METHANE PRODUCTION BY A PACKED-BED ANAEROBIC DIGESTER FED DAIRY BARN FLUSH WATER

A Thesis

Presented to

the Faculty of California Polytechnic State University,

San Luis Obispo

In partial fulfillment

of the Requirements for the degree

Master of Science in Civil and Environmental Engineering

by

Sean Richard Thomson

December 2014

COMMITTEE MEMBERSHIP

TITLE:	Methane Production by a Packed-Bed Anaerobic Digester Fed Dairy Barn Flush Water
AUTHOR:	Sean Richard Thomson
DATE SUBMITTED:	December 2014
COMMITTEE CHAIR:	Dr. Tryg Lundquist, Associate Professor Civil & Environmental Engineering
COMMITTEE MEMBER:	Dr. Yarrow Nelson, Professor Civil and Environmental Engineering
COMMITTEE MEMBER:	Dr. Sean Hurley, Professor Agribusiness Department

ABSTRACT

Methane Production by a Packed-Bed Anaerobic Digester Fed Dairy Barn Flush Water

Sean Richard Thomson

Packed-bed digesters are an alternative to covered lagoon digesters for methane production and anaerobic treatment of dilute wastewaters such as dairy barn flush water. The physical media of packed-beds retain biofilms, often allowing increased treatment rates. Previous studies have evaluated several types of media for digestion of dilute wastewaters, but cost and media fouling have setback commercial development. A major operational cost has been effluent recirculation pumping.

In the present effort, a novel approach to anaerobic digestion of flush dairy water was developed at pilot-scale: broken walnut shells were used as a low-cost packed-bed medium and effluent recirculation was replaced by reciprocation mixing to decrease pumping costs and the risk of media clogging.

Three packed-bed digesters containing walnut shells as media were constructed at the on-campus dairy and studied for about six months. Over that time, several organic loading rates (OLRs), measured as both chemical oxygen demand (COD) and volatile solids (VS) were applied to the new packed-bed digesters to allow modeling of methane production. The influence of temperature on methane production was also investigated. Additionally, the study measured solids accumulation in the walnut shell packed-bed as well as the effectiveness and durability of walnut shells as packing media. Finally, a simple economic analysis was developed from the methane model to predict the financial feasibility of packed-bed digesters at flush water dairies under similar OLR conditions.

Three methane production models were developed from organic loading: saturation-type (following the form of the Monod equation), power and linear. The models were evaluated in terms of regression analysis and the linearity of experimental to predicted methane production. The best model was then chosen to develop the economic predictions. Economic predictions for packed-bed digesters were calculated as internal rate of return (IRR) using the methane models along with additional input variables. Comparisons of IRRs were made using electric retail rates of \$0.10 to \$0.20 per kilowatt-hour and capital cost subsidies from zero to 50%.

Sludge accumulation in the packed-bed was measured via change in porosity, and walnut shell durability was measured as the change in mass of representative walnut shells over the course of the study.

The linear-type model of methane production from volatile solids OLR best represented this data set. Digester temperature was not found to influence methane production in this study, likely due to the small daily average ambient temperature range experienced (14°C to 24°C) and the greater influence of organic loading. Porosity of the walnut shell packed-bed decreased from 0.70 at startup to 0.34±0.06 at the end of the six-month study, indicating considerable media fouling. Sludge accumulated in each digester from zero at startup to 281±46 liters at termination. Walnut shells in the packed-bed lost on average 31.4±6.3% mass during the study period which may be attributed to degradation of more readily bio-degradable cellulose and hemi-cellulose within the walnut shells.

Given the predicted methane production and media life, at present, the economic outlook for packed-bed digesters at commercial dairies is quite dependent on utility electrical rates, available subsidies and future improvements to packed-bed digester technology. The predicted IRRs ranged from below 0% (at 0% capital subsidy and $0.10/kWh) up to 25% (at 50% capital subsidy and $0.20/kWh) at large dairies (3000 milking cows). Increases in organic loading were not shown to necessarily increase IRR, particularly at OLRs above 10 g/L_{liquid}-d (as COD or VS). Ultimately, to better assess the value of packed-bed digesters for flush dairies, additional study is needed on topics such as sludge accumulation prevention, long-term walnut shell degradation, dairy barn flush water mixing, and more detailed economic analysis.

Keywords: Methane, anaerobic digestion, attached growth, fixed-film, packed-bed, organic loading, temperature, dairies, modeling, scale-up, economics, electricity, power.

ACKNOWLEDGMENTS

I would like to thank the following for their support of this research opportunity

Funding: USDA National Institute of Food and Agriculture

Dr. Tryg Lundquist, P.E., PhD.	Adviser
Dr. Yarrow Nelson, PhD.	Committee Member
Dr. Sean Hurley, PhD.	Committee Member

My Family –Thank you for your unwavering encouragement and support.

Neal Adler –You taught me the true meaning of teamwork and were always there to make the best of any situation, no matter how messy. I was lucky to have had a chance to work with you.

Cal Poly Dairy & Farm Operations:
Dr. Rich Silacci, Kevin Piper and Boomer Wadsworth – Thank you for supporting all the needs of this project at the dairy and answering many, many questions about dairy management.

David Wendt, Nutrinut Inc., Visalia, CA – Thank you for providing all the walnut shells for the packed-bed digesters. The research would not have been possible without your support.

To the following research staff and professors for their expertise and lab equipment:

Ruth Spierling	Matt Hutton, P.E.	Trevor Harding, PhD.
Ian Woertz, P.E.	Tracy Thatcher, PhD.	Xi Shen

To the following graduate students who shared the labs and offered helpful suggestions

Kyle Fooks	Matt Rodrigues	Ankita Kashyap
Seppi Henneman	James Starnes	Michael Lehrer
Jason Kane	Franco Trabucco, PhD.	Shasta Billings
Elliot Ripley	Louis Lefevbre	Michael Chang

To the following student assistants

Aaron Gao, Andrew Armstrong, Ashley Kachedorian, Cole Harrington, Gabriela Villanueva, Hasit Chetal, Hedieh Esfahani, James Fuchs, Janna Dolin, Jason Coontz, Jennifer Thompson, Jonathan Bellesbach, Jose Ascencio, Justin Kraetsch, Kaitlyn Beesley-Campos, Kevin Powell, Loratious Presley, Max Wallack, Michael Chang, Michael Goymerac, Nate Goekel, Nathaniel Olivas, Nick Lazarakis, Paul Peabody, Ruben Mendoza, Samuel Dennis, Sheila Magladry, Hernan Cortez, Marcos Sanchez, Stephen Neumayr, Alexandra Macedo, Marissa Liccese, Ryan Sinnott, Michelle Kolb

Finally, Kay Kibbe and Amy Sinclair for their administrative support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 INTRODUCTION

Methane (CH_4) gas is a by-product of the microbial degradation of carbonaceous wastes such as cow manure in anaerobic conditions (Toerien & Hattingh 1969; Narihiro & Sekiguchi 2007) where it may bex collected, treated and combusted to produce energy at California's dairies. In 2012, at least 1,563 dairies were operating in the state of California, with a milking cow population of 1.82 million plus calves and non-lactating or "dry" cows. In that year, 41.4 billion pounds (18.8 billion kilograms) of milk was produced at an approximate value of seven billion dollars, making milk the leading agricultural commodity in the state (California Milk Advisory Board 2013). Manure from these dairies is a potentially large source of methane fuel (Wise et al. 1979) however it must be dealt with in a manner which promotes the safety of the animals, protects public health and prevents environmental damage (Hart & Turner 1965; Wilkie 2003, Krich et al. 2005).

Of the 1,563 dairies operating in California, 87% were located in California's San Joaquin Valley (Fresno, Kern, Kings, Madera, Merced, San Joaquin, Stanislaus and Tulare Counties) with an average regional milking cow population per dairy of 1,510, not including calves (California Milk Advisory Board 2013). The average milking cow and heifer weighing 625 kg and 441 kg respectively excrete up to 81.4 kg and 24.5 kg of manure daily (NRCS USDA 2008). On average, lactating cows at and heifers represent 56% and 17% of the cow population at California dairies (Spierling et al. 2009). With that population demographic, the above mentioned excretion rates and statewide population of lactating cows and heifers, the annual manure from California dairies is at least 33 million tons. Calves and dry cows likely contribute many more millions of tons annually. Manure left to decay may be a substantial source of uncontrolled and uncontained methane as a greenhouse gas (GHG) (NRCS USDA 2008). Methane contributes about 21 times more global warming potential than CO_2, making it a serious climate change concern (IPCC 2007). In 2006, dairies in California's San Joaquin Valley were estimated to produce 39.4 million metric tons of carbon dioxide equivalent (CO_2e) greenhouse gases annually, which included methane (Mitloehner 2006). Conversely, 14.6 billion cubic feet (413.7 million m^3) of methane are produced each year from California's dairies (Krich et al. 2005), which corresponds to about 277,000 metric tons of CH_4 annually at normal temperature and pressure (20°C and 1 atmosphere). Thus, the capture and utilization of methane derived from dairy cow manure may provide power for the region as well as economic benefits and savings to dairy farmers (Bryant 2006; Dusault 2007). Additional environmental benefits of anaerobic digestion at dairies includes a reduction of odors and wastewater treatment (Wilkie 2003; Krich et al. 2005)

Many dairies in California operate a recirculating flush system to remove manure from barns, producing flushed dairy manure water (flush water) which increases the overall volume of waste produced by dairies (Powers et al. 1997). In California, flush water is typically contained in multi-acre anaerobic "lagoons" where solids settle and supernatant water is re-circulated back to the barns to flush more manure (Martin 2008). Anaerobic lagoons are major sources of methane and carbon dioxide (CO_2) GHGs (Krich et al. 2005; Lory et al. 2010) as well as odors (Wilkie 2003).

Anaerobic lagoons may be covered to capture naturally occurring methane produced from the breakdown of manure and flush water. These lagoons are covered by an impermeable plastic membrane and are typically several acres in size with typical hydraulic retention times (HRT) around 40 days (Williams & Gould-Wells 2003; Krich et al. 2005). Large tanks have also been used as a vessel for anaerobic digestion of flush dairy manure however these are quite expensive compared to covered lagoons. Land costs and/or availability of property may influence the decision as to install a covered lagoon or tank digester at dairies (Spierling et al. 2009).

Another method of anaerobic digestion, attached-growth is used to treat diluted, low-strength substrate (Wilkie 2005). Attached-growth digesters contain media which provides ample surface area to host microbial communities, thus reducing the HRT as low as three days. As the microbial reactions are contained within the media, attached growth digesters are much less susceptible to washout. The design also allows for smaller vessel sizes, reducing capital costs (Wilkie 2003; Zaher et al. 2008). This paper focuses on the establishment of an attached-growth, packed-bed digester using walnut shells (*Juglans regia)* as the support media for microbial growth. Walnut shells are another abundant waste product of the agriculturally concentrated San Joaquin Valley (National Agricultural Statistics Service, USDA 2012) and also contain a high lignin concentration which is slow to degrade (Bugg et al. 2011).

An overall understanding of the pilot scale digesters was desired to better assess the relationship between influent flush dairy water and methane production in a novel, packed-bed and reciprocated mixing environment. Mathematical modeling between independent variables of organic loading rates (OLR) and temperature were plotted against the dependent variable, methane production in units of methane volume per digester liquid volume (L_{liquid}) per day (L CH_4/L_{liquid}-d).

The main purpose of the mathematical model was to understand the quantity of methane which could be produced from influent flush water by the walnut shell packed-bed digesters. Thus, finding a relationship between methane output and organic loading is crucial for both environmental quality improvements at dairies as well as for providing additional revenue or energy savings for dairy farmers.

The primary distinction between the models introduced in this paper and other anaerobic digestion models is the implementation of attached-growth media compared to suspended culture models such as a covered lagoon or continuously stirred tank reactors (CSTRs). There is limited research on attached growth digesters at dairies in general (Liao & Lo 1985; Wilkie et al. 2004; Umaña et al. 2008; Zaher et al. 2008) and the kinetic modeling of these types of digesters is even less understood (Yu et al. 1998). This study attempted to provide a model for methane production from a digester fed flush dairy manure water substrate with a walnut shell packed-bed.

California has been on the frontlines of United States climate action legislation in the past decades and anaerobic digestion has played an important but tenuous role. To reduce GHG emissions, California has implemented many measures. In 2001, California Senate Bill 5X (SB5X) was introduced to provide $15 million in funding to qualifying dairies who wished to install an anaerobic digester and produce electricity (Austin 2013). Biogas power generation, as a result of SB5X however was subject to air emission controls, in particular the limitation of nitrogen oxides (NO_x), which may form ozone, a respiratory health hazard (CARB 2008). A regulatory limit for NO_x of 9-11 ppm was set which has been difficult for many dairies generating biogas power to achieve (Austin 2013). Digesters have also been spotlighted as a source of renewable energy in

California's Assembly Bill 32 (AB32), The Global Warming Solutions Act which aims to reduce GHG emissions to 1990 levels by 2020 (CARB 2006). Additionally, California Senate Bill X1-2 (SBX1-2), implemented in 2011 requires 33% of all electricity generated in California to be sourced from renewable energy or carbon credits purchased by utilities. Methane produced from anaerobic digesters is considered a renewable energy source under that bill (Nahai et al. 2011).

State requirements for continued emissions reduction and increased production of sustainable energy will likely keep anaerobic digestion in focus as a promising technology for use at dairies into the future. Despite the demands for renewable energy, many challenges remain. The overall process of generating power from manure-derived biogas at dairies requires many complex and costly components such as feasibility studies, construction costs, capital costs, maintenance and operation of digester systems (Zhang 2007; PERI 2008). Continued research and collaboration between dairy farmers, scientists, engineers and regulatory agencies has the potential for many exciting and improved anaerobic digester technologies, including the walnut shell packed-bed digester which is the focus of this paper.

In summary, flush water anaerobic digestion at dairies with packed-bed media may create a sustainable, local source of electricity while supporting California's goals for GHG emissions reduction, minimizing odors and decreasing waste.

2 BACKGROUND

Manure at many California dairies is removed by gravity from the barns by a flush water system (Spierling et al. 2009). Depending on the dairy, approximately 0.32 m^3 (Spierling et al. 2009) to 0.90 m^3 (Silacci pers. comm. 2011) of flush water is required per animal unit (AU) of 454 kg each day. Flush water is continually recycled from the anaerobic lagoon back to the barns to remove additional manure, lowering fresh water demands. Fresh water however is used to flush manure from maternity or sick barns where risk of pathogen exposure is high or where food production standards must be met (Silacci pers. comm. 2011). Storm water from rain also contributes to the re-circulated flush as it flows into lagoons during the wet season.

Primary treatment, including settling and screening is applied to flush water before entering the anaerobic lagoon which has been shown to remove between 46% and 70% of total solids (TS) in flush water (Adler 2013). After primary treatment, the flush water enters the anaerobic lagoon where any remaining solids settle and the supernatant is recycled back to the barns for the next flush. Preliminary solids removal extends lagoon lifespan of a lagoon by decreasing the rate of solids cleanout, a process which requires emptying the lagoon and using heavy equipment to manually remove any accumulated solids (Silacci, pers. comm 2011). Primary solids treatment for flush water is particularly important for packed-bed digesters as it reduces the tendency for fouling in the media.

Organic loading (OLR) of digesters at dairies is based on the number of cows, flushing system and re-circulation rates which ranged from 0.109 to 1.18 as COD (g COD/L_{liquid}-d), and from 0.11 to 0.74 as VS (g VS/L_{liquid}-d) (Williams & Gould-Wells 2003; Wilkie et al. 2004; Martin 2008). Typical solids concentration for flush dairies is less than 2% and may contain many remaining micro fibers (<1 mm in size) which settle when undisturbed (SJFAP 2005).

Biogas, which includes methane, is formed via a process known as methanogenesis from carbonaceous wastes through several steps in an ecosystem of various facultative and obligate anaerobic microorganisms (Narihiro & Sekiguchi 2007) which results in a mixed gas containing 60% to 80% methane (Wilkie et al. 2004; Zhang 2007), with residual carbon dioxide (CO_2), nitrogen (N_2), hydrogen sulfide (H_2S), ammonia (NH_3) and other organic vapors. Several complex processes are involved in the conversion of waste material to methane, including hydrolysis of substrate (hydrolysis), volatile fatty acid (VFA) production (acidogenesis) and methane fermentation (methanogenesis) (Lawrence and McCarty 1969; Metcalf and Eddy 2003). Methane formation may occur in a well-mixed, suspended culture or on surfaces in a biofilm as an attached-growth culture (Metcalf & Eddy 2003). Typical methane production ($L\ CH_4/L_{liquid}$-d) for operating flush water covered lagoon digesters is between 0.018 and 0.140 (Williams & Gould-Wells 2003; Williams 2005; Martin 2008) and has reached 0.443 for attached-growth, fixed-film digesters (Wilkie et al. 2004).

Covered lagoon anaerobic digesters contain a suspended microbial community for methane production and are a common digester at dairies in California (Zhang 2007). Well-mixed reactor tanks, typically larger than 350 m^3 (PERI 2008) and a few attached-growth digesters (Wilkie et al. 2004; Umaña et al. 2008; Zaher et al. 2008) have also been used at dairies. Covered lagoon digesters typically occupy about 1 hectare, with depths up to 7.3 m and are lined with a plastic geo-membrane or compacted clay to prevent groundwater contamination (Krich et al. 2005; Zaher et al. 2008; Martin 2008). Covered lagoon digesters operate at hydraulic retention times of 30 to 40 days and are unheated (Spierling et al. 2009). Periodic draining and removal of accumulated solids is necessary for continued operation (Krich et al. 2005; Silacci pers. comm. 2011).

Anaerobic digestion of flush water with attached-growth media such as fixed-films or packed-beds is a promising option for flush water dairies (Wilkie et al. 2004; Zaher et al. 2008). Attached-growth media includes engineered plastics and corrugated pipes, rock and recycled aggregates as well as natural organics such as wood chips, coconut husks nut shells and used auto tires (Vartak et al. 1997; Lee et al. 2007; Zaher et al. 2008). Engineered plastic media is relatively expensive compared to natural media however it has a low density and is available in a wide variety of shapes and sizes (Metcalf & Eddy 2003). Organic media may be more cost effective, especially if found locally (Lee et al. 2007) however it may be prone to degradation as later discussed in this paper (Antal et al. 2000; Bugg et al. 2011).

Fixed-film digesters contain an engineered arrangement of media which provides sufficient surface area and minimizes any chance of clogging or fouling in the media. The benefits of fixed-film are minimization of microbial washout while allowing for higher hydraulic throughput and a smaller overall reactor size as well as HRTs below three days. The fixed-film is also designed to prevent fouling and accumulation of sludge (Powers et al. 1997; Wilkie 2000).

In contrast, packed-bed digesters contain a random arrangement of media to increase surface area and are common in laboratory settings (Lee et al. 2007; Vartak et al. 1997; Hill & Bolte 1992; Powers et al. 1997), but rarely found at dairies with the exception of a used auto tire digester in Oregon (Zaher et al. 2008). As of 2011, up to five commercial attached-growth digesters have been operated in the United States but little information is available on their specifics (EPA AgStar 2011).

Substrate mixing is an important consideration for proper digester operation to ensure substrate is being utilized (Metcalf & Eddy 2003). Various mixing techniques including recirculation (Wilkie 2000; Lee et al. 2007), fluidization of media (Hill & Bolte 1992) or mechanical mixing (Powers et al. 1997) have been used to deliver substrate to anaerobic microorganisms.

Reciprocation is a promising method of mixing and is described in the companion thesis (Adler 2013). Modeled after aerobic/anoxic nitrogen removal research (Henneman 2011; Kane 2010), a reciprocated digester contains two packed-bed tanks where pumps transfer wastewater back and forth (reciprocation) between the two tanks. Applied to anaerobic digestion, reciprocation was thought to minimize channelization and sludge accumulation in the packed-bed and use less energy than conventional mixing techniques or recirculation (Adler 2013).

Kinetic models for anaerobic digestion have been developed by researchers attempting to understand the rate limiting or slowest step in the conversion of substrate to methane. These models have included parameters such as the hydraulic retention time (HRT) and VFAs, including acetate, butyrate and propionate (Lawrence & McCarty 1969; Batstone et al. 2002; Bialek et al. 2013). Models resulting from methane production studies with HRT as the predictor variable typically have had stable substrate concentrations (Hashimoto 1982) compared to freestall dairies where influent substrate concentrations are more variable (Wilkie et al. 2004; this study).

