = \text{pH}_2 * \text{pHMult}_2$$

16: Z=X+F (P34)

1: 5 X Loc [pH_1]
2: 7 F
3: 5 Z Loc [pH_1]

17: Z=X+F (P34)

1: 6 X Loc [pH_2]
2: 7 F
3: 6 Z Loc [pH_2]

; Gas Meter Monitoring

18: Pulse (P3)
1: 2 Reps
2: 1 Pulse Channel 1
3: 2 Switch Closure, All Counts
4: 7 Loc [Click_1]
5: 1.0 Mult
6: 0.0 Offset

19: If time is (P92)
1: 0 Minutes (Seconds --) into a
2: 1 Interval (same units as above)
3: 10 Set Output Flag High (Flag 0)

20: Set Active Storage Area (P80)
1: 3 Input Storage Area
2: 9 Loc [min_tot]

21: Totalize (P72)
1: 2 Reps
2: 7 Loc [Click_1]

$$Q_1 = (\text{Click}_1 * 0.055) / 1$$

$$Q_2 = (\text{Click}_2 * 0.055) / 1$$

22: Set Active Storage Area (P80)
1: 1 Final Storage Area 1
2: 1 Array ID

23: Sample (P70)
1: 1 Reps
2: 9 Loc [min_tot]

24: Sample (P70)
1: 1 Reps
2: 10 Loc [Q_1]

25: Sample (P70)
1: 1 Reps
2: 11 Loc [Q_2]

26: Sample (P70)

1: 11 Reps

2: 1 Loc [Voltage]

; Execution Intervals, Sampling and Flag Status

27: Do (P86)

1: 10 Set Output Flag High (Flag 0)

28: Real Time (P77)

1: 220 Day,Hour/Minute (midnight = 2400)

29: Sample (P70)

1: 13 Reps

2: 1 Loc [Voltage]

30: Sample (P70)

1: 2 Reps

2: 20 Loc [Tfeed]