Modeling of biological processes and substrate utilization has been studied for over a century and is described in detail for enzyme utilization kinetics (Michaelis and Menten 1913) and bacterial growth (Monod 1949). These studies describe a common saturation-type model for maximum substrate utilization rate or microbial growth rate with a given substrate concentration of the form:

$$\mu = \mu_{max} \frac{S}{S + K_s}$$

In this case, known as the Monod model, where μ is the microbial growth rate, μ_{max} is the maximum rate of microbial growth, S is the substrate concentration and K_s is the half saturation constant (Monod 1949). The mathematical form of the Monod equation provides a comprehensive solution to the first, second and zero order microbial growth rates found throughout microbiology (Metcalf & Eddy 2003).

An adaptation of the Monod model to describe methane production as the dependent variable and various forms of organic input as the independent variable is common. There is likely a connection between methane production and growth rates of the Monod model as methane is a byproduct of microbial metabolism (Metcalf and Eddy 2003). The relationship between microbial growth rates and methane production are then likely to be proportional, making the mathematical form of the Monod model acceptable for methane production modeling (Yu et al. 1998). Both methane production (L CH_4/L_{liquid}-d) and methane yield (L $CH_4/g_{substrate}$-d) have been modeled and the differences in the definitions should be noted. Methane production is a common output variable in the literature (Martín et al. 1991; Yu et al. 1998; Lin et al. 2011; Raposo et al. 2004; Senturk et al. 2013). Monod-type equations for output of methane yield (Ma et al. 2013) and by an inverse methane yield relationship (Ahn & Forster 2000) have also been developed. Independent variables in the Monod-type models include organic loading (Yu et al. 1998; Ahn & Forster 2000), concentration of influent substrate (Martín et al. 1991; Lin et al. 2011; Senturk et al. 2013; Ma et al. 2013), concentration of effluent substrate (Raposo et al. 2004) and destroyed substrate (Hill 1983).

Additional models for methane output as either production or yield include adaptation of microbial growth rate equations including: first-order, Grau, Chen and Hashimoto (Ma et al. 2013). These models are more complex, requiring many additional inputs such as maximum microbial growth rate, endogenous decay, HRT and VFA concentrations (Grau et al. 1975; Chen & Hashimoto 1980; Ma et al. 2013).

It is important to note that most of the literature review regarding methane modeling is from laboratory experiments where organic loading, substrate concentration, temperature and other parameters could be well-controlled. Most of these studies did not use flushed dairy manure as a substrate. About half of the cited studies used a form of attached growth, with the remaining studies grew cultures in continuously-stirred tank reactors (CSTRs). Although the substrate and reactor designs varied among the literature regarding modeling, the focus of the literature review was to understand the *overall* methane production modeling procedure rather than attempt to find specific studies regarding dairies as those appear to be limited in scope.

The process of digesting flush water, creating methane biogas and then converting methane into power via a generator requires many complex steps. Raw biogas from anaerobic digestion typically contains between 60% and 80% methane, with CO_2, nitrogen (N_2), hydrogen sulfide (H_2S), water vapor and other organic gases making up the rest of the composition (Krich et al. 2005; Wilkie et al. 2004; ARD 2008). These remaining impurities must be removed before methane may be combusted to produce heat or power (Wilkie 2013). Hydrogen sulfide in particular is a flammable, toxic and odorous substance known for its signature "rotten egg" smell (OSHA n.d.) and is highly corrosive to metallic equipment and piping (EPA 1991). Exhaust from methane combustion in the San Joaquin Valley must not exceed 9 parts per million (ppm) or 0.15 grams per brake horsepower-hour or oxides of nitrogen (NO_X) (Austin 2013) which may be removed via catalysis (Spierling et al. 2009).

The intricacy of converting waste material into biogas, methane and ultimately energy requires many complex steps and a variety of equipment. The sequential process train for anaerobic digestion at dairies requires preliminary flush water treatment (if not already installed), anaerobic reactor vessel (covered lagoon(s), tank(s), etc.), piping, H_2S

scrubbers, activated carbon for NH_3 and organic vapor removal, CO_2 absorption, electrical generator, an exhaust catalyst for NO_X prevention as well as a flare for system bypass (Krich et al. 2005; Spierling et al. 2009; CalEPA 2011; Wilkie 2013). Typical capital costs for covered lagoons are above one million dollars (Zhang 2007; Martin 2008) and the lower average capital cost is about $4,500 per generated kilowatt (Krich et al. 2005). Once operating, maintenance for digesters is estimated to cost $0.015 per generated kilowatt-hour (Krich et al. 2005; Martin 2008).

After power is generated, it may be connected to the utility grid for wholesale or delivered directly to dairy facilities in the form of utility retail power savings. Utility connection rates and net meters for dairy digesters have ranged from $12,728 to $71,436 before 2007 (Zhang 2007) and have more recently ranged between $65,000 and $100,000 (Hurley & Summer 2013). Wholesale rates of generated power to utilities of $0.04, $0.0605 and $0.10 per kilowatt-hour have been negotiated by dairies through power purchase agreements with utility companies (Martin 2008; Zhang 2007; PERI 2008). Retail electrical costs for dairies are variable depending on time of day and time of year, total required power as well as individual pumps and equipment which may have sudden peak needs (SCE[a] 2014; PG&E[a] 2014). Non-peak rates in winter may be as low as $0.09942/kWh (PG&E[b] 2014) or $0.05280/kWh (SCE[b] 2014) while peak summer rates may reach $0.36651/kWh (PG&E[b] 2014) or $0.40049/kWh (SCE[b] 2014) depending on the utility. Off-grid use of generated power can save electrical costs by avoiding retail rates however an unconnected dairy is subject to the performance of its digester and equipment and if grid power is needed, demand charges to reconnect a dairy to a utility can exceed $7.00 per kilowatt during peak usage (PG&E[a] 2014). A hybrid method which allows for biogas generation and retail power is known as time-of-use (TOU) electrical metering. A TOU meter can measure bi-directional flow of power either from the utility or the biogas generator with an annual bill or credit depending on the power outcome (PG&E[c] 2014).

Power requirements at dairies in California have ranged between 300 to 1500 kilowatt hours (kWh) per cow annually (SCE 2004) and older estimates put the average needs around 500 kWh per cow (Collar et al. c1995). Small dairies with less than 500 milking cows require about 480 annual kWh (Shelford 2012). In theory, large dairies may be able consolidate or bundle power usage to lower the unit costs and annual power needs per cow.

A previous measure of the economic success of anaerobic digesters at dairies is controlled by a recommended "hurdle" internal rate of return (IRR), estimated at 17% which has been established due to the various complexities and risks associated with anaerobic digestion, power generation and utility interconnection at dairies (PERI 2008). A few dairy covered lagoon anaerobic digesters have exceeded this hurdle with IRRs between 19.02% and 22.82%. One reached 8.64% however many others have not been economically viable, with negative IRRs (PERI 2008). It is important to note that those dairy digesters with the highest IRRs were supported through SB5X and received capital subsidies between 40% and 57% (PERI 2008; Zhang 2007). Additional benefits from methane production and generation at dairies may increase in the near future with the implementation of cap and trade programs (CARB 2012).

Attached-growth and particularly packed-bed digesters may be more economically feasible for methane production at dairies because of smaller required lagoon or tank sizes, reduced land area and a higher concentration of methane, up to 80% (Wilkie 2000) in the biogas. At the time of writing, packed-bed digesters have been implemented at only one large-scale flush water dairy (Zaher et al. 2008) with no available data or specific operating procedures. A limited scope economic analysis for packed-bed digesters was evaluated from this research. However, given the above described complexities and highly variable economic outcomes of methane generation and power production, it is rather limited in scope and only showcases a range of probable outcomes for dairies interested in establishing packed-bed digesters.

2.1 Study Objectives

Several questions arose from the literature review regarding the development of the pilot-scale packed-bed digesters in regards to performance, long-term success and implementation at commercial dairies. These questions include:

1. Is there a relationship between input flush water constituents, temperature and the resulting methane production? If a relationship exists, can it be mathematically modeled to predict methane production estimates for commercial dairies interested in investigating packed-bed digesters?
2. Do solids (sludge) accumulate in the packed-bed and at what rate?
3. How suitable are walnut shells for packed-bed digesters?

The following study objectives address these questions:

1. Understand the influence of the organic loading rate (OLR) of organic matter, as chemical oxygen demand (g COD/L_{liquid}-day) and volatile solids (g VS/L_{liquid}-day), as well as temperature on methane production (L CH_4/L_{liquid}-day). Evaluate a mathematical model which best describes this relationship.
2. Periodically measure the porosity of the packed-bed and estimate the rate of sludge accumulation within the walnut shell packed-beds over the study period.
3. Estimate the rate of degradation and viability of walnut shell packed-bed media.

Additionally, a limited scope economic analysis for commercialization of packed-bed digesters was estimated over a range of parameters and constraints.

Further information of the packed-bed digesters including: influent and effluent water quality characteristics, evaluation of reciprocation performance, quantification of the degree of hydraulic short-circuiting through the packed-bed, COD percent removal correlation based on OLR and first-order removal parameters are presented in the companion thesis (Adler 2013).

3 METHODS

Three pilot-scale tank digester systems were constructed with walnut shell packed-beds and were fed with free stall barn flush water. The digesters were located at the California Polytechnic State University Dairy in San Luis Obispo, CA (latitude 35°18’25N, longitude 120°40’30W). Construction of the pilot-scale digesters took about eight months from August 2011 to April 2012. Operation began on April 27, 2012 and six experimental conditions were applied during the nearly six month study beginning June 25, 2012 and ending on December 9, 2012.

This chapter describes the process flow of the existing preliminary flush water treatment at the Cal Poly Dairy and also the construction and operation of the pilot-scale digesters. Sampling procedures for liquid and gasses, gas and liquid flow rates and the accompanying laboratory testing procedures are also discussed. Additionally, this section describes the individual experiments, procedure for modeling methane production as well as an explanation of the prediction and economic methods for commercial packed-bed dairy digesters.

3.1 Dairy Barn Flushing and Wastewater Process

The Cal Poly Dairy herd averaged 211 milking cows (Jersey and Holstein), 89 heifers and 109 calves during the study period. Milking cows included actively lactating and dry cows. The cows were housed in three barns, two of which used re-circulated flush water and one which used tap water for manure removal. Tap water was also used to clean the milking parlor (**Figure 3.1**) and also entered the dairy waste stream. Each day, an average of 245 m^3 of re-circulated flush water and 95 m^3 of tap water from the nursing barn and milking parlor were flushed into the 0.62-hectare west anaerobic lagoon

(Silacci, pers. comm. 2011). Any manure excreted in the dairy's dry lots was manually removed and was not flushed into the wastewater treatment system.

After collecting manure from the free stall barns, the flush water flowed by gravity and entered the primary treatment area for solids removal (**Figure 3.2**). Primary treatment included a sand trap, inclined screen and secondary settler. An agitator pit with pump moved flush water to the inclined screen, which separated manure fibers greater than one millimeter in size from the flush water. Additional solids were removed at the secondary settler. The sand trap and secondary settler were cleaned weekly with a front loader and sent to a composting operation. A concrete distribution box with approximate capacity of 3.3 m^3 was located downstream from the secondary settler and was situated directly before flush water reentered the lagoon. The distribution box was the source of influent flush water used to feed the digesters (**Figure 3.3**).

Figure 3.1 The Cal Poly Dairy and flush water treatment area. Flush water was pumped from the West Lagoon to the Recirculation Tank (white lines) where it then collected manure and flowed by gravity through the freestall barns to the treatment area (black lines). For health reasons, the nursing barn and milking parlor were cleaned with tap water rather than re-circulated lagoon water.

Figure 3.2 Primary flush water treatment area. Pilot digesters under construction here. The distribution box was the source of influent flush water for the digester systems.

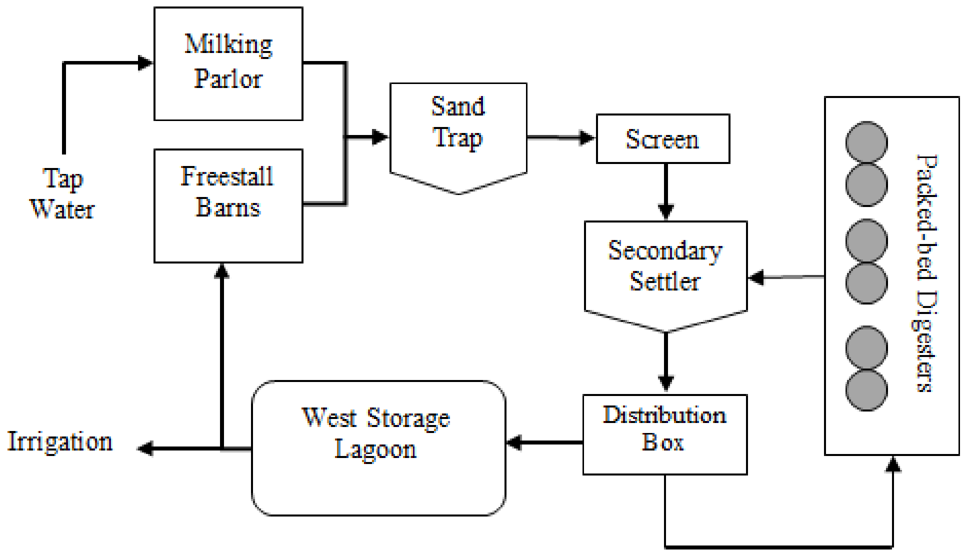


Figure 3.3: Dairy process flow diagram. Included are the pathways for re-circulated flush water and digester influent.

3.2 Digester Configuration

The three digesters were aligned in a north to south configuration on gravel next to the preliminary dairy flush water treatment system. The north to south alignment minimized the shadowing of the digesters on each other, lessening temperature differences between the digesters. Temperature fluctuations were further reduced by covering the sides and top of each digester tank with 5-cm thick foam and aluminum foil insulation with thermal R-value of 11.6 (Insulfoam, Puyallup, Washington) (**Figure 3.4**).

Each digester system consisted of two tanks, a “feed” tank and a “reservoir” tank (**Figure 3.5**). Flush water was transferred between the two tanks by reciprocation as a novel mixing method. The purpose of reciprocation was to reduce sludge accumulation and channeling of flush water through the packed-bed.

The six total tanks were made of high density polyethylene (HDPE) with dimensions of 206-cm height and 88-cm diameter with 41-cm diameter access port on the top (IA3581, Chem-tainer Industries Inc., West Babylon, New York). The tanks were specially sealed for pressurization up to about 20 cm water column by plastic welding the access port of each tank shut with solid sheets of HDPE by a forced air welder (Chicago Welding 96712 plastic welder, Camarillo, California). Inner tubes were also attached to each digester system to prevent a vacuum as flush water left the digesters. The naming schemes for the individual digester systems were; D1, D2 & D3. Individually, each tank was named D1A, D1B, D2A, D2B, D3A and D3B. The reservoir tanks were designated with an “A” and feed tanks were denoted with the letter “B” (**Figure 3.4**).

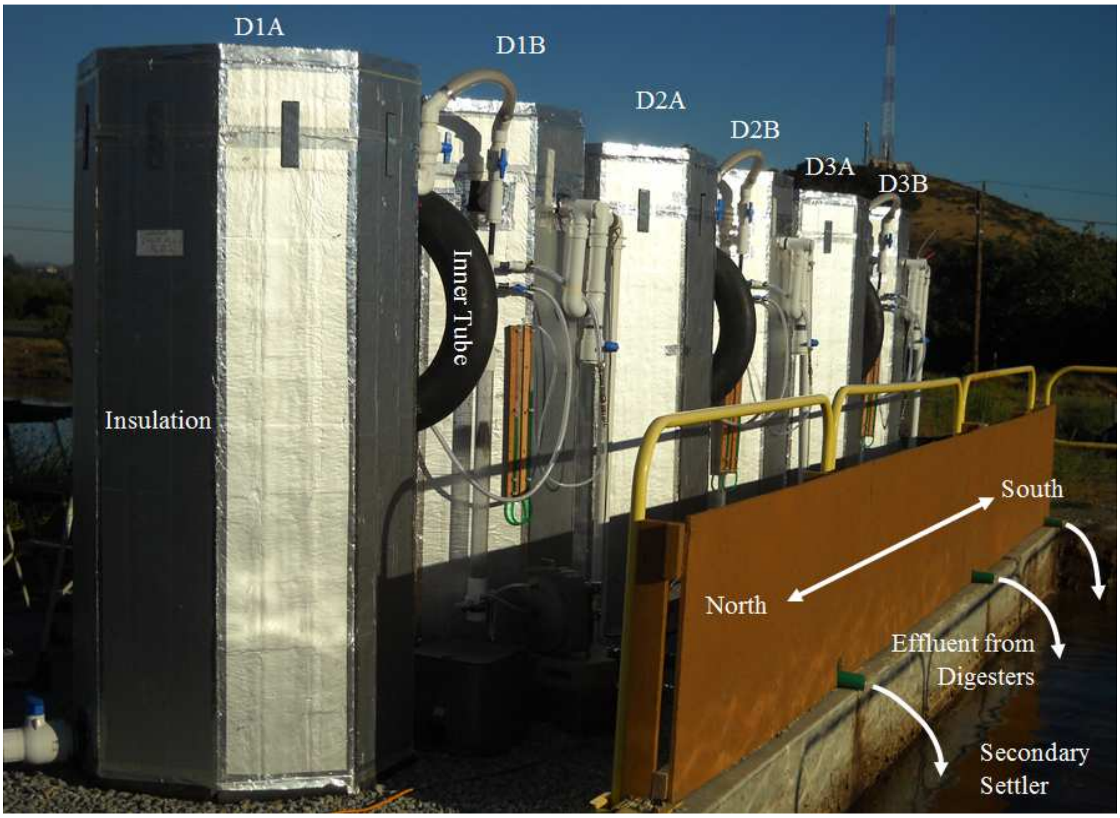


Figure 3.4: Labeled pilot digesters with foam insulation covering the HDPE tanks. Note the north-south alignment, proximity to the secondary settler and inner tubes for pressure normalization.

Vertically-aligned PVC sumps of 15.2-cm inner diameter and 200-cm height were attached to each tank for delivery of influent flush water to each digester as well as allowing reciprocation transfer between tanks. The sumps were connected to a 5.1-cm diameter bulk head fitting near the floor of the tank (**Figure 3.5**). Submersible pumps (PE-2.5F-PW, Little Giant, Oklahoma City, Oklahoma) were placed at the bottom of each sump to reciprocate flush water between tanks via a 1.27-cm flexible reciprocation flow tube. Biogas also flowed between the two tanks during reciprocation to account for displaced liquid volume (**Figure 3.6**).

Figure 3.5: Reciprocated flow between tanks. One tank was full while the other remained empty. The water levels were then switched during the reciprocation cycle by sump pumps via the reciprocation flow tube. Photo taken before insulation was installed around green tanks.

Influent flush water entered the digesters through a sump connected to each feed tank (**Figure 3.7**). The reservoir tank was used to accommodate flush water as it was reciprocated (**Figure 3.6**). Three submersible sump pumps (PE-2.5F-PW, Little Giant, Oklahoma City, Oklahoma) programmed with digital timers (HB800RCL, Intermatic Inc., Spring Grove, Illinois) transferred flush water into each digester system from the distribution box. Minute fibers in the flush water were removed prior to entering each digester with a PVC pipe framed screen box, doubly wrapped with window screen containing the submersible pumps (**Figure 3.8**). The screen box was cleaned several times each week with a water jet from a hose.

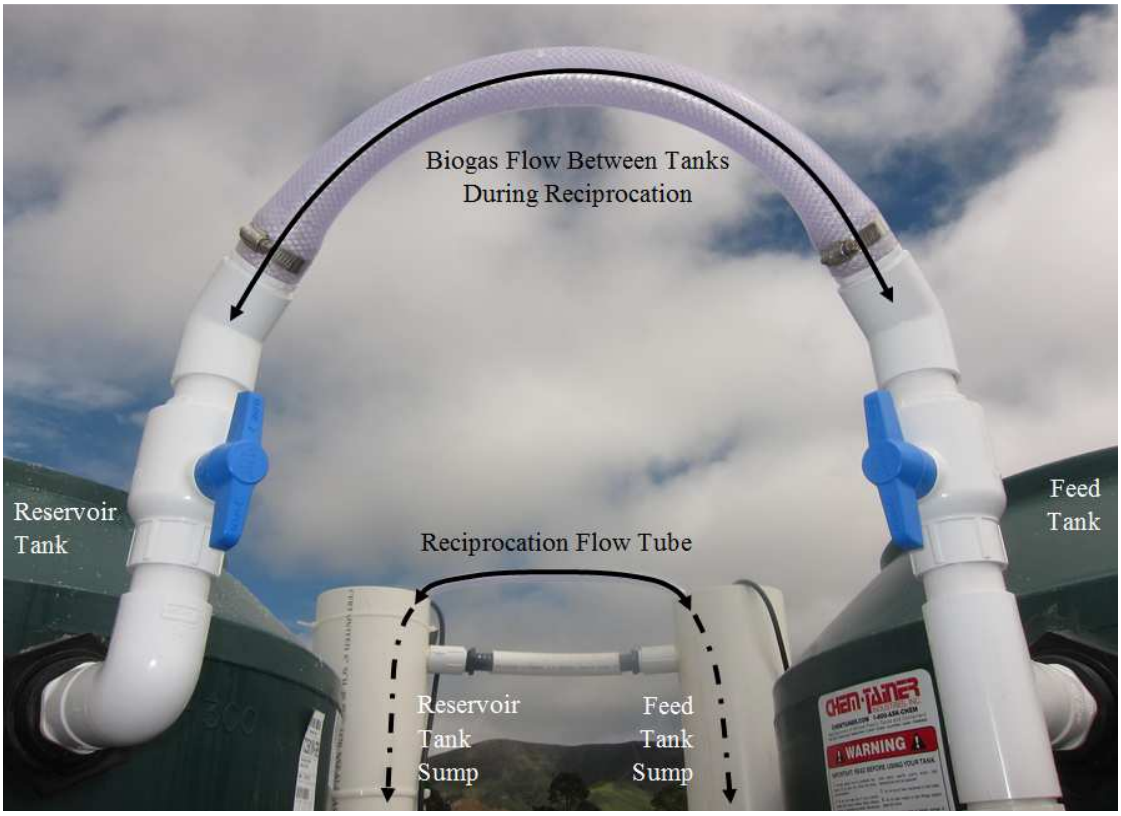


Figure 3.6: Configuration for reciprocation between tanks. Liquid levels were raised and lowered within the two tanks as flush water was pumped from one tank to the other and then back. Biogas was also distributed between tanks to account for displaced liquid volumes caused by reciprocation and keep digester system pressures relatively constant. Submersible pumps were located inside and near the floor of the sumps. Photo taken before attachment of silver insulation around green tanks.

Effluent was discharged from each digester system during each of the ten daily influent periods (**Figure 3.4**). An effluent manifold made of PVC pipe was connected to a 5.1 cm bulk head fitting near the top of the feed tank. The manifold contained a U-trap which prevented any air from entering the digester systems (**Figure 3.9**).

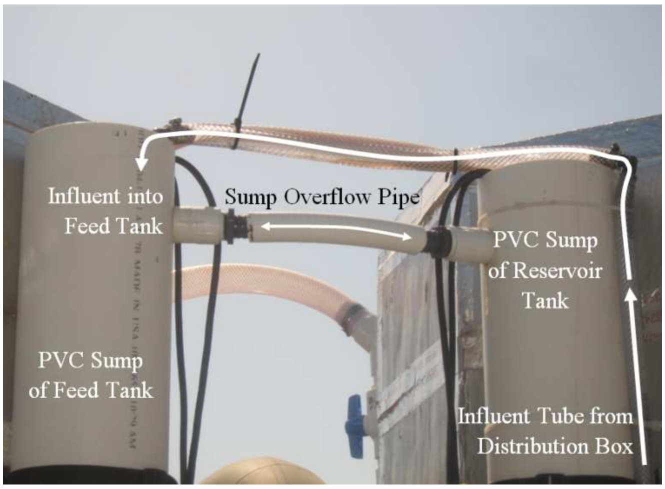


Figure 3.7: Influent flush water tubing with sumps and sump overflow pipe.

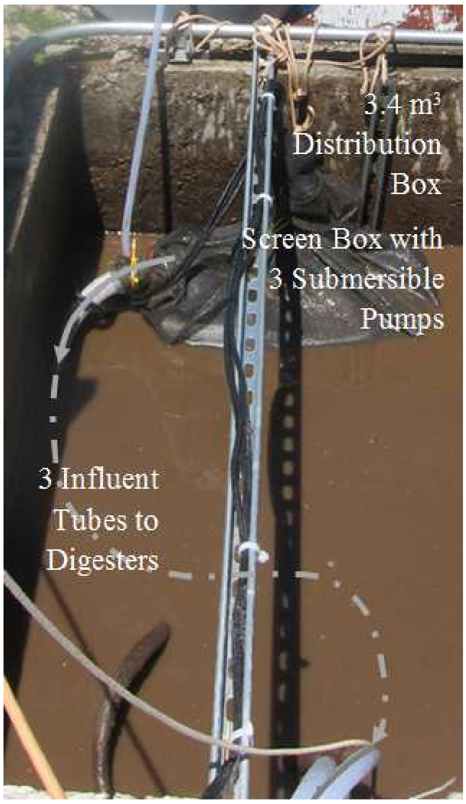


Figure 3.8: Flush water influent screen box inside the distribution box with tubes to each digester.

A PVC pipe manifold was installed to remove biogas from each digester tank. Biogas exited each tank about 2.5 cm below the top of the tank lid through a 3.8-cm bulkhead on both tanks and could then be passed through the gas meter or into the other digester tank during reciprocation. The biogas connection between the feed and reservoir tanks prevented pressure accumulation in the tanks during a reciprocation cycle by replacing the liquid volume with that of the biogas (**Figure 3.10**). A pressure manometer was also attached to the biogas manifold to measure total digester system pressure of each digester. Three Wet-tip gas meters (Speece, Nashville, Tennessee) measured biogas leaving each digester system and were connected to a data logger and computer.

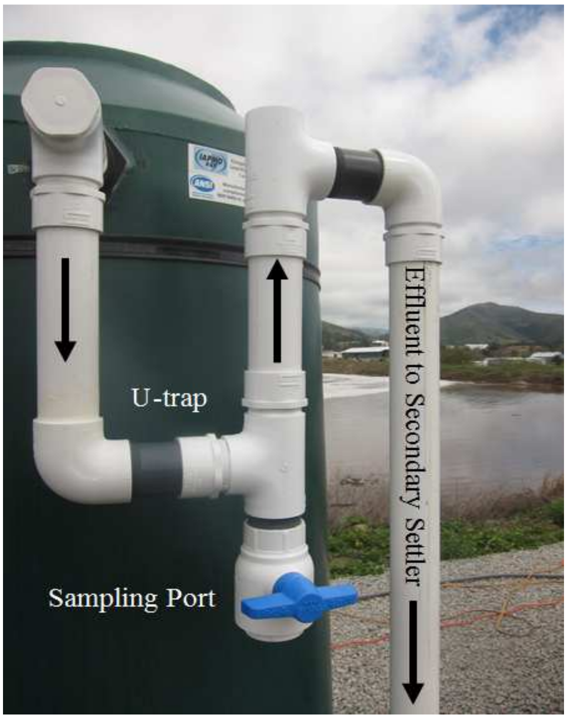


Figure 3.9: Effluent manifold with U-trap. Sampling port and discharge pipe to the secondary settler shown. Insulation was later placed around the green tank.

Figure 3.10: Biogas manifold. Reciprocation flow directions, manometer and pipe to gas meter shown. Photo taken before placement of insulation.

Several tons of English walnut shells (*Juglans regia*) were brought to the site from a walnut processing plant (Nutrinut, Inc., Visalia, California). Two wood-framed screens were built with 1.27-cm (½") hardware cloth screen to sieve and remove smaller shell fragments. The retained shells, with minimum dimension of 1.27 cm, bulk density of 0.245 kg/L and specific surface area of 360 m^2/m^3 were placed into each of the six digester tanks as the packed-bed with approximate height of 132 cm and occupying about 0.75 m^3 of tank volume (**Figure 3.12**). Walnut shells were chosen as the packed-bed media for this study due to their availability in California (Wendt, pers. comm. 2011; USDA 2012) as well as their potential durability (Antal et al. 2000). The utilization of walnut shells as packed-bed media provided an additional environmental benefit as they are a waste product from the walnut industry.

An underdrain was constructed to support the walnut shell packed-bed (**Figure 3.11**) and was made of 30 cm tall septic tank leach field chambers (Model ARC18, ADS, Hilliard, Ohio) surrounded by randomly packed PVC pieces (approximately 10-cm long 5.7-cm diameter, Schedule 40), covered with a plastic geonet with 9.5-mm openings (SKAPS, Commerce, Georgia).

To allow for a "core sample" of the packed-bed for sludge and walnut shell degradation study, a slotted 140-cm, 10.2-cm diameter PVC pipe was installed in the center of the walnut shell packed-bed of each digester tank. Within the pipe was a 122-cm long vertical cylindrical geonet wattle with 9.5-mm openings containing randomly packed walnut shells. Flush water could freely enter the geonet wattle through the slotted PVC, thus mimicking flow into the walnut shell packed-bed but allowing removal for investigation. Flush water could also enter the geonet wattle from the base of the uncapped core pipe, flowing upwards through the walnut shell core.

Figure 3.11: Underdrain arrangement. ARC18 chamber, packed PVC pipe and geonet shown.

Figure 3.12: Walnut shell packed-bed. Shown before digester operation. Note the slotted PVC pipe at center, which housed the geonet wattle.

3.3 Operation and Monitoring

After construction, each tank was filled with tap water and the timers, pumps, piping and other components were carefully inspected and tested before the digester systems were ready for inoculation and initial influent flush water. Each digester system was inoculated equally with 10% by volume (114 L) of mature digester sludge from the San Luis Obispo Municipal Water Reclamation Facility on April 27, 2012.

During startup and experiments, the field site was monitored daily by the researchers and undergraduate assistants. One hour per day was typically spent monitoring the site and included a thorough inspection of all components, leak checking, biogas data logger readouts, influent flow rates, sampling and in field alkalinity test.

3.4 Sampling and Field Measurements

Liquid influent flush water, digester effluent and biogas were regularly sampled for laboratory analyses. Daily composite samples were also taken where water quality was expected to change over the course of the day. Flow rates of influent flush water into each digester and biogas from each digester system was also measured. Alkalinity and ammonia were also measured weekly to assess digester system health.

3.4.1 Influent Flush Water and Effluent Sampling

Samples of influent flush water and effluent wastewater were either obtained by manual "grab" or automatic sampling using two composite auto samplers (Sigma 900 Max, Hach Co., Loveland, Colorado). Grab samples of flush water were collected from the influent tube discharge, located at the top of the PVC sump on D1. Influent composite samples were collected by a hose extending from the auto sampler into the screen box located within the distribution box, directly adjacent to the digester influent pumps. Effluent grab samples were collected at the invert point of the effluent manifold pipe, directly above the secondary settler. Composite effluent samples were collected via a hose extended from the auto sampler into the U-trap of the effluent manifold, located about 1.5 meters off the ground.

The need for composite sampling was determined by settling of solids in the distribution box and irregular free stall flushing events at the dairy. Solids concentrations within the distribution box were shown to decrease with time after the end of a flush event (Adler 2013). The exact daily schedule of the free stall barn flushes and the duration of those flushes were manually controlled and were subject to some variability as described in later sections of this paper.

Composite samples were gathered once per week over a 24 hour period. Influent flush water or digester effluent was collected by the auto samplers during ten influent or effluent events per day. One auto sampler was dedicated to collecting influent flush water *every* week. The other auto sampler collected digester effluent from one digester at a time and was rotated weekly to collect effluent among each of the three digesters. Each auto sampler contained 24 collection bottles. A total of 20 bottles with 195-mL capacity were collected weekly as duplicate samples for each of the ten influent or effluent events. The 20 bottles were removed from the auto sampler, mixed well and poured into a bucket. The contents of the bucket were again well stirred and the final composite sample was poured into a screw top bottle and taken to the lab. Before sample collection, ice was added to each of the auto samplers to limit any reactions in the liquid. Typical composite sample temperatures were 7°C at the time of collection, 24 hours after the initial composite pull.

All liquid samples were stored in well labeled HDPE bottles and either tested at the lab within an hour of collection or placed in a refrigerator at 4°C for testing within 48 hours. A portion of each sample was acidified to pH<2 and refrigerated for chemical oxygen demand (COD) and total ammonia nitrogen (TAN) measurements.

3.4.2 Influent Flush Water Flow Rate

Influent sump pumps were located within the screen box, submerged into the distribution box. Sump pumps were controlled via timers (HB800RCL, Intermatic Inc., Spring Grove, Illinois). The flow rates of influent flush water were measured daily by the time required to fill a 4-L graduated cylinder, located at the same elevation as the influent discharge point of each digester, so that the elevation head would be the same during measurement and operation. Based on the flow rates, influent timers could be adjusted to change the daily influent volume to correspond with the desired hydraulic retention time.

3.4.3 Biogas Sampling

Biogas was sampled weekly for composition using 1-L Tedlar bags with septa valves (EG-PP1, Zefon International, Ocala, Florida). Sample bags were flushed with biogas twice before collection to minimize air or contaminant presence. Collection bags were kept under slight pressure until biogas was tested with gas chromatography.

3.4.4 Biogas Flow Rate

Biogas exited each digester tank through a gas manifold that was connected to a Wet-tip gas meter (Speece, Nashville, Tennessee). The gas meter was connected to a digital HOBO data logger (Onset, Pocasset, Massachusetts). The meter was carefully calibrated and biogas readings were recorded from the data logger to a computer spreadsheet.

3.5 Water Quality and Biogas Analyses

Several field and laboratory tests were conducted to augment methane and organic loading modeling as well as indicate the presence of inhibitors (**Table 3.1**).

Data quality was assured by frequent calibration of laboratory equipment, testing of blanks, standards, splits, and spikes in each analytical batch. Sample and measurement precision was confirmed by with duplicates or triplicates. For splits and/or triplicates, a 10% measurement error was allowed for all tests to account for small sampling and testing variation. Percent error for triplicates was calculated by the percent difference of the lowest and highest values of the three results.

Table 3.1: Lab and field measurements, frequency, materials and methods used. APHA method numbers refer to *Standard Methods for Examination of Water and Wastewater* (APHA 2006).

Test	Frequency	Materials & Method
Alkalinity & pH	3-7 times/week	H_2SO_4 Acid Titration (APHA 2320 B)
Total Ammonia Nitrogen (TAN)	Weekly	Orion 9512 NH_3/NH_4^+ Selective Electrode (APHA 4500-NH_3 D)
Carbonaceous Biochemical Oxygen Demand ($cBOD_5$)	Weekly	5 day, 20°C (APHA 5210 B)
Chemical Oxygen Demand (COD)	Weekly	CHEMetrics 0-1500 ppm Vials, 2-hour digestion at 150°C (APHA 5220 D)
Solids (TS, VS, TSS, VSS)	Weekly	Fisherbrand G4 (1.2µm) Glass Fiber Filters, Mettler Toledo AG245 4-Point Balance (APHA 2540 B, D, E)
Biogas Flow rate	Continuous	Tipping Gas Meters and Onset Electronic Data Logger
Biogas Composition	Weekly	SRI 8610 Gas Chromatograph, TCD and 1.8 m Packed Columns
Water and Gas Temperature	Continuous	Onset Temperature Sensors and Electronic Data Logger

Alkalinity was measured by acid titration and an Oakton pH 11 Series digital meter (Thermo Fisher Scientific, Waltham, Massachusetts) and a Sensorex S200C combination pH electrode probe (Sensorex, Garden Grove, California). Total ammonia nitrogen (TAN) was measured at pH>11 with a Corning pH/ion Analyzer (355, Corning Co., Corning, New York) and Orion electrode probe (9512HPBNWP, Thermo Scientific, Waltham, Massachusetts). The test for carbonaceous biochemical oxygen demand ($cBOD_5$) used nitrogen inhibitor packets and a dissolved oxygen meter to measure changes in oxygen over five days at 20°C. Chemical oxygen demand (COD) tests used 0-1500 ppm EPA approved COD calibration vials (CHEMetrics, Midland, Virginia) with either a DR700 or DR890 colorimeter (HACH, Loveland, Colorado). Total suspended, total volatile and volatile suspended solids were measured weekly using aluminum weighing dishes (08-732-100, Thermo Fisher Scientific, Waltham, Massachusetts). Suspended solids were filtered with a vacuum pump (1HAB-25B-M100X, GAST, Benton Harbor, Michigan). A calibrated, four-point balance (AG245, Mettler Toledo, Columbus, Ohio) was used to weigh the masses of solids.

Biogas was measured weekly using a gas chromatograph (8610, SRI Instruments, Torrance, California) operating at 40°C and 45 psi with double packed 1.8 m columns, TCD sensors and argon carrier gas (Praxair, Danbury, Connecticut). Samples were collected in 1-L Tedlar Bags (EG-PP1, Zefon International, Ocala, Florida) and injected into the gas chromatograph with 1-mL syringes and #23 needles (301025, BD, Franklin Lakes, New Jersey). The procedure for gas chromatography is further described in **Appendix A.1**.

3.6 Experimental Design

The thesis experiments were developed to understand the relationship between organic loading and methane production for walnut shell packed-bed digesters fed dairy barn flush water. From June 25, 2012 to December 10, 2012, six experimental conditions were tested where hydraulic residence time (HRT) and reciprocation (mixing) rates were controlled (**Table 3.2**). Further experiments including: sludge accumulation and porosity in the packed-bed, endogenous decay of sludge to methane (starvation) and walnut shell degradation additionally supported the research.

Table 3.2: Experiment names, dates, and characteristics in each of the three digester systems.

#	Experiment Name	Hydraulic Residence Time (days)	Reciprocations per day	Experiment Duration (days)	Start Date (2012)	End Date (2012)
1	Reciprocation 1	6 (all)	1, 5, 10	21	Jun 25	Jul 15
2	Re-circulated Flush 1	1, 3.5, 6	1 (all)	17	Jul 17	Aug 2
3	Tap Water Flush 1	1, 3.5, 6	1 (all)	33	Aug 3	Sept 4
4	Tap Water Flush 2	0.5, 3.5	1 (all)	23	Sept 18	Oct 10
5	Re-circulated Flush 2	0.5, 3.5	1 (all)	20	Oct 11	Nov 1
6	Reciprocation 2	0.25, 0.5	0, 1, 1	36	Nov 1	Dec 6
7	Sludge to Methane "Starvation"	0 (all)	--	3.89	Sept 6	Sept 10
8	Porosity and Sludge Accumulation	--	--	<1 each	Three times during study	
9	Walnut Shell Degradation	--	--	2	Beginning and end of study	

The organic loading and flush water COD and VS concentrations were reduced during Experiments 3 and 4, between August 3, 2012 and October 10, 2012 (**Table 3.2**) when tap water was used to flush the barns rather than re-circulated flush water. That operational change was out of the control of the researchers and caused a reduction in all water constituent concentrations. Methane production at that time was not consistent with the rest of the study during normal re-circulated flushing conditions. As a result, data during fresh water flushing was not used for methane production modeling as described in the next section.

3.7 Methods of Methane Modeling

A variation of the Monod-type saturation model was selected based on the literature as the focal model for prediction of methane production from substrate. In this case, methane production replaced microbial growth rates on the dependent axis (y axis). The independent variable (x axis) of substrate concentration, found in the Monod Model was replaced with organic loading rates (OLRs). In this study, digester influent flush water concentration was an uncontrolled variable subject to the barn flushing schedule and the duration of the flush. Although many methane production models use concentration as an independent variable (Martín et al. 1991; Raposo et al. 2004; Lin et al. 2011; Senturk et al. 2013), it was decided to normalize the substrate by multiplying the concentration by the daily flow rates and dividing by the liquid volume of the digester (L_{liquid}) to produce the organic loading rate (OLR) in units of g/L_{liquid}-d as volatile solids (VS) or of chemical oxygen demand (COD) (Yu et al. 1998; Ahn & Forster 2000) (**Figure 3.13**).