End Program

APPENDIX B
THE EFFECT OF MACERATION ON BIOGASIFICATION OF SUGAR BEET TAILINGS

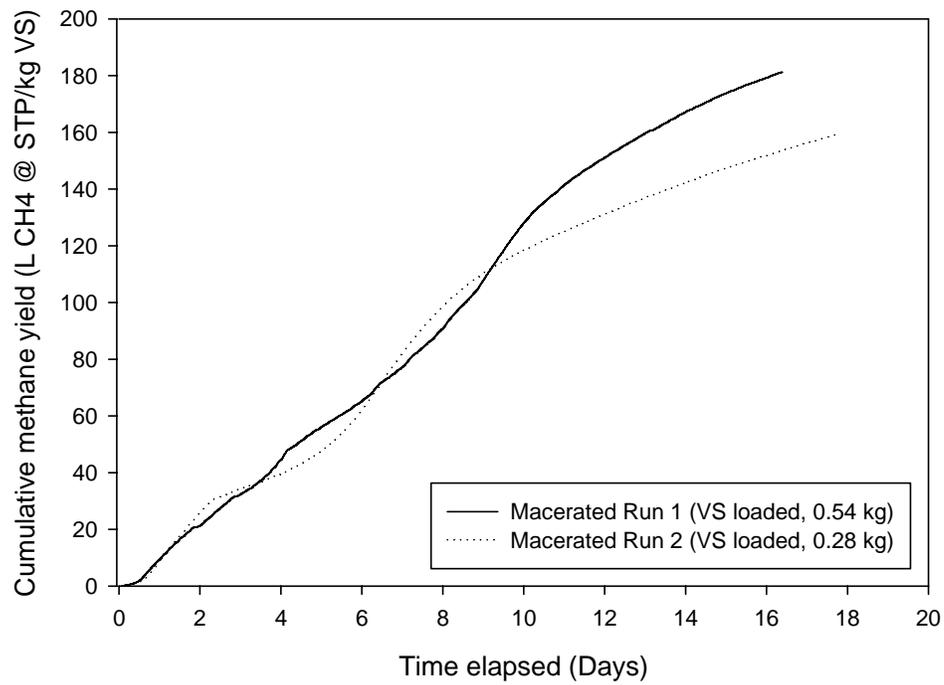


Figure B-1. Cumulative methane yield of macerated sugar beet tailings

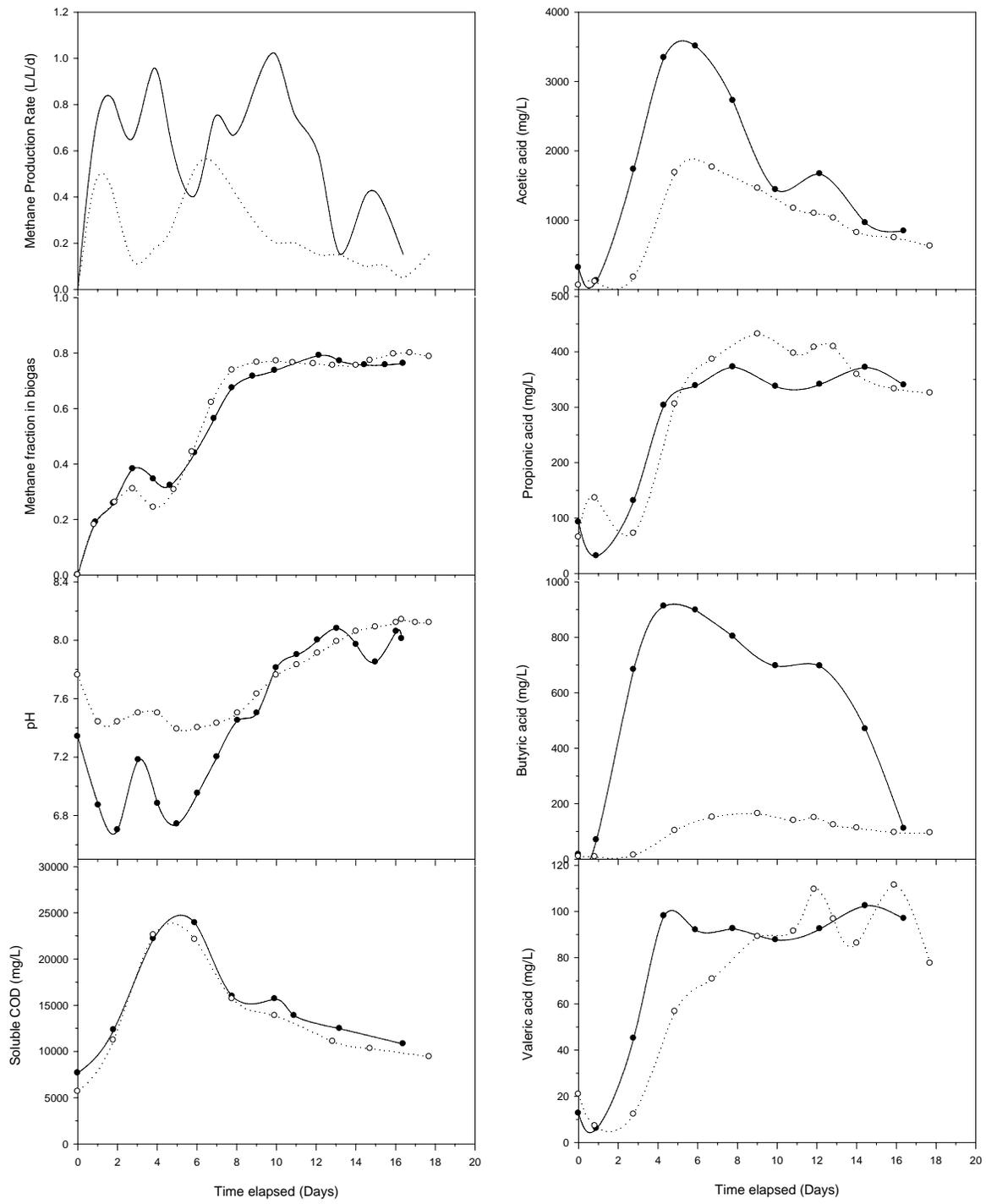


Figure B-2. Biogasification parameters for macerated sugar beet tailings

APPENDIX C
ACTIVITY TEST ON DORMANT INOCULUM

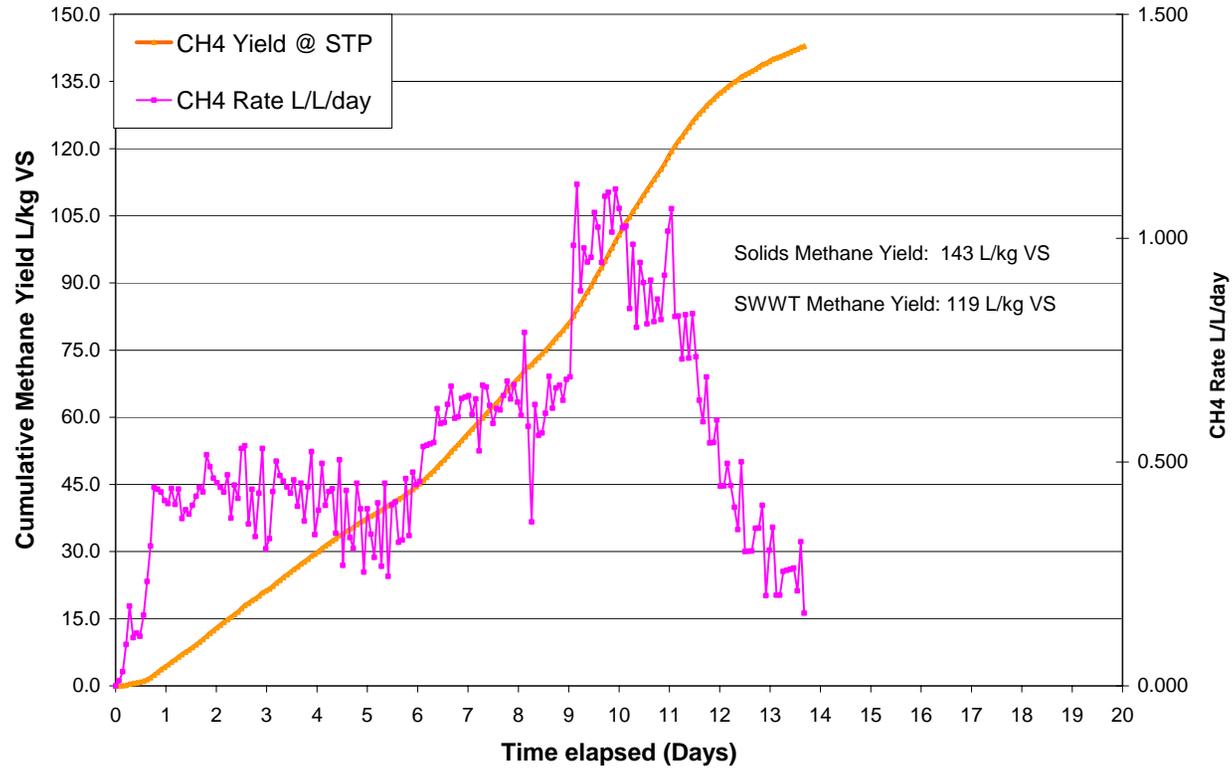


Figure C-1. Inoculum activity test run

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BIOGRAPHICAL SKETCH

Ioannis M. Polematidis was born (on December 17, 1981) in Athens, Greece and immigrated to the United States with his mother in 1990. He received his Bachelor of Science degree in chemical engineering (graduating magna cum laude) from the University of Florida in April 2005. Thereafter, he worked as a research assistant for 2 months in the Bioprocesses lab aiding Dr. Pullammanappallil on an on-going biofuels project, before enrolling in the graduate school at the University of Florida. He obtained a Master of Science degree in agricultural and biological engineering in August 2007. After completing his graduate studies, he plans to work in the field of environmental engineering that will use the technical skills acquired during his studies and experiences as a student.