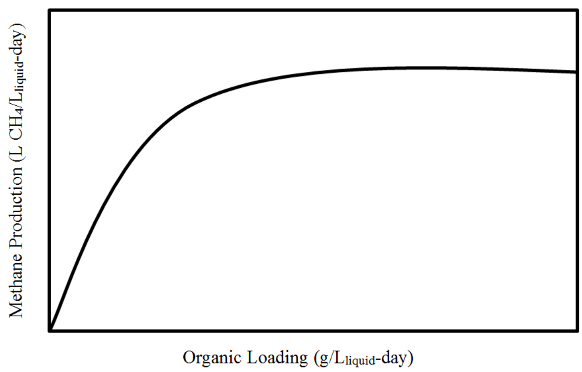


Figure 3.13: **Monod-type model.** Methane production as a function of organic loading can be represented by a saturation curve (Yu et al. 1998; Lin et al. 2011) with a slight decline at higher organic loading due to inhibitory compounds, particularly ammonia (after Henze & Harramoës 1983).

Normalization of substrate concentration into OLR changes the model from one based on substrate concentration to the actual mass of substrate entering the digester each day. The OLR thus provides a more representative independent variable for use in this model due to the real world constraints of the pilot study. Another benefit of OLR is the included digester volume term (L_{liquid}) which may be used to size a digester at an ideal (or minimal) methane production for economic benefits as described later in this paper.

3.7.1 Modeling Data

Data for modeling was collected either daily or weekly between June 25, 2012 and December 9, 2012. Several data points were systematically omitted from the modeling dataset. The largest section of removed data was during the freshwater flushing of the barns as described in **Section 3.6** between August 2, 2012 and October 10, 2012. Organic loading rates (OLR) and methane production at that time were not comparable to measurements during recirculation of flush water through the barns. Further, fresh water barn flushing would not likely be feasible at a commercial dairy operating a flush water system (Silacci 2011, pers. comm.). Additional data points were removed during the final high loading experiment (#6) from November 2, 2012 to December 9, 2012 due to unstable and increasing methane production. The runtime of that experiment was not long enough to reach a steady state methane production. Any remaining data greater than two standard deviations (outliers) from the mean were identified in Minitab® 16.1.1 using a simple box plot method and removed. Lastly, any unmeasured or zero values were also removed from the data set.

Methane production values were carefully adjusted to omit the influence of sludge decomposition to methane inside the packed-bed. The accumulation of sludge was undesirable due to its potential to foul a packed-bed, resulting in limited treatment and methane production due to reduced biological surface area. The procedure is further explained in **Section 3.9**, **Appendix A.2** and **Appendix A.4**.

Acceptable daily data points from each experiment were then averaged resulting in nine points which represented three experiments (1, 2 & 5) for each of the three digesters. These were the final condensed data points used in the mathematical modeling of organic loading to methane production. Note that experiments 3, 4 and 6 were omitted from the data set as described above.

3.7.2 Modeling Procedure

Minitab® 16.1.1 was used to make the OLR and methane production models with kinetic parameters. An iterative approach with three promising model types, including Monod-type saturation (Michaelis-Menten), linear and power was performed. Minitab® provided statistical information about the models and in particular the standard error of the regression, or S value, which may be used for model comparison for a particular data set. The S value provides a direct interpretation of the percentage of data spread from the regression line. The lower the S value, the better the regression model predicts the data set. The standard error of the regression is favorable over an R^2 value as it represents a realistic description of the modeled data rather than an arbitrary value (Frost 2014).

The Monod-type saturation model was the focal point of modeling for this study as it is common in the literature (Martín et al. 1991; Yu et al. 1998; Lin et al. 2011; Raposo et al. 2004; Senturk et al. 2012). It is important to note that it follows the *mathematical form* of the Monod or Michaelis-Menten equations and does not seek to evaluate enzyme utilization rates, or microbial growth as those models do. The equation form is:

$$y = \frac{aX}{b + X}$$

Where y is the methane production, a and b are kinetic parameters and X is the organic loading rate of either COD or VS (as g/L_{liquid}-day).

Additionally, the power equation was attempted as a two-parameter model with the same variables as the Monod saturation model above:

$$y = aX^b$$

And finally, the linear model was also attempted for this data set:

$$y = aX + b$$

Once developed, these models were compared by S value and validated by a linearity test as described further on in the methods section. The best model was chosen to predict methane production values as the basis for economic outcomes for commercial dairies wishing to install a packed-bed digester.

3.7.3 Temperature Modeling

An attempt to discover the kinetic response of methane production from temperature changes was also performed. Temperature is known to affect microbial growth rates (Metcalf & Eddy 2003) and as methane is a byproduct of microbial growth in methanogens (Yu et al. 1998), it is reasonable to interpret that methane production by microbes is thus affected by temperature (Safley & Westerman 1994; Kim et al. 2006).

Temperature based Arrhenius-type rate equations have been applied to wastewater treatment removal models for flush dairy manure. These have appeared as a multiplicative term to organic loading or removal efficiency models in the form of:

$$y = (loading\ or\ removal\ model) * {k_T}^{T-20°C}$$

Where y is the function output as concentration reduction or fraction of removal, k_T is the temperature induced kinetic rate, T is the temperature and 20°C is a mean or normalized temperature (Kane 2010; Henneman 2011; Adler 2013). Although temperature could forcefully be mathematically applied to a data set in Minitab®, it was important to first validate the influence of temperature on methane production before applying a third model term.

To uncover the effects of temperature on methane production, two short hypothesis tests were created in Minitab® to produce p-values for test comparison with a one way analysis of variance (ANOVA) at low loading rates. The null hypothesis stated temperature did not influence methane production, while the alternate hypothesis stated that there is evidence to suggest that methane production is positively affected by temperature changes. Because temperature changes were relatively small (ranging from 14°C to 24°C) for this data set, temperature categories were grouped in two ways to develop the hypothesis tests and calculate p-values. The first method found the mean data set temperature and categorized the resulting methane produced as occurring either above or below the mean temperature, to see if methane production might be higher with the above-mean temperatures. The second method categorized temperature into one degree increments and calculated a p-value based on the differences one degree temperature increments may have on the production of methane.

To provide visual evidence of the potential temperature influence on methane production, temperatures were averaged by experiment, grouped by digester and graphed to see if a correlation between temperature and methane production existed.

In this study, temperature was an uncontrolled variable subject to weather conditions. The digesters were located outside and were insulated to minimize temperature fluctuations however it was not possible to heat or cool the influent flush water or the interior of the digesters. Ultimately, temperature was not included as a model variable and kinetic parameters were not calculated. The results section describes these inconsistencies.

3.7.4 Model Validation

Two sequential methods were used to determine the most representative model for methane production by organic loading.

The first was the standard error of regression, or S value, which is a statistical measure of deviation of data from a regression line derived by Minitab®. It may be used to make correlation comparisons for different models within the same data sets only. The lowest S value indicates the best fit of data to a regression line (Frost 2014). Therefore, methane production from organic loading of COD cannot be directly compared to methane production from organic loading of VS.

The second step in methane production model validation included a test for linearity which compared actual methane production data to estimated methane production data using the models by inputting the organic loading. The actual and estimated methane production values were plotted on an equal-axis graph, and the resulting line slopes were compared. The linearity graph with the slope closest to one was then considered the best for the given data sets. Linear validation is seen in the literature for kinetic models of methane production or yield (Martín et al. 1991; Raposo et al. 2004; Senturk et al. 2012).

3.8 Porosity and Sludge Accumulation Methods

Porosity and sludge accumulation were estimated by a field method of removing and measuring the volume of flush water within the void space of the walnut shell packed-bed. Given the volume of water measured, the vertical change in water level (read from the sump) in the tank and the initial walnut shell porosity of 0.70, it was possible to calculate the void percentage and sludge accumulation at a particular time. Porosity measurements were performed three times during digester operation. Estimated daily porosity and sludge accumulation values were interpolated between the experiment dates. Detailed procedures are described in **Appendix A.2**.

3.9 Contribution of Methane from Accumulated Sludge

The production of methane from the decay of sludge accumulated within the walnut shell packed-bed digesters was calculated as part of the 14-day "starvation" period from September 4, 2012 to September 17, 2012 where influent flush water was prevented from entering all digesters. The purpose of the starvation experiment was to determine the amount of endogenous decay in the sludge which could be contributing to additional methane production on top of the production from the flush water. Although additional methane production from sludge is not inherently problematic, accumulated sludge may increase fouling in the packed-bed (Lee et al. 2007), leading to system failure. On September 5, 2012, three digester tanks were set up for the sludge starvation test and all flush water in the packed-bed of each effluent tank was evacuated to the reservoir tanks via the reciprocation pumps. By removing flush water from one tank, the sludge in the packed-bed was effectively isolated from the flush water and the tank was considered "dry". Note that both digester tanks remained sealed and anaerobic at that time. The recorded starvation period of the three tanks lasted for 3.89 days from September 6, 2012 until September 10, 2012. The contribution from sludge to methane was calculated with the following known inputs: the total methane produced in the “dry” tank during the starvation period, the sludge volume in each tank, the concentration of COD and VS in the sludge and the “starvation” time period. See **Appendix A.4** for additional methods and calculations.

3.10 Walnut Shell Degradation

The degradation rate of walnut shells in the packed-bed was measured to better understand the durability of organic packed-bed media over time. The experiment compared the change in mass of ten walnut shells throughout the eight month digester operation. Initially, a small ~0.6-cm hole was drilled into each of the ten walnut shells, and they were soaked overnight in deionized water. Once the membrane was removed, the shells were dried overnight and carefully weighed. Colored zip ties were looped through the ~0.6-cm holes to assist in locating later. The shells were placed inside the wattle “core” within the reservoir and feed tanks of digester D1. The shells were removed on December 9, 2012 and re-weighed to identify changes in mass. A thorough explanation of the methods is described in the **Appendix A.3**.

3.11 Economic Feasibility for Commercial Scale Packed-bed Digesters

The best validated methane production models from COD and VS organic loading rates (OLRs) were used to predict the quantity of methane and subsequently the potential range of economic outcomes for packed-bed digesters at commercial dairies operating with a recycled flush water system. A spreadsheet was developed for calculations and to account for several input ranges and assumptions as well as costs. Input variables and assumptions included: milking cow population, organic loading rates (as COD or VS), retail electric rates, capital subsidies, generator efficiency and a breakdown of capital costs (**Table 3.3**). Manure excretion rates were calculated based on the cow population demographics and a flush water rate of 0.432 m^3 per animal unit (AU) was used (Spierling et al. 2009).

Table 3.3: **Input variables and assumptions for estimation of methane.** Methane output (L/d) and economic conditions also shown.

Adjustment Factor	Value	Units	Comments	Source
COD Organic Loading	1 to 10	g COD/L_{liq}-d	Range of pilot study	--
VS Organic Loading	1 to 10	g VS/L_{liq}-d	Range of pilot study	--
Milking Cows at Dairy	500 to 3000	cows	56% is avg. milk cows per dairy	a
Total Cows at Dairy	893 to 5357	cows	Remaining 44% of cows	--
Electrical Rates	$0.10 and $0.20	$/kWh	Approximate mid-range rates	b,c
Subsidy Rate	0% and 50%	% of Capital	57% is maximum provided	d
Generator Efficiency	28%	--	--	e
Generator Run-time	90%	--	Annual operating time	a
Percent CH_4 in Biogas	80%	--	Approximate pilot study results	--

a - Spierling et al. 2009
b - PG&E 2014 (b)
c - SCE 2014 (b)
d - Zhang 2007
e - Krich et al. 2005

Organic loading rates (OLRs) and daily manure and flush COD and VS masses based on the cow population were used to make digester liquid volume (L_{liquid}) calculations. Digester liquid volume directly affected digester size and thus capital and equipment costs.

$$L_{liquid} = \frac{(\frac{M}{day})_{manure} + (\frac{M}{day})_{flush}}{OLR}$$

Where:

L_{liquid} = Liquid volume of digester

M = Mass of COD or VS

manure = Mass from actual manure

flush = Mass from re-circulated lagoon water before flushing the barns

OLR = Normalized loading rate as COD or VS (g/L_{liquid}-d)

The total reactor size was further increased by addition of walnut shell volume, five percent headspace and ten percent underdrain volumes. Two outcomes for digester liquid volume may be calculated based on the COD and VS manure and flush water masses as well as the COD and VS OLRs. The resulting digester volumes calculated by COD and VS were then averaged to present one approximate digester liquid volume.

A spreadsheet for economic analysis made calculations for the development of a packed-bed covered lagoon digester at a supposed commercial dairy. Essentially, the hypothetical design was a covered lagoon filled with a walnut shell packed-bed and supported by a series of underdrains. Although tanks were considered, the covered lagoon was chosen over tanks as many dairies already have an anaerobic lagoon and could potentially use their existing infrastructure for an excavated covered lagoon packed-bed digester. Tank costs by comparison to covered lagoons are also quite high (Spierling et al. 2009). Capital costs were estimated by required size, equipment, land price, walnut shell costs and utility interconnection. Engineering consulting and site work rates were estimated at an additional 26% and 10% of capital (Spierling et al. 2009). A more detailed method of the capital cost breakdown with equipment and subcategories is further explained in **Appendix C**.

Annual benefits as retail electric savings were calculated from the total daily output of methane, energy density of methane, generator efficiency and run-time, retail electrical rates and capital cost subsidies. Wholesale of power to utilities was not included in this study as it was revealed to be unprofitable due to low rates and high utility interconnection fees, later discussed. These benefits were then converted to internal rates of return (IRRs) over a 10 year investment period with up-front capital costs and subsequent yearly income. The purpose of the economic analysis was to estimate the "high" and "low" ranges for economic outcomes, represented as IRRs or actual profitability rather than capital costs or simple payback. The range of economic outcomes could then be used to estimate the financial feasibility of packed-bed digesters operating at dairies by directly comparing to a "hurdle" IRR of 17% recommended for dairies interested in developing anaerobic digesters (PERI 2008). Maintenance costs were subtracted from benefits at a rate of $0.015/kWh generated (Krich et al. 2005) and at a bi-annual walnut shell replacement cost of $30/ton (Southam 2010).

Internal rate of return (IRR) was chosen over modified IRR (MIRR) and net present value (NPV) as a financial investment indicator in this study. In part, this was due to its simplicity where the annual cash flow of benefits from methane generation was expected to remain positive throughout the investment period. If annual cash flows in this analysis had changed signs between positive and negative values, a modified internal rate of return (MIRR) would have predicted a more conservative and controlled investment return (CIMA 2012). Conversely, net present value (NPV) analysis requires a discount rate for prediction (Schmidt 2013). NPV was not chosen because the discount rate for this type of anaerobic digester at dairies has not been established as this is a novel technology. Without a representative discount rate, financial predictions using NPV would likely be less valid than IRR for this study.

Two economic analyses were prepared with the available input variables to provide a range of outcomes. The first analysis calculated IRR at various organic loading rates under four conditions: 0% capital subsidy and \$0.10 per kWh, 0% subsidy and \$0.20/kWh, 50% capital subsidy and \$0.10/kWh, and finally, 50% subsidy and \$0.20/kWh. Subsidy fractions at 50% are close to the highest known subsidy for a dairy digester project found in the literature, at 57% (Zhang 2007). The milking cow population was held constant at 1,510 for the first analysis as this is the average milking cow population per dairy in the San Joaquin Valley of California (California Milk Advisory Board 2013) (**Table 3.4**). The second analysis estimated IRR at various milking cow populations with the organic loading (as COD or VS) held at 5 g/L_{liquid}-d (the median of the pilot results) using the same four subsidy and rate conditions as described above (**Table 3.4**). The different analyses were produced to allow those interested in constructing a commercial scale packed-bed digester to calculate an economic range based on organic loading rates as well as milking cow population.

Table 3.4: **Conditions for economic analyses.**

	Dependent Variable	Subsidy	\$/kWh	Outcome	Comments
Analysis 1	Organic Loading Rate (as COD or VS)	0%	\$ 0.10	IRR	Fixed milking cow population of 1,510 (at 56% milking cows per dairy)
		0%	\$ 0.20		
		50%	\$ 0.10		
		50%	\$ 0.20		
Analysis 2	Milking Cow Population	0%	\$ 0.10	IRR	Fixed organic loading rate of 5 g/L_{liquid}-d (as COD or VS)
		0%	\$ 0.20		
		50%	\$ 0.10		
		50%	\$ 0.20		

notes: 1 Generator efficiency of 28%
2 Annual generator runtime of 90%

It is important to note that the economic methods and results were not developed as a feasibility study for a particular dairy or group of dairies. As a result, there are many local conditions and constraints which cannot be satisfied in the economic model as the study is hypothetical.

4 RESULTS AND DISCUSSION

The results of this study are described in the following sections:

1. Influent flush water and effluent characteristics
2. Biogas composition and methane production
3. Methane production models
4. Packed-bed porosity and sludge accumulation
5. Degradation of walnut shells
6. Commercial digester performance and economic predictions

4.1 Influent and Effluent Water Quality Characteristics

Several water quality constituents from the influent flush water and digester effluent were measured between June 25, 2012 and December 10, 2012 and are presented as global averages below (**Table 4.1**). Digester health was gauged by tests for pH, alkalinity and ammonia (as an inhibitory compound). Water quality tests which influenced methane modeling included measurement of volatile solids (VS), chemical oxygen demand (COD) concentrations as well as temperature. Additional tests such as total solids (TS), total suspended solids (TSS), volatile suspended solids (VSS) and biochemical oxygen demand ($cBOD_5$) were also conducted but were not used for modeling purposes.

Table 4.1: Average water quality results for each digester. Includes effluent and influent flush water from 6/25/2012 to 12/10/2012 with standard deviations after the ± symbol.

Test	Influent			D1			D2			D3		
Alkalinity (mg/L)	1785	±	683	2074	±	730	2117	±	578	2220	±	654
pH	7.85	±	0.29	7.32	±	0.31	7.64	±	0.27	7.65	±	0.29
TAN (mg N/L)	144	±	59.1	169	±	52.3	163	±	50.5	157	±	54.4
$CBOD_5$ (mg/L)	800	±	186	423	±	260	402	±	206	450	±	190
COD (mg/L)	4274	±	1493	2564	±	1168	2485	±	906	2797	±	1009
TS (g/L)	6.02	±	1.76	4.35	±	1.38	4.27	±	1.31	4.3	±	1.38
VS (g/L)	2.95	±	1.1	1.88	±	0.66	1.78	±	0.56	1.88	±	0.62
TSS (g/L)	2.32	±	1.25	0.91	±	0.48	0.92	±	0.38	1.04	±	0.37
VSS (g/L)	1.8	±	0.91	0.79	±	0.4	0.81	±	0.32	0.92	±	0.29
Temperature (°C)	21.5	±	1.72	20.4	±	1.28	20.5	±	1.34	21.1	±	1.47

Weekly average COD and VS concentrations, organic loading rates and temperature results are presented in graphical form below (**Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4, Figure 4.5**). Vertical lines along the graphs indicate experiment separations as identified in methods (**Section 3.6**). Gray shaded areas on the figures below denote the "starvation" experiment where the sludge and flush water were digested separately to expose their individual influence on the production of methane, as described in methods (**Section 3.9)**.

The concentration of all measured water chemicals decreased during experiments three and four, from August 3, 2012 to October 10, 2012 where the barns were flushed with tap water rather than re-circulated lagoon water. The decrease in concentration at that time was evident in the following graphs for COD and VS concentration (**Figure 4.1**, **Figure 4.2**) as well as organic loading (**Figure 4.3**, **Figure 4.4**). The concentration peak measured on October 12, 2012 was attributed to a temporary lapse in flushing for a few days due to pump malfunction which caused manure accumulation in the barns.

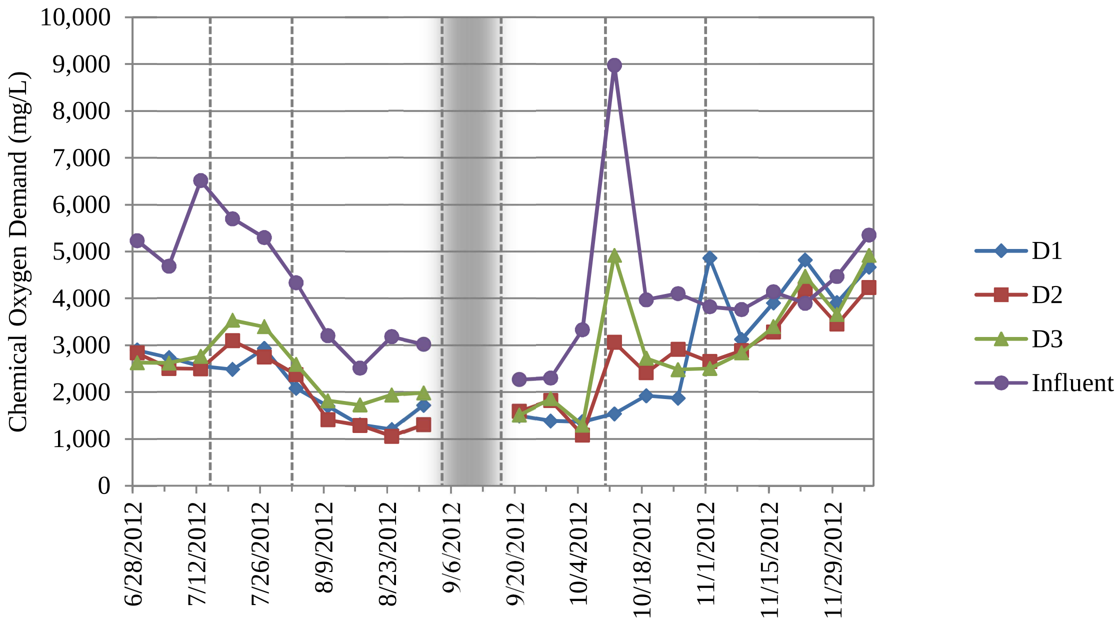


Figure 4.1: Weekly Average COD Concentration. Vertical lines indicate experiment boundaries. Gray shaded area indicates "starvation" experiment where digesters were not loaded.

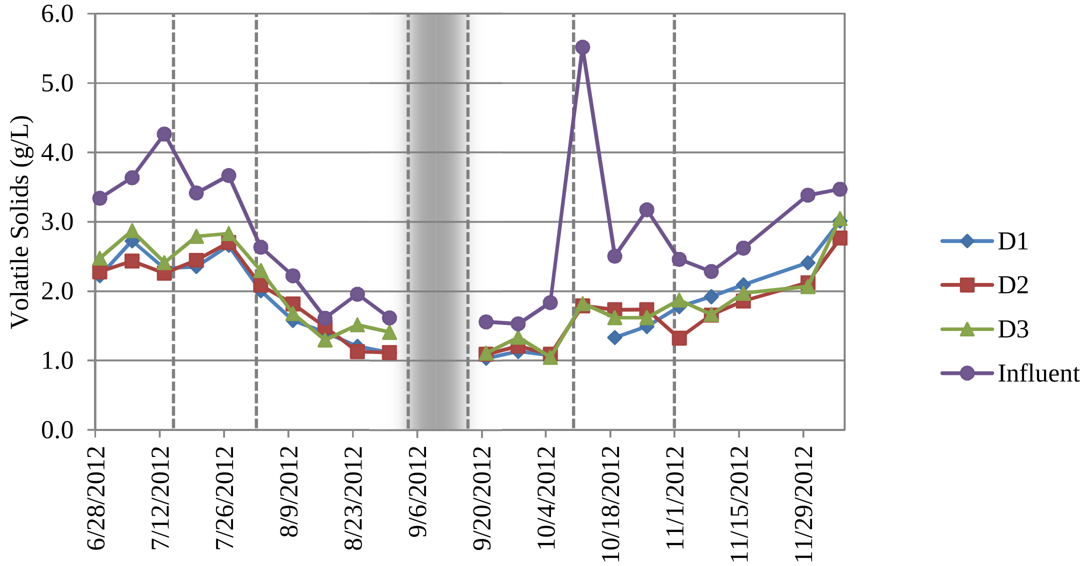


Figure 4.2: Weekly average VS concentration. Vertical lines indicate experiment boundaries. Gray shaded area indicates "starvation" experiment where digesters were not loaded.

Organic loading (OLR) was calculated from the daily masses of COD and VS entering the digesters, liquid flush water influent flow rates and the digester liquid volume (L_{liquid}) which remained constant at 1135 L. Organic loading of the digesters increased during the research (**Figure 4.3**, **Figure 4.4**) to study methane output and water treatment at higher loading rates. Organic loading was affected by barn flushing schedules and amount of flushed manure which could not be controlled by the author during the study period.

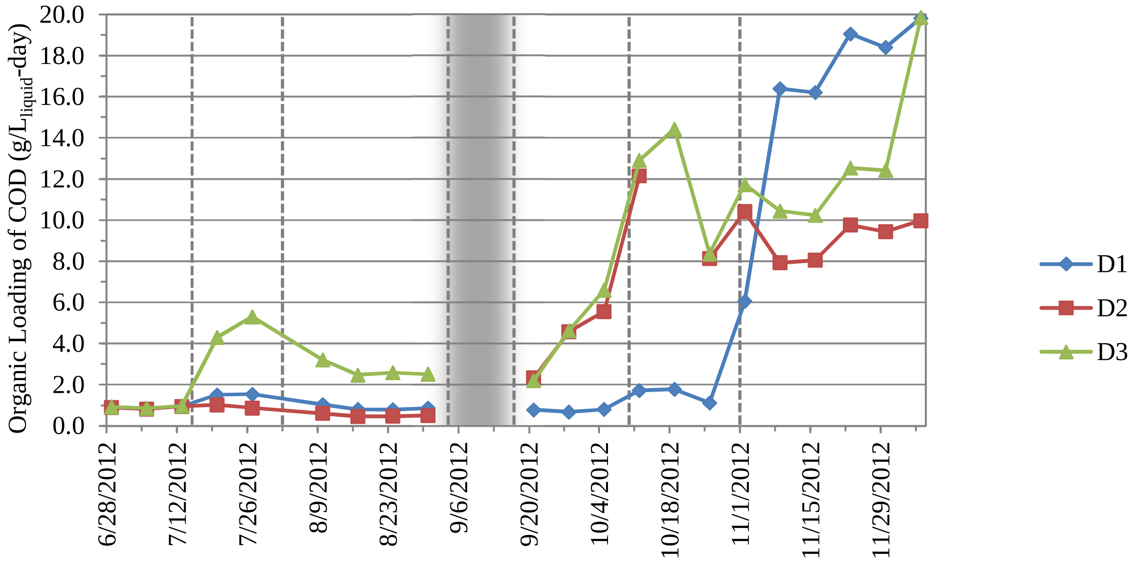


Figure 4.3: Weekly average organic loading of chemical oxygen demand (COD). Vertical lines indicate experiment boundaries. Gray shaded area indicates "starvation" experiment where digesters were not loaded.

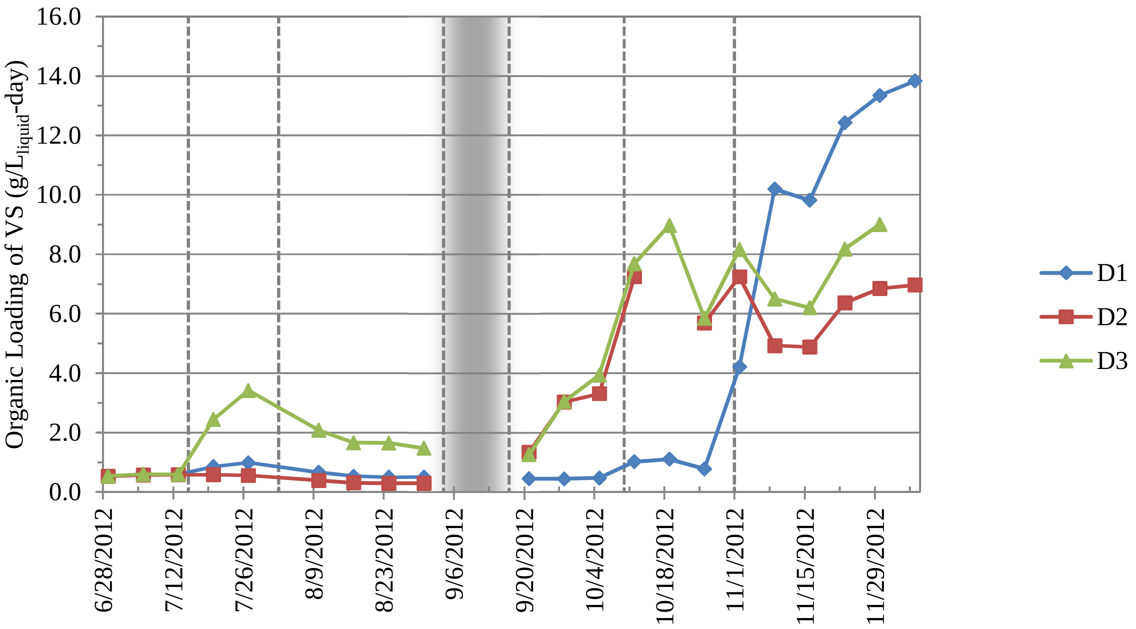


Figure 4.4: Weekly average organic loading of volatile solids (VS). Vertical lines indicate experiment boundaries. Gray shaded area indicates "starvation" experiment where digesters were not loaded.

The average daily temperature of the packed-bed digesters ranged from 14°C to 24°C during the study period. Each digester tank was insulated as described in the methods section to minimize temperature fluctuations. As the study period approached the winter season, the average daily temperature began to decline (**Figure 4.5**).

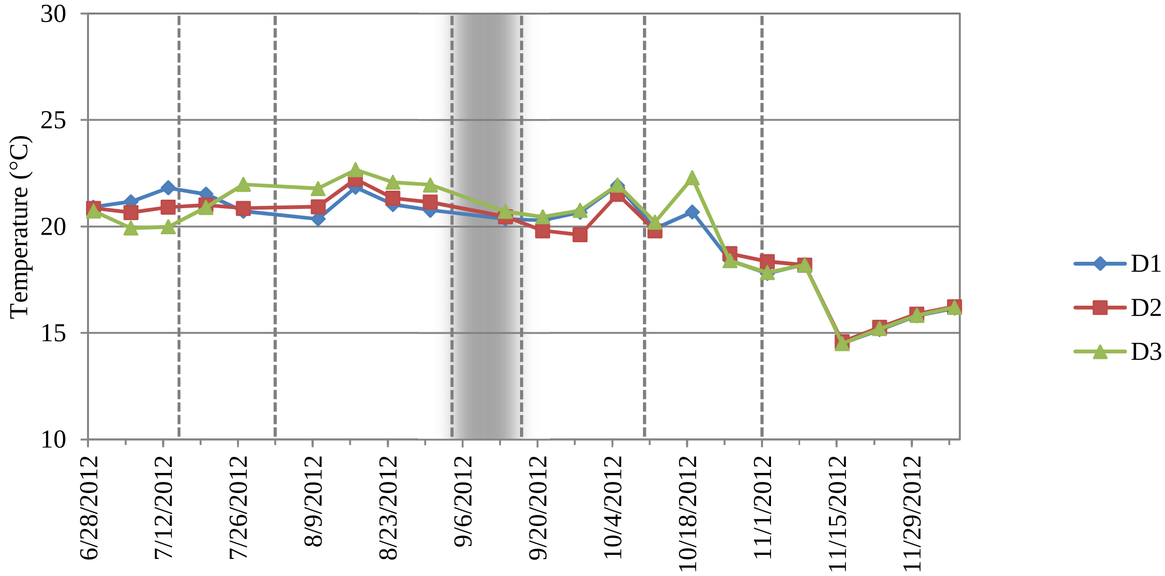


Figure 4.5: Digester internal average weekly temperature. Vertical lines indicate experiment boundaries. Gray shaded area indicates "starvation" experiment.

4.2 Biogas Composition and Methane Production

The majority component of the biogas emitted from the digesters was methane with average concentrations of 85.9%, 84.6% and 86.7% in digesters D1, D2 and D3 respectively over the study period (not including startup). These methane concentrations correspond closely to other packed-bed or fixed-film digesters with low HRTs and high hydraulic loading around 80% methane (Powers et al. 1997, Wilkie 2000). Carbon dioxide (CO_2) accounted for most of the remaining gas, while nitrogen was occasionally present above the detection limit of the gas chromatograph. Hydrogen sulfide (H_2S) was also present in the biogas due to its signature “rotten egg” odor however its concentration was not measured during the study period.

The concentration of methane in biogas continued to gradually increase in all digesters over the study period (**Figure 4.6**). A theory for the increase in methane concentration may have been the increasing hydraulic loading of the digesters over the study period which may have allowed for greater CO_2 solution into the flush water. This theory however remains unsolved and further study would be necessary understand the gradual increase of methane in the biogas.

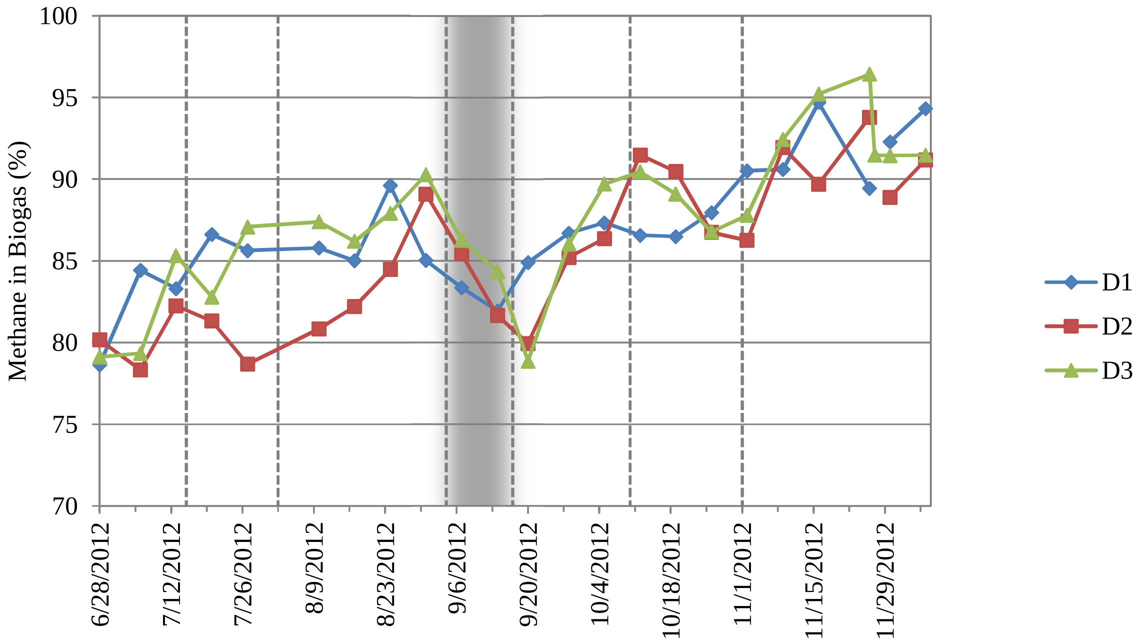


Figure 4.6: Weekly average methane concentration in biogas. Vertical lines indicate experiment boundaries. Gray shaded area indicates "starvation" experiment where digesters were not loaded but methane concentration continued to be measured.

4.2.1 Methane Production

Methane production generally increased over the study period, in parallel with rises in organic loading rate (**Figure 4.7**). The correlation between organic loading rates and methane production are discussed at length in the following methane modeling sections.

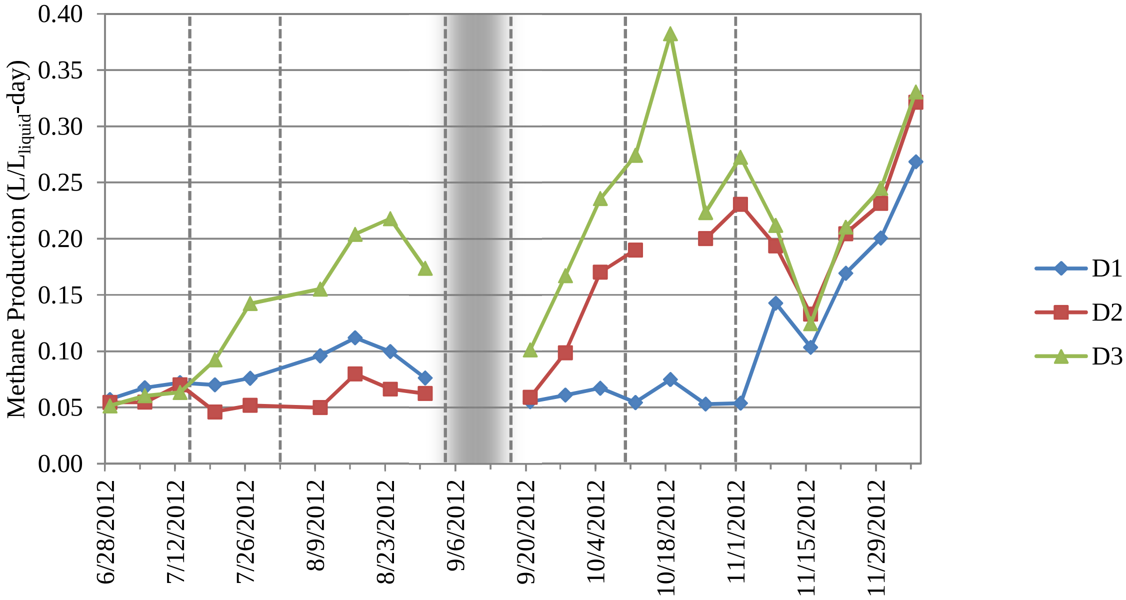


Figure 4.7: Weekly average methane production from each digester. Vertical lines indicate experiment boundaries. Gray shaded area indicates "starvation" experiment where digesters were not fed but methane production continued (not shown here) as detailed in **Appendix A.4.**

The fluctuations in methane production during each of the experiments were likely attributed to the internal movement of biogas due to the reciprocation and perhaps temperature swings. Approximately 9 cm of water column pressure was needed for biogas to pass through the gas meters. Occasionally, several hours were needed until pressure increased above the 9 cm threshold and biogas could be measured.

The source of methane production was categorized into two groups; from loading and from sludge degradation. From the sludge starvation test, sludge was found to contribute between 4.9% and 24% of daily methane production (Adler 2013). The production from sludge was subtracted from the total daily methane production before modeling as the focus of the paper was to evaluate the methane production from flush water. **Appendix A.4** further details the procedure of subtracting methane produced from decomposing sludge accumulated in the reactor.

4.3 Results of Methane Modeling

One hundred fifty three data points were used for methane production modeling by the three digesters. The resulting data was then averaged by the three remaining experiments (1, 2 & 5) as described in the methods section, resulting in nine averaged points for modeling. The mean and standard deviation of these experimental points may be viewed in the table below (**Table 4.2**).

Table 4.2: Mean experimental results for the selected data modeling set with standard deviations (SD) and sample points (n).

Exp.	n	Dig.	CH_4 Production (L/L_{liq}-d)			VS Load (g/L_{liq}-d)			COD Load (g/L_{liq}-d)			Temperature (°C)		
			Mean		SD	Mean		SD	Mean		SD	Mean		SD
1	20	D1	0.068	±	0.007	0.58	±	0.02	0.92	±	0.06	21.4	±	0.7
2	14	D1	0.077	±	0.005	0.96	±	0.07	1.52	±	0.17	20.6	±	0.7
5	19	D1	0.059	±	0.020	0.93	±	0.16	1.42	±	0.33	19.3	±	1.6
1	19	D2	0.058	±	0.015	0.58	±	0.02	0.91	±	0.08	20.8	±	0.3
2	14	D2	0.054	±	0.012	0.54	±	0.04	0.87	±	0.11	20.8	±	0.5
5	17	D2	0.246	±	0.051	6.75	±	1.36	10.32	±	2.63	19.0	±	1.5
1	21	D3	0.060	±	0.010	0.58	±	0.03	0.92	±	0.07	20.2	±	0.5
2	16	D3	0.133	±	0.018	3.22	±	0.39	5.16	±	0.86	21.8	±	0.5
5	13	D3	0.289	±	0.069	6.50	±	1.19	9.69	±	2.31	19.2	±	1.7

The resulting data points were graphed in Minitab® to yield three individual models of methane production with kinetic parameters from the organic loading of chemical oxygen demand (**Figure 4.8**) and three models for organic loading of volatile solids (**Figure 4.9**). The six attempted models for both organic loading of COD and VS included Monod-type saturation (Michaelis-Menten) model, a power model and a linear model as described in the methods section. The three models in each of the same data sets were directly compared for fit by the standard error of the regression (S) (**Figure 4.8**, **Figure 4.9**). **Section 4.3.2** further compares the models by validation.

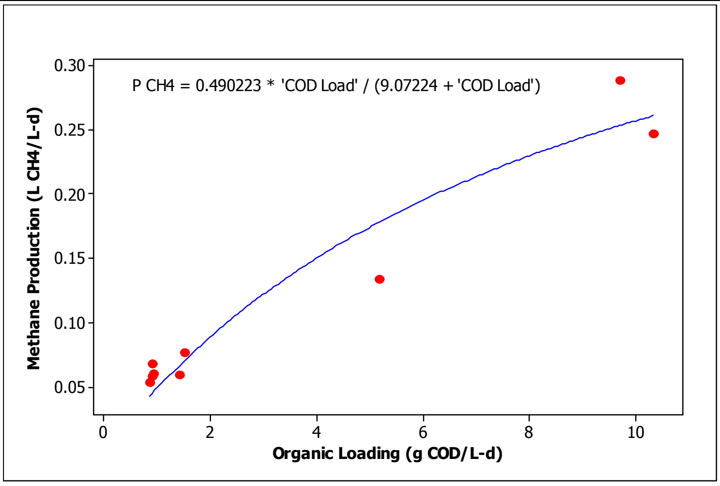
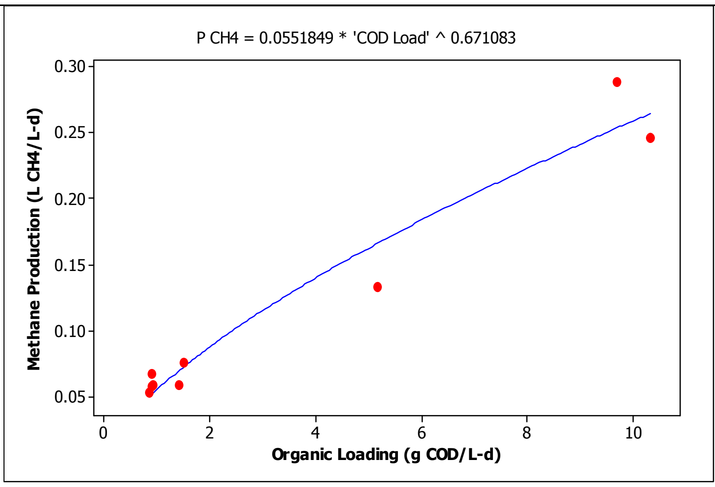
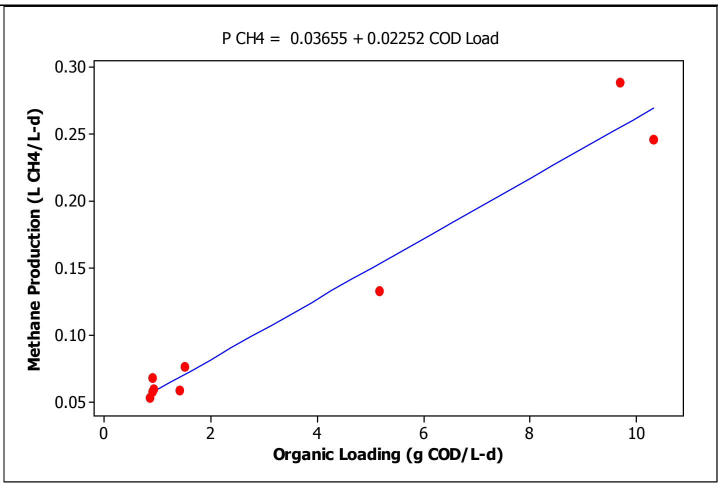
Model Type	Minitab® Output and Equation	Statistical Information
COD Monod (Michaelis-Menten) Saturation Model		Iterations 11 S 0.0255160
COD Power Model		Iterations 11 S 0.0210813
COD Linear Model		S 0.0180400 R^2 0.965 R^2 (adj.) 0.96

Figure 4.8: Monod, power and linear models developed by Minitab® for methane production at experimental average chemical oxygen demand (COD). Minitab® statistical information is provided and an example output is in **Appendix B.1**.

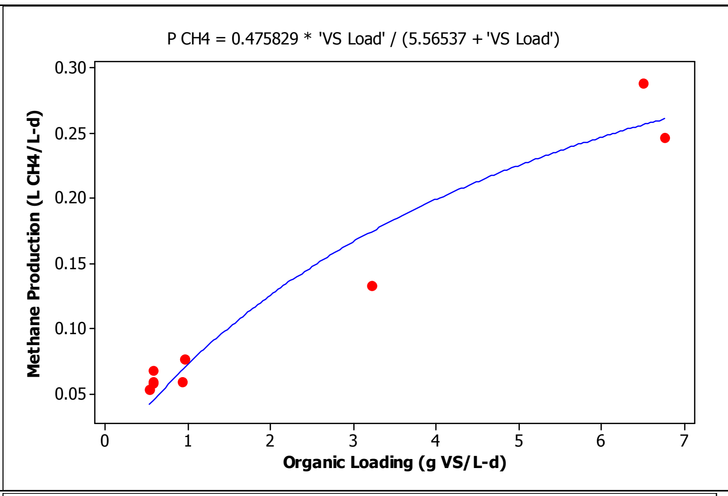
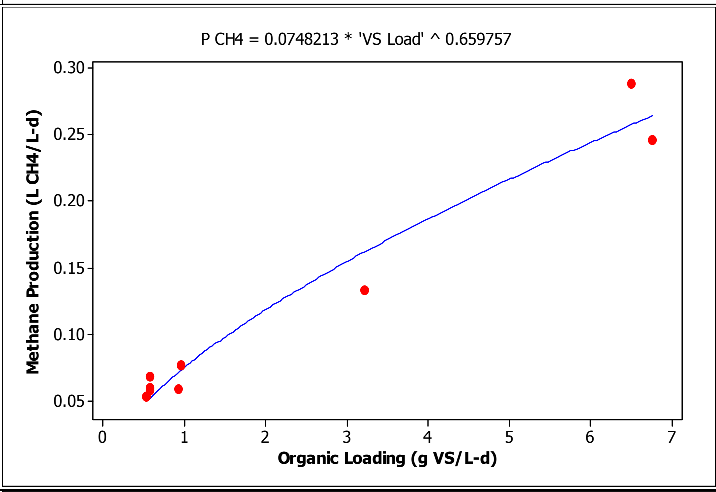
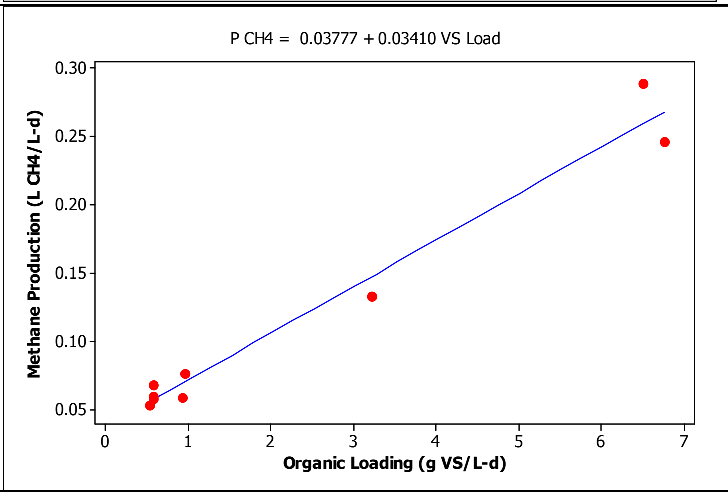
Model Type	Minitab® Output and Equation	Statistical Information
VS Monod (Michaelis-Menten) Saturation Model		Iterations 11 S 0.0242121
VS Power Model		Iterations 11 S 0.0192634
VS Linear Model		S 0.0159344 R^2 0.972 R^2 (adj) 0.969

Figure 4.9: Monod, power and linear models developed by Minitab® for methane production at experimental average volatile solids (VS) organic loading rates. Minitab® statistical information is provided and an example output is in **Appendix B.1**.

The linear model for both COD and VS data sets for methane production has the lowest S value when comparing models of the same data set. Although expected to outperform the other models based on the literature, the Monod-type model was not the best fit for the given data sets, likely due to limited mid-range data from organic loading and methane production. Mid-range organic loading was designed to be measured during experiments 3 and 4 however as the barns were flushed with fresh water at that time, the data was not used for modeling as it was not representative of typical dairy flushing operations (Silacci, pers. comm 2011). If more mid-range data under normal re-circulated flushing conditions been gathered, the Monod-type model may have been more representative for methane modeling by organic loading.

4.3.1 Temperature Modeling

The influence of temperature on methane production was also evaluated during the experiment. Unfortunately, no regressive or practical model of temperature induced methane production may be evaluated from the available data set.

Temperature did not have a significant effect on the production of methane for this study. When experimentally averaged methane production from each digester was grouped between low, medium and high loading, temperature effects on methane production were insignificant in comparison to the effects by organic loading. At low average experiment loading, between 0.867 and 1.521 g COD/ L_{liquid}-d and 0.539 and 0.955 g VS/L_{liquid}-d, methane production remained relatively constant between 19°C and 21.5°C. At medium loading of 5.164 g COD/ L_{liquid}-d and 3.223 g VS/L_{liquid}-d, methane production was clearly higher. Finally, at high average loading rates, between 9.690 and 10.321 g COD/ L_{liquid}-d and 6.501 and 6.754 g VS/L_{liquid}-d, methane production was nearly six times higher (shown as triangles below) than the low average loading rates (shown as diamonds below), even at similar temperatures around 19°C (**Figure 4.10**).

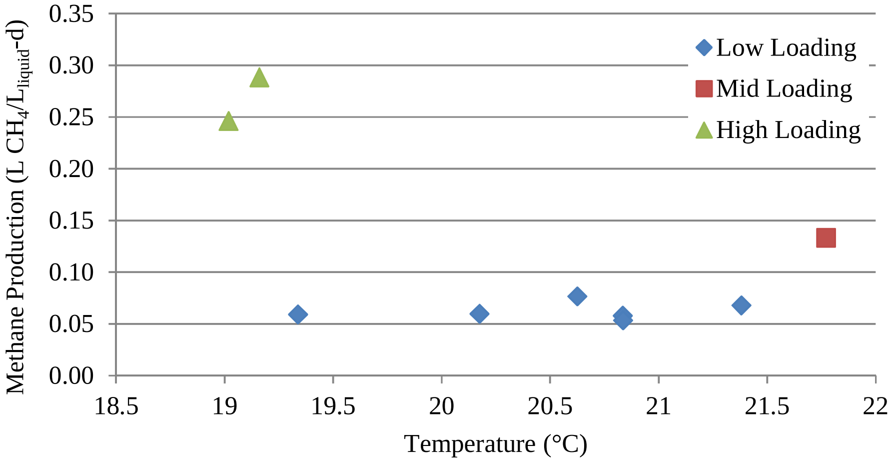


Figure 4.10: Temperature vs. methane production. Experimental results grouped by loading conditions. At low loading, methane production was unaffected by experimentally averaged temperature changes and at near-equal temperatures (19°C) a nearly six fold increase in methane production was identified.

To provide statistical evidence for the inconclusive influence of temperature on methane production, two simple hypothesis tests were generated through analysis of variance (ANOVA) for temperature categorized as above or below the mean of data set temperature of 20.52°C or in one degree increments between 19°C and 22°C (**Table 4.3**). Temperatures below 19°C and above 22°C were not included as there are limited data points in that range.

Table 4.3: Two hypothesis test conditions for temperature influence of methane. For production at low loading rates, grouped with mean methane production (L CH_4/L_{liquid}-d), standard deviation (SD) and the resulting p-value and total samples (n).

Hypothesis Test	Test Grouping	n	Mean Methane Production	SD of Methane Production	p-value
1	Below 20.52°C	40	0.059	0.016	0.131
	Above 20.52°C	67	0.064	0.014	
2	19°C - 20°C	16	0.062	0.017	0.122
	20°C - 21°C	41	0.060	0.014	
	21°C - 22°C	36	0.066	0.013	

Both hypothesis tests suggest that there was insufficient evidence of temperature influence on methane production. With a confidence interval of 0.95, the resulting p-values of 0.131 and 0.122 for these tests are well above 0.05 needed to reject the null hypothesis. Thus the alternate hypothesis was rejected and temperature was not influential on methane production. As a result, temperature was not included as a parameter in the methane production models.

Although research suggests an influence by temperature on methane production (Safley & Westerman 1994; Kim et al. 2006), and temperature conditions clearly affect microbial growth rates (Metcalf & Eddy 2003), the reason for the lack of temperature correlation may be due to daily and weekly temperature swings or the small average temperature range (14°C to 24°C). Further research in a controlled environment where temperature and organic loading could be more carefully regulated might provide evidence toward the influence of temperature on the production of methane for packed-bed digesters. As such, for this data set, no temperature factor was recommended for the models.

4.3.2 Model Validation

Model predicted methane production was plotted against the actual methane production by a linearity test. The linear methane production models from both the OLR of COD and VS were most representative, with the lowest S values and slope closest to one (**Figure 4.11**, **Figure 4.12**, **Table 4.4**). The VS loaded linear model was the best overall predictor of methane production from OLR (**Table 4.4**).

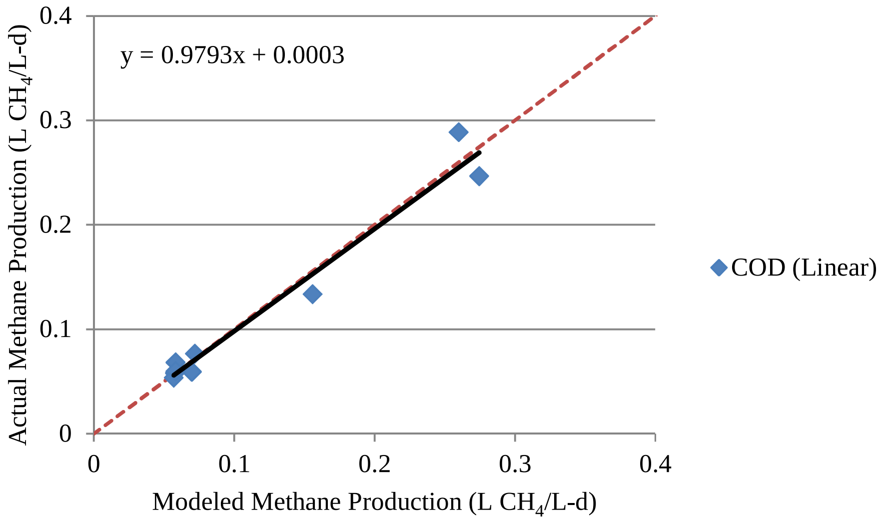


Figure 4.11: Linearity test of COD modeled methane production. Shown with actual methane production. The slope here was 0.9793 and the dashed red line indicates a slope of 1 (1:1).

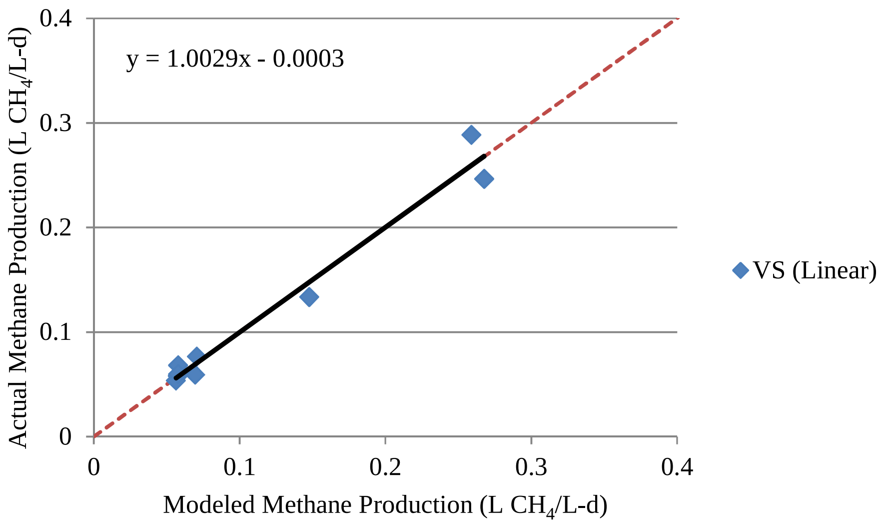


Figure 4.12: **Linearity test of VS modeled methane production.** Shown against actual methane production. This linearity test validated the linear VS loaded methane production model as being the most representative overall. The slope here is 1.0029 and the dashed red line indicates a slope of 1 (1:1).

Comparisons of the six attempted models from organic loading of COD and VS are tabulated for direct comparison (**Table 4.4**).

Table 4.4: Methane modeling results. Kinetic parameters (a & b), standard error of the regression (S) and linearity test slopes for COD and VS loading for the Monod, Power and Linear models, with equations. The best model is bolded.

Model Type	Equation	Loading Type	Kinetic Parameters a	b	S	Slope
Monod (Michaelis-Menten)	$y = \frac{aX}{b+X}$	COD	0.490	9.07	0.0255	0.939
		VS	0.476	5.57	0.0242	0.808
Power	$y = aX^b$	COD	0.055	0.671	0.0211	0.984
		VS	0.075	0.660	0.0193	0.979
Linear	$y = aX + b$	COD	0.023	0.037	0.0180	0.979
		VS	0.034	0.038	**0.0159**	**1.003**

Overall, the linear model from OLR of COD and VS proved to be the best fit for the experimentally averaged data sets, with the VS loading model being the most representative. The data from the VS model was both closest to the regression line by the standard error of the regression (S) as well as being closest in slope to an ideal model representing the data. The COD linear model however was also used throughout later sections of this paper as its statistical and linear validation results are very close to the VS model, allowing for use of both a COD and VS models for calculation and estimation purposes for a commercial scale dairy.

More data would have likely provided a better understanding of the influence of OLR on methane production. Approximately two months of methane production data could not be used for modeling during the freshwater flushing of the barns (August 2, 2012 to October 10, 2012) as the substrate itself was not representative of normal dairy operations at that time (R. Silacci 2012, pers. comm.). If the dairy had been recirculating water from the lagoon under normal conditions during that time, the data may have provided more mid-range OLRs and methane production values, which may have favored the Monod-type saturation model.

The stability of methane production in the final loading experiment (#6) was not reached due to time constraints. Such an unstable data set was not ideal for modeling and was not included. If stability had been achieved, saturation of methane production at higher loading rates may have been more evident and the linear model would have likely been less representative in comparison to Monod or power type models.

4.4 Porosity and Sludge Accumulation in the Walnut Shell Packed-bed

Several porosity tests were conducted over the course of the pilot digester experiments to highlight the rate of fouling and accumulation of sludge in the walnut shell packed-bed. On average, the initial porosity of 0.700 in the clean packed-bed was reduced to 0.341 by the end of the study and filled with an average sludge volume of 281.3 L (**Table 4.5**).

The degree of sludge accumulation was clearly evident when the packed-bed was opened at the end of the study. The rates of porosity reduction and sludge accumulation increased with time over the course of the experiments, indicating that fouling of the packed-bed was likely inevitable.

Table 4.5: Total tank porosity and sludge accumulation.

Tank	Date of Porosity Test	Porosity	% Porosity Change	Sludge Accumulation (L)
1A	9/13/2012	0.670	3%	23.8
1A	11/1/2012	0.575	12%	98.1
1A	12/10/2012	0.444	26%	200.6
1B	9/13/2012	0.613	9%	68.1
1B	11/1/2012	0.473	23%	178.5
1B	12/10/2012	0.315	38%	301.8
2A	9/13/2012	0.678	2%	16.9
2A	12/10/2012	0.362	34%	265.1
2B	12/10/2012	0.312	39%	304.3
3A	9/13/2012	0.676	2%	19.2
3A	11/7/2012	0.448	25%	197.6
3B	9/13/2012	0.566	13%	105.2
3B	12/10/2012	0.273	43%	334.9
Average porosity on 12/10/2012		0.341	36%	281.3

As a result, sludge accumulation was clearly problematic. Methods for sludge removal are necessary for continued operation of a packed-bed digester and are discussed in the companion thesis (Adler 2013).

4.5 Walnut Shell Degradation Results

Of the ten initially tagged walnut shells, eight were recovered from the packed-bed wattle cores of tanks D1A and D1B. Once cleaned, the digested shells were darker and grayer in appearance but maintained their rigidity. From digester inoculation in April, 2012 to the end of the study in December 2012, the tagged walnut shells lost an average of 31.4% of their original mass with a range of 20.7% to 42.6% (**Table 4.6**).

Table 4.6: Walnut shell degradation during digestion. Four samples were tested in each the feed and reservoir tanks of D1. Two samples were not recovered. No samples were collected from digesters D2 & D3.

Digester Tank	Initial Shell Mass (g)	Final Shell Mass (g)	% Change
1A	1.871	1.073	-42.6%
1A	1.528	1.076	-29.6%
1A	1.690	1.072	-36.6%
1A	1.477	1.074	-27.3%
1B	1.494	1.097	-26.6%
1B	1.623	1.078	-33.6%
1B	1.661	1.097	-33.9%
1B	1.349	1.070	-20.7%
Average	1.587	1.080	-31.4%

To generally understand biological degradation, four fresh walnut shells were incinerated at 550°C and an average ash content of 3.45% and a volatile (organic) fraction of 96.55% were recorded (**Table 4.7**).

Table 4.7: Volatile solids results for fresh walnut shells.

Sample	Shell (g)	% VS by Mass	% Ash
1	2.250	94.6%	5.40%
2	2.317	97.1%	2.89%
3	2.198	96.9%	3.15%
4	1.951	97.6%	2.37%
Average	2.179	96.6%	3.45%

The experiment then attempted to categorize the organic fraction of walnut shells into readily biodegradable and slow degrading components based on the cellulose, hemicellulose, lignin and ash composition of walnut shells at 21.0%, 18.8%, 32.7% and 2.02% respectively (**Table 4.8**) as percent of the total mass of the shell (Antal et al. 2000). Lignin is a non-carbohydrate organic molecule and is not considered to be easily biodegradable (Bugg et al. 2011). Cellulose and hemicellulose are considered more readily biodegradable and combined, they account for an average of 38.4% of the total walnut shell mass (**Table 4.8**).

Table 4.8: Readily biodegradable organic components of walnut shells. Based on fractions of lignin, hemicellulose and cellulose (Antal et al. 2000).

Sample	Volatile Mass (g)	Lignin (g)	Hemicellulose (g)	Cellulose (g)	% Readily Biodegradable
1	2.129	0.6961	0.4002	0.4470	37.7%
2	2.250	0.7358	0.4230	0.4725	38.7%
3	2.128	0.6960	0.4001	0.4469	38.5%
4	1.905	0.6228	0.3580	0.3999	38.9%
Average	2.103	0.6876	0.3953	0.4416	38.4%
% Total	96.6%	31.6%	18.1%	20.3%	38.4%

Assuming the loss of mass may be attributed to degradation, most of the readily biodegradable mass of the walnut shells was consumed within the eight month digestion period. It is likely however that the rate of degradation may slow as lignin becomes the majority component of the walnut shells once cellulose and hemi-cellulose have been degraded (Antal et al. 2000). Further and more careful testing of anaerobic walnut shell degradation is necessary to assess the long term viability for packed-bed digesters.

4.6 Economic Feasibility of Commercial Scale Packed-bed Digesters

Using the developed linear mathematical models for methane production with given organic loading rate, the quantity of methane and subsequent power and economic benefits for a hypothetical dairy were calculated. The inputs required to make these calculations are described in the methods section and further detailed in **Appendix C**. The overall economic outlook for dairies interested in packed-bed digesters is dependent on a multitude of factors. This paper attempts to describe the best and worst case situations, rather than choosing one particular set of input values. The best and worst case outcomes were estimated for economic feasibility as annual generated kilowatt hours and internal rates of return (IRRs). The two analyses, as described in the methods section were based respectively on the organic loading rate (as either COD or VS) and the population of milking cows at a dairy, assuming 56% of all cows, on average at dairies are milking cows (Spierling et al. 2009).

The linear model for methane production was chosen to predict methane output by population of milking cows and from organic loading rates. The results were calculated at 28% generator efficiency and 90% generator run time based on the organic loading rate and population of milking cows per dairy (**Figure 4.13**, **Figure 4.14**).

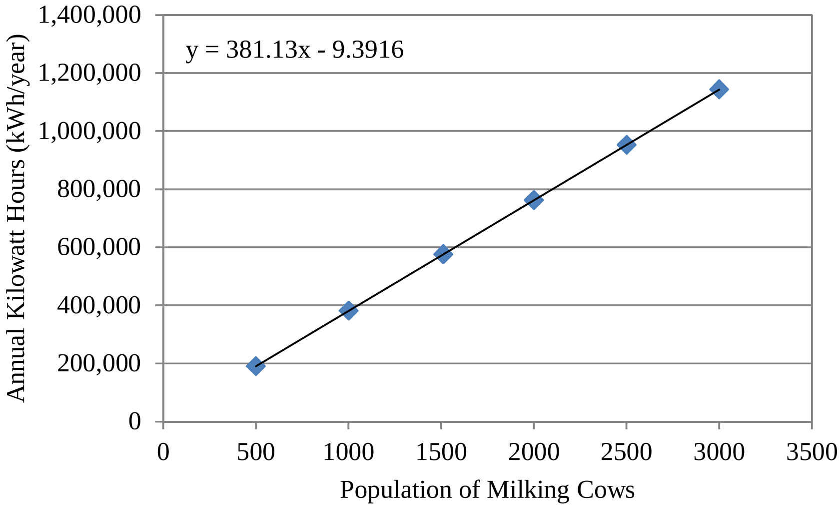


Figure 4.13: Annual kilowatt-hours of generated power based on milking cow population. Results are shown at a steady OLR of 5 g/L_{liquid}-d as COD or VS.

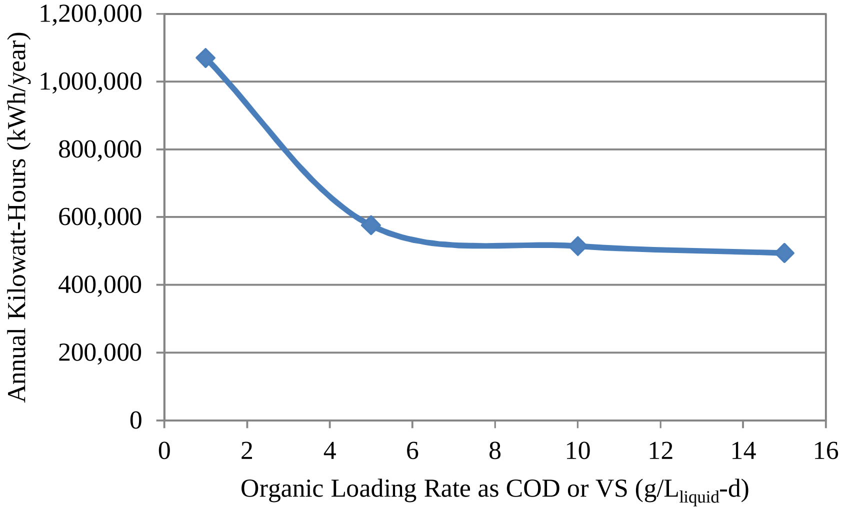


Figure 4.14: Annual kilowatt-hours of generated power based on organic loading rate (OLR). Milking cow population was held at 1,510 for this model.

Economic results were then introduced as IRRs. The results of the first analysis, based on organic loading, electrical rates (as $/kWh) and capital cost subsidies was rather poor, with the highest return at a 50% subsidy and electric rate of $0.20/kWh hovering just over 10% (**Figure 4.15**). As a result, higher loading rates do not substantially increase IRR for packed-bed digesters. As loading rate increases, the digester size decreases along with capital costs, however the daily output of methane was also reduced with digester size, nominally changing the benefits for high loading of packed-bed digesters.

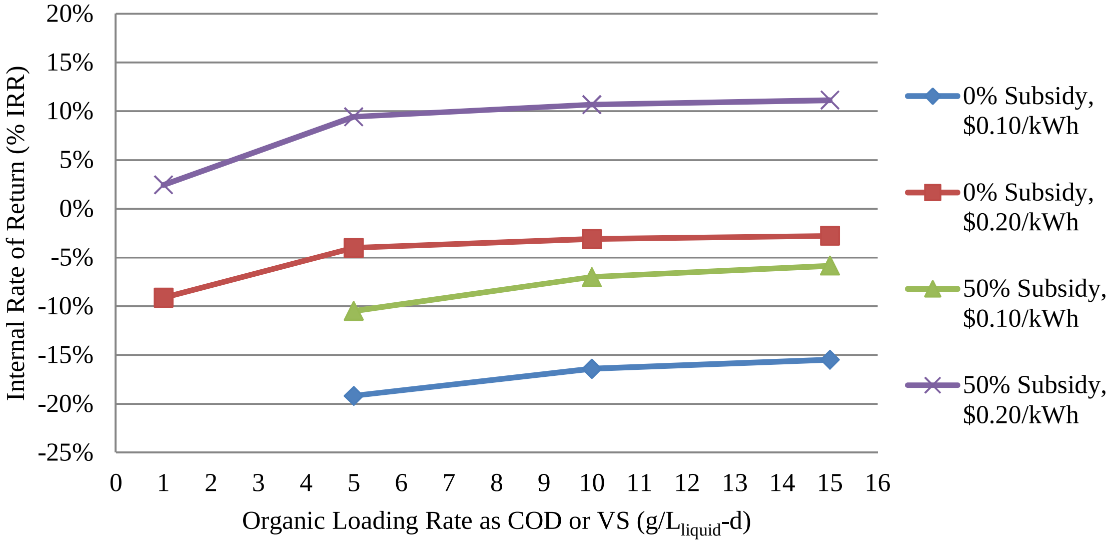


Figure 4.15: Benefits (IRR) for various rate and subsidy conditions by organic loading rate. Milking cow population for this analysis was held constant at 1,510 cows per dairy. The lowest loading rates for the bottom two curves are well below economic feasibility and were not included.

The second analysis presents the IRR based on milking cow population at the same subsidy and electrical rate parameters as described above. Organic loading was held at 5 g/L_{liquid}-d, which was the approximate mid-point of the pilot study (**Figure 4.16**).

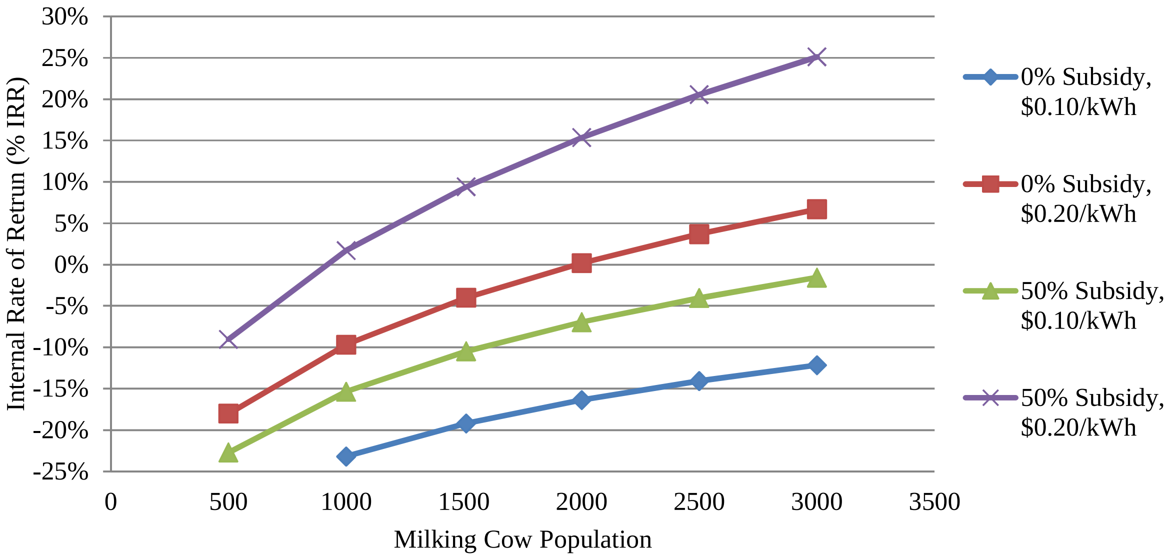


Figure 4.16: Benefits (IRR) for various rate and subsidy conditions by milking cow population. Organic loading for this analysis was held at 5 g/L_{liquid}-d as COD or VS.

As expected, an increase in subsidies and electric rates improves the economic outlook for dairies interested in packed-bed technology. Unfortunately, most of these conditions in both analyses describe a relatively poor economic outlook for packed-bed digesters as the “hurdle” IRR of 17% (PIER 2008) was rarely met to avoid investment risks.

Several conditions may improve the economic outlook for dairies interested in constructing a packed-bed digester, including: further subsidies, obtaining used equipment, use of pre-existing infrastructure (anaerobic lagoons, primary treatment, etc.), better electric rates, lower interconnection charges, recirculation and reduction in sludge accumulation.

5 CONCLUSIONS

The three walnut shell packed-bed digesters were operated for 226 days at the California Polytechnic State University, San Luis Obispo Dairy. Freestall flush water was digested under a variety of loading conditions and the resulting effluent and biogas characteristics were measured and analyzed. Each digester comprised of two 1135-L tanks which were mixed by reciprocation and filled with walnut shells as a packed-bed media for biofilm attachment. The influence of methane production from organic loading rates (OLRs) of chemical oxygen demand (COD) and volatile solids (VS) as well as temperature were investigated by mathematical modeling. The best model was validated and used to predict methane production at commercial-scale dairies. A basic economic analysis was then performed to investigate the financial feasibility of commercial-scale packed-bed digesters. Additional studies measured the accumulation of sludge in the walnut shell packed-bed as well as the degradation rates and feasibility of walnut shells as media for packed-bed digesters. The objectives are summarized below.

5.1 Biogas Characteristics, Methane Production and Organic Loading

During the study period biogas contained an average methane concentration of 86.7 ± 4.4% and a carbon dioxide concentration of 10.7 ± 5.7% with the remaining gases a balance of nitrogen, hydrogen sulfide and organic compounds. Over time, the concentration of methane in the biogas steadily increased while the carbon dioxide concentration decreased. The reduction of carbon dioxide in the biogas may be attributed to an increase of CO_2 solution into the flush water as the hydraulic loading was simultaneously increased. Weekly average methane production during the study period ranged from 0.046 to 0.382 L CH_4/L_{liquid}-day with an average of 0.135 ± 0.083 L

CH_4/L_{liquid}-day. The term L_{liquid} was the actual combined liquid flush water inside both tanks of each digester which remained constant at 1135 L. Organic loading was calculated as COD or VS in units of g/L_{liquid}-day. Organic loading by COD ranged from 0.139 to 19.855 g COD/L_{liquid}-day with an average of 5.490 ± 5.777 g COD/L_{liquid}-day. Organic loading by VS ranged from 0.081 to 13.87 VS/L_{liquid}-day with an average of 3.59 ± 3.88 g VS/L_{liquid}-day.

5.2 Methane Modeling Conclusions

Three models of the forms: Monod-type saturation, power and linear were attempted for both organic loading data sets, of COD and VS. The best model was found by statistical comparison of the standard error of the regression (S) as a measure of closeness of fit and then validated with a test for linearity as described in the methods section. For the two COD and VS data sets, the best models for estimation of methane production were linear (y=ax+b) with alpha and beta parameters for COD loading at 0.023 and 0.037 respectively, while for VS loading those parameters were 0.034 and 0.038. The Monod-type model was expected to outperform others for the data sets based on literature review (Yu et al. 1998; Ahn & Forster 2000) however its representation of the methane production curves was the poorest for this study. The power model was the second-best model for methane production.

The influence of temperature on methane production was also evaluated as a potential second input parameter to the production models. Temperature however was not found to significantly influence methane production and was not included in the methane production models.

5.3 *Porosity and Sludge Accumulation*

Fouling of the walnut shell packed-bed by sludge and the associated decrease in porosity was an unfavorable result of the study. On average, 281 ± 46 liters of sludge accumulated in each of the digester tanks by the end of the study and the porosity dropped from 0.70 at startup (clean walnut shells) to an average of 0.34 ± .06, a 36% reduction in pore space volume. Accumulation of sludge in the packed-bed was found to reduce hydraulic retention times as well as treatment of COD and reciprocation mixing did not appear to reduce accumulation (Adler 2013).

5.4 *Walnut Shell Durability and Degradation*

The short and long term durability of walnut shells was estimated by initial and final investigation from which several tagged shells were placed into the digester for approximately eight months from startup in April 2012 to the end of the study in December 2012 and were then assessed at the end of the study. The shells lost an average mass of 31.4 ± 6.3% over the digestion period. Walnut shells comprise of mostly volatile matter including: lignin, hemicellulose and cellulose with some additional non-volatile material. Lignin is more difficult to degrade (Bugg et al. 2011) while cellulose and hemicellulose is considered “readily biodegradable” (Antal et al. 2000). This experiment makes the assumption that the average mass lost during the study period was associated with decomposition of readily biodegradable components of the walnut shell. Lignin, being more difficult to degrade would therefore be the remaining predominant compound of the shells once the readily biodegradable substances had been consumed by microbes in the digester, suggesting that the rate of degradation may slow once the more readily degradable substances of the walnut shell have been consumed. It is interesting to note that after losing nearly one third of their mass during the digestion period, the walnut shells retained much of their rigidity and continued to "crack" with applied pressure.

5.5 Economic Feasibility for Commercial-Scale Packed-Bed Digesters

The economic feasibility of packed-bed digesters was calculated based on an extensive spreadsheet which estimated the annual kilowatt-hours of power which could be produced based on the organic loading rate and the milking cow population of a dairy. Annual electricity (as kilowatt-hours) increased linearly from 191,000 to 1,143,000 kWh/year as milking cow population increased from 500 to 3000. Annual power decreased with organic loading from 1,069,000 kWh per year and leveling at approximately 495,000 kWh per year. Methane production in a smaller digester will yield less overall methane and annual power when converted to kilowatt hours per year. With the predicted annual power production, the economic feasibility represented as internal rate of return (IRR) was calculated as a 10 year investment and was based on retail electric prices as well as available subsidies. Retail rates of \$0.10 and \$0.20 per kilowatt-hour and capital cost subsidies ranging from zero to 50% provided a range of outcomes from worst to best case scenarios. IRRs were calculated based on milking cow population as well as organic loading. IRR increased substantially with milking cow population, with the highest calculated economic results above 25%. Many outcomes however are below the "hurdle" IRR for dairies, at 17% (PERI 2008) and several are below zero. The economic outlook based on organic loading was less favorable with a maximum IRR at 11.1% at high subsidy and electrical rates and again with several outcomes below zero at low subsidies and electric rates. These ranges are an attempt to categorize packed-bed digesters for further comparison by those interested in the development of packed-bed digester technology on a commercial scale. Ultimately, the current economic outlook for packed-bed digesters operating at dairies is not particularly feasible however increased focus and study may make them a viable solution for power production and GHG reduction in the future.

5.6 Limitations of Study

The three digesters were constructed outdoors at the dairy and were subject to weather, temperature fluctuations and occasional mechanical breakdowns. Barn flushing was controlled by dairy staff and neither the volume of flush water nor the concentration of flush water chemicals was constant. Research was further hampered by the two month, fresh water flushing of the barns as described in the methods section. Finally, the use of fresh water at a commercial dairy, particularly given the current severe drought in California would not be a likely commercial-scale solution to cleaning freestall barns.

5.7 Future Research

A replication of this study in a laboratory setting with well controlled temperature, flush water COD and VS concentrations and organic loading would likely reveal more suitable data for methane production modeling. A more detailed evaluation of the effects of temperature on anaerobic digestion of flush dairy manure, carefully controlled in the laboratory would likely reveal a positive trend of methane production and increased temperature (Safley & Westerman 1994; Kim et al. 2006) which could further benefit the methane production model.

Evaluation of techniques for the elimination or reduction of sludge accumulation may allow for longer continued operation of packed-bed digesters in the future. These techniques may include backwashing, gas sparging or the use of media with larger voids for sludge to settle and be removed via gravity or vacuum.

Long term (>1 year) evaluation of walnut shells and other nut or organic residues as packed-bed media should be studied for anaerobic digesters. Other crop residues may be suitable for packed-bed digesters and comparisons should be made to assess the best media for a particular location.

Further evaluation and comparison of the economic feasibility of packed-bed digesters at commercial dairies is needed. This paper attempts to make a basic assessment, however the limitations of the study, modeling results and lack of temperature influence on methane production likely affect the overall economic results. A multi-disciplinary study of packed-bed digesters under more ideal conditions would likely provide further and more representative economic predictions for commercialization.

REFERENCES

Adler, N. (2013). “Dairy Manure Flushwater Treatment By Packed-Bed Anaerobic Digesters”. MS Thesis, Civil and Environmental Engineering Department, California Polytechnic State University, San Luis Obispo.

ADS (2014). “Arc Chambers.” Retrieved September 2014. <http://www.ads-pipe.com/en/product.asp?page=arc_chambers>

Ahn, J.-H., Forster, C. F. (2000). “Kinetic analysis of the operation of mesophilic and thermophilic anaerobic filters treating a simulated starch wastewater.” *Process Biochemistry (36)*, pp 19-23.
PII: S0032-9592(00)00166-7.

Alberta Agriculture and Rural Development (ARD), Navaratnasamy, M., Jones, J., Partington, B. (2008). “Biogas: cleaning and uses.” Retrieved July 2014. <http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/agdex12276>

American Public Health Association (APHA). (2006). “Standard Methods for the Examination of Water and Wastewater”. *American Water Works Association, and Water Environment Federation.*

Antal M.J., Allen, S.G., Dai, X., Shimizu, B, Tam, M.S., Grønli, M. (2000). “Attainment Of The Theoretical Yield Of Carbon From Biomass”, *Industrial & Engineering Chemistry Research (39)*, pp. 4024-4031.
DOI: 10.1021/ie000511u

Austin, Anna (2013). “Methane Migrane.” Retrieved June, 2013. <http://biomassmagazine.com/articles/3377/methane-migraine>

Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A., Sanders, W. T. M., Siegrist, H., Vavilin, V. A. (2002). “The IWA anaerobic digestion model No. 1 (ADM1).” *Water Science and Technology (45)* 10, pp 65-73.

Bialek, K., Cysneiros, D., O’Flaharty, V. (2013). “Low-temperature (10°C) anaerobic digestion of dilute dairy wastewater in an EGSB bioreactor: microbial community structure, population dynamics, and kinetics of methanogenic populations.” *Hindawi Publishing Corporation;Archaea (2013)*, Article ID 346171, 10 Pages.

Bryant, D. (2006). “Methane digester converts dairy manure to electricity.” *Western Farm Press.* Accessed July, 2014. < http://westernfarmpress.com/methane-digester-converts-dairy-manure-electricity>

Bugg, T.D., Ahmad, M., Hardiman, E. M., Rahmanpour, R. (2011). “Pathways for degradation of lignin in bacteria and fungi.” *Nat. Prod. Rep 28(12)*, pp 1883-1896.
DOI: 10.1039/c1np00042j

California Air Resources Board (CARB) (2006). “California global warming solutions act of 2006.” Retrieved March 2013. <http://www.leginfo.ca.gov/pub/05-06/bill/asm/ab_0001-0050/ab_32_bill_20060927_chaptered.pdf>

California Air Resources Board (CARB) (2008). “Ozone And Ambient Air Quality Standards”. Retrieved October 2013. <http://www.arb.ca.gov/research/aaqs/caaqs/ozone/ozone.htm>

California Air Resources Board (CARB) (2012). “Compliance Offset Protocol Livestock Projects.” Retrieved July, 2013. <http://www.arb.ca.gov/cc/capandtrade/protocols/livestock/livestock.htm>

California Environmental Protection Agency (CalEPA) (2011). “Permit guidance for anaerobic digesters and co-digesters.” *Version 2*. Retrieved June 2014. <http://www.calepa.ca.gov/digester/Documents/GuideDigester.pdf>

California Milk Advisory Board (2013). “California – The Nation’s Dairy Leader.” Retrieved April, 2013. <http://www.californiadairypressroom.com/Press_Kit/Nations_Dairy_Leader>

Chen, Y. R., Hashimoto, A. G. (1980). “Substrate utilization kinetic model for biological treatment processes.” *Biotechnology and Bioengineering (22)*, pp 2081-2095.

Chartered Institute of Management Accounts (CIMA) (2012). “Spreadsheet skills: modified internal rate of return (MIRR).” Retrieved November, 2014. <http://www.cimaglobal.com/Thought-leadership/Newsletters/Insight-e-magazine/Insight-2012/Insight-March-2012/Spreadsheet-skills-modified-internal-rate-of-return-MIRR/>

Collar, C., T. Shultz, N. Peterson, A. Wubishet, G. Higginbotham (c1995). *California Dairy Energy Project*, Dairy and Livestock Research Report, UC Cooperative Extension, pp. 10.

Dusault, A., (2007). “Mitigating methane emissions from dairy waste; The California challenge.” *Sustainable Conservation.* Retrieved July 2014. <http://www.arb.ca.gov/cc/symposium/030507symp/docs/8dusault_methane.pdf>

EPA AgStar. (2011). “Recovering Value From Waste. Anaerobic Digester System Basics.” Retrieved October 2013. <http://www.epa.gov/agstar/documents/recovering_value_from_waste.pdf>

Frost, J. (2014). “Regression analysis: how to interpret S, the standard error of the regression.” *The Minitab Blog*, *Minitab Inc.* Accessed June, 2014. < http://blog.minitab.com/blog/adventures-in-statistics/regression-analysis-how-to-interpret-s-the-standard-error-of-the-regression>

Grau, P., Dohányos, M., Chudoba, J. (1975). “Kinetics of multicomponent substrate removal by activated sludge.” *Water Res. (7)*9, pp 637–642.
DOI: 10.1016/0043-1354(75)90169-4

Hart, S. A., Turner, M. E. (1965). “Lagoons for livestock manure.” *J. Water Pollution Control Federation), 37* (11) pp. 1578-1596.

Hashimoto, A. G. (1982). “Methane from cattle waste: effects of temperature, hydraulic retention time, and influent substrate concentration on kinetic parameter (K).” *Biotechnology and Bioengineering (24),* pp. 2039-2052.

Henneman, S. (2011). “Water and air quality performance of a reciprocating biofilter treating dairy wastewater.” Master’s Thesis at California Polytechnic State University, San Luis Obispo.

Henze, M., & Harremoës, P. (1983). “Anaerobic treatment of wastewater in fixed film reactors—a literature review.” *Water Science & Technology, 15*(8-9), 1-101.

Hill, D. T. (1983). “Simplified Monod kinetics of methane fermentation of animal wastes.” *Agricultural Wastes (5),* pp 1-16.

Hill, D. and Bolte, J. (1992). “Bio-Retentive Properties Of Synthetic Media For Anaerobic Digestion Of Animal Waste.” *American Society of Agricultural Engineers,* vol. 35, issue 2.

Hurley, S., Summer, M. D. (2013). “An economic analysis of six dairy digester systems in California; Report 2 of 2.” *Prepared for: California Energy Commission.*

IPCC – Intergovernmental Panel on Climate Change, (2007). “2.10.2 Direct Global Warming Potentials.” *IPCC Fourth Assessment Report: Climate Change 2007: Working Group I: The Physical Science Basis,* Ch. 2.10.2. Retrieved November 2013. <http://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-10-2.html>

Kane, J. (2010). “Water quality performance of a reciprocating biofilm reactor for treatment of dairy wastewater.” Master’s Thesis at California Polytechnic State University, San Luis Obispo.

Kim, J., Oh, B., Chun, Y., Kim, S. (2006). “Effects of temperature and hydraulic retention time on anaerobic digestion of food waste.” *Bioscience and Bioengineering (102)*4, pp 328-332.
DOI: 10.1263/jbb.102.328

Krich, K., Augenstein, D., Batmale, J. P., Benemann, J., Rutledge, B., Salour, D. (2005). “Biomethane from dairy waste; A sourcebook for the production and use of renewable natural gas in California.” *Prepared for: Western United Dairymen.*

Lawrence, A. W., McCarty, P. L. (1969). “Kinetics of Methane Fermentation in Anaerobic Treatment.” *Water Pollution Control Federation (41)* 2, pp R1-R17.

Lee, Seunghwan., Lee, H., Lee, S., Chitapornpan, S., Chiemchaisri, C., Polprasert, Ahn, K. (2007). “Media configuration and recirculation of upflow anaerobic floating filter for piggery wastewater treatment.” *Korean Journal of Chemical Engineering 24(6),* pp. 980-988.

Liao, P. H., Lo, K. V. (1985). “Methane production using whole and screened dairy manure in conventional and fixed-film reactors.” *Biotechnology and Bioengineering, 27,* pp 266-272.

Lin, Y., Wang, D., Li, Q., Huang, L. (2011). “Kinetic study of mesophilic anaerobic digestion of pulp and paper sludge.” *Biomass and Bioenergy (35),* pp 4862-4867. DOI:10.1016/j.biombioe.2011.10.001

Lory, J., Massey, R., Zulovich, J. (2010). “An Evaluation Of The Usepa Calculations Of Greenhouse Gas Emissions From Anaerobic Lagoons.” *Journal of Environmental Quality (39),* pp. 776-783.
DOI: 10.2134/jeq2009.0319.

Ma, J., Yu, L., Frear, C., Zhao, Q., Li, X., Chen, S. (2013) “Kinetics of psychrophilic anaerobic sequencing batch reactor treating flushed dairy manure.” *Bioresource Technology (131),* pp 6-12. DOI:10.1016/j.biortech.2012.11.147

Martin, J. H. (2008). “An Evaluation of a Covered Anaerobic Lagoon for Flushed Dairy Cattle Manure Stabilization and Biogas Production.” *AgSTAR Program*. Accessed April, 2013. <http://www.epa.gov/agstar/documents/flushed_dairy_cattle.pdf>

Martín, A., Borja, R., García, I., Fiestas, J. A. (1991). “Kinetics of methane production from olive mill wastewater.” *Process Biochemistry (26),* pp 101-107.

Metcalf & Eddy (2003). "Wastewater Engineering, Treatment and Reuse.” New York, McGraw-Hill Companies Inc.

Michaelis, L., Menten, M. (1913). “Die kinetik der invertinwirkung/The kinetics of invertase action.” Translated from German by Goody, R. and Johnson, K.

Mitloehner, F. Ph.D. (2006). “Measurement of GHG Emissions from Dairy Farms.” *Climate Change Research Conference, Sacrament, California,* September 13, 2006. <http://www.climatechange.ca.gov/events/2006_conference/presentations/2006-09-13/2006-09-13_MITLOEHNER.PDF>.

Monod, J. (1949). “The growth of bacterial cultures.” *Annual Review of Microbiology (3),* pp 371-394.

Nahai, D., Lewis, Brisbois, Bisgaard & Smith, (2011). “California’s SB X 1-2 Law Walks Renewable Energy Tightrope,” Retrieved September 2013. <http://www.renewableenergyworld.com/rea/news/article/2011/06/californias-sb-x-1-2-walks-renewable-energy-tightrope>

Narihiro, T., Sekiguchi, Y. (2007). “Microbial communities in anaerobic digestion processes for waste and wastewater treatment: a microbiological update.” *Current Opinion in Biotechnology, (18)*, pp 273-278. DOI: 10.1016/j.copbio.2007.04.003

National Agricultural Statistics Service, USDA (2012). “2012 California walnut objective measurement report.”

Natural Resources Conservation Service (NRCS) – USDA, (2008). “Agricultural Waste Characteristics.” *Agricultural Waste Management Field Handbook*, ch. 4, pp 13. <ftp://ftp.wcc.nrcs.usda.gov/wntsc/AWM/handbook/ch4.pdf>

Occupational Safety and Health Administration (OSHA), (n.d.). “Hydrogen Sulfide.” Retrieved September 2014. <https://www.osha.gov/SLTC/hydrogensulfide/hazards.html>

Pacific Gas & Electric Company (PG&E), (2013). Electric Rates: Large Agricultural (OCT 1, 2013-Present).” Retrieved October 2013. <http://www.pge.com/nots/rates/tariffs/electric.shtml>

Pacific Gas & Electric Company PG&E[a] (2014). “Agricultural customers.” Retrieved July 2014. <http://www.pge.com/about/rates/rateinfo/rateoptions/agricultural/>

Pacific Gas & Electric Company PG&E[b] (2014). Electric schedule AG-4 time-of-use agricultural power.” Retrieved July 2014. <http://www.pge.com/tariffs/tm2/pdf/ELEC_SCHEDS_AG-4.pdf>

Pacific Gas & Electric Company PG&E[c] (2014). “Net energy metering for biogas digester generators.” Retrieved March 2014. <http://www.pge.com/b2b/newgenerator/netenergymetering/biogasnem/index.shtml>

Powers, W., Wilkie, A., Van Horn, H., Nordstedt, R. (1997). “Effects of hydraulic retention time on performance and effluent odor of conventional and fixed-film anaerobic digesters fed dairy manure wastewaters.” *Transactions of the ASAE (40)*5, pp. 1449-1455.

Princeton Energy Resources International, LLC (PERI). (2008). “Economic Study of Bioenergy Production from Digesters at Dairies in California.”

Raposo, F., Borja, R., Sánchez, E., Martín, M. A., Martín, A. (2004). “Performance and kinetic evaluation of the anaerobic digestion of two-phase olive mill effluents in reactors with suspended and immobilized biomass.” *Water Research (38),* pp 2017-2026.
DOI:10.1016/j.watres.2004.01.007

Safley, L. M., Westerman, P. W. (1994). “Low-temperature digestion of dairy and swine manure.” *Bioresource Technology (47),* pp 165-171.

San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel (SJFAP). 2005. “An Assessment of Technologies for Management and Treatment of Dairy Manure in 30 California’s San Joaquin Valley.” Accessed May, 2013. <http://www.arb.ca.gov/ag/caf/dairypnl/dmtfaprprt.pdf>

Senturk, E., Ýnce, M., Onkal Engin, G. (2013). “Assessment of kinetic parameters for thermophilic anaerobic contact reactor treating food-processing wastewater.” *Int. J. Environ. Res. (7)*2, pp 293-302. *ISSN: 1735-6865*

Shelford, T. (2012). “Estimating farm size required to economically justify anaerobic digestion on small dairy farms.” *Got Manure? Enhancing Economic and Environmental Sustainability.* Retrieved July 2014.
<http://www.epa.gov/agstar/documents/conf12/11b_Shelford.pdf>

Schmidt, R. (2013). “Understanding the difference between NPV vs IRR.” Retrieved November, 2014.
<http://www.propertymetrics.com/blog/2013/06/28/npv-vs-irr/>

Silacci, R (2013). Personal communication, Dairy Herd Manager, California Polytechnic State University, San Luis Obispo, March 21, 2013.

Southern California Edison (SCE). (2004). “Dairy Farm Energy Management Guide: California.”
<https://www.sce.com/NR/rdonlyres/60CC09E0-2EE1-4087-B46F-51527CC0906D/0/CompleteGuide_102005REV.pdf>

Southern California Edison SCE[a] (2014). “Agricultural and pumping rates.” Retrieved July 2014. <http://goo.gl/32i1vi> Note: URL shortened by Google.

Southern California Edison SCE[b] (2014). “Schedule TOU-PA-2 time-of-use agricultural and pumping – small to medium.” Retrieved July 2014.
<https://www.sce.com/NR/sc3/tm2/pdf/CE340.pdf>

Southam, J. (2010). Personal communication, Farmer, Southam Farms, Inc, Butte City, California. November 2010.

Spierling, R.E., Albinger, L.C. & Lundquist, T.J. (2009). “Projected Performance And Costs Of Wastewater Treatment At California Flush Dairies.” Final report, USEPA, Region 9, Award No. EP089000064.

Toerien, D. F., Hattingh, W. H. J. (1969). “Anaerobic Digestion I. The microbiology of anaerobic digestion.” *Water Research, 3,* pp. 385-416.

Umaña, O., Nikolaeva, S., Sánchez, E., Borja, R., Raposo, F. (2008). “Treatment of screened dairy manure by upflow anaerobic fixed bed reactors packed with waste tyre rubber and a combination of waste tyre rubber and zeolite: effect of the hydraulic retention time.” *Bioresource Technology, 99,* pp 7412-7417. DOI:10.1016/j.biortech.2008.01.009

United States Environmental Protection Agency (EPA), (1991). “Hydrogen Sulfide Corrosion: Its Consequences, Detection and Control.” *Office of Water, Article WH-595.* Retrieved September 2014. <http://nepis.epa.gov/Exe/ZyPDF.cgi/200048ZZ.PDF?Dockey=200048ZZ.PDF>

Vartak D.R., Engler, C.R., McFarland, M.J., Ricke, S.C. (1997). “Attached-Film Media Performance In Psychrophilic Anaerobic Treatment Of Dairy Cattle Wastewater.” *Bioresource Technology,* (62) 79-84. PII: S0960-8524(97)00135-1

Wendt, D. (2011). Personal communication. Manager, Nutrinut, Inc., Visalia, California, June 15, 2011.

Wilkie, A. C. (2000). “Reducing dairy manure odor and producing energy.” *BioCycle (41) 9,* pp. 48-50.

Wilkie, A. C. (2003). “Anaerobic digestion of flushed dairy manure.” Proceedings from Anaerobic Digester Technology Applications in Animal Agriculture – A National Summit, Alexandria, Virginia. *Water Environment Federation*, pp. 350-354

Wilkie, A.C., Castro, H. F., Cubinski, K. R., Owens, J. M., Yan, S. C. (2004). “Fixed-film anaerobic digestion of flushed dairy manure after primary treatment: wastewater production and characterization.” *Biosystems Engineering*, *89*(4), pp 457-471. DOI:10.1016/j.biosystemseng.2004.09.002

Wilkie, A. C. (2005). “Anaerobic Digestion Of Dairy Manure: Design And Process Considerations.” *Dairy Manure Management: Treatment, Handling, and Community Relations. NRAES (176),* pp 301-312.

Wilkie, A. C. (2013). “Biogas use.” Retrieved July 2014. <https://biogas.ifas.ufl.edu/uses.asp>

Williams, D., Gould-Wells, D. (2003). "Biogas Production From A Covered Lagoon Digester And Utilization In A Microturbine," *American Society of Agricultural Engineers*, Presented on July 30, 2003, ASAE Annual International Meeting, Las Vegas, Nevada.

Williams, D. (2005). "What the future looks like in farm-scale digestion." *BioCycle*, Presented March 7-9, 2005, BioCycle 5th Annual Conference on Renewable Energy from Organics Recycling, San Francisco, California.

Wise, D. L., Wentworth, R. L., Ashare, E. (1979). "Methane production from biomass and agricultural residues." *Ind. Eng. Chem. Prod. Res. Dev. 18* (2).

Yu, H., Wilson, F., Tay, J. (1998). "Kinetic analysis of an anaerobic filter treating soybean wastewater." *Wat. Res. 32* (11), pp 3341-3352.
PII: S0043-1354(98)00102-X

Zaher, U., Frear, C., Pandey, P., Chen, S. (2008). "Evaluation of a new fixed-bed digester design utilizing large media for flush dairy manure treatment." *Bioresource Technology, 99*, pp 8619-8625.
DOI:10.1016/j.biortech.2008.04.034

Zhang, Z., (2007). "Lessons Learned On California Dairy Digesters." *Power-Gen Renewable Energy and Fuels, Conference, March 6-8, 2007.*

Appendix A Detailed Methods

Specific details for biogas measurement by gas chromatography, porosity measurement methods, sludge accumulation and walnut shell degradation are presented in the following sections.

A.1 Biogas Analysis by Gas Chromatography

Biogas emitted from the digesters was brought to the lab and tested for a variety of compounds using a gas chromatograph (GC). Gases of interest were methane, carbon dioxide, nitrogen and oxygen. Hydrogen sulfide, although apparent due to its signature "rotten egg" odor, was not tested as its concentration was below the detection limit of the equipment. Oxygen was measured to signal any digester leaks or explosion potential when mixed with methane.

Biogas from each of the three digesters was measured on a weekly basis using the gas chromatograph (GC) column method with an SRI Gas Chromatograph (8500, SRI Instruments, Torrance, California) operating at 40°C and 45 psi with Argon Spec carrier gas (Praxair, Danbury, Connecticut). Samples were collected from each digester via quick-connect fittings into 1-L Tedlar bags (EG-PP1, Zefon International, Ocala, Florida). One milliliter gas samples were obtained through septa valves located on the Tedlar bags and were then inserted into the GC with a #23 BD needle (301025, BD, Franklin Lakes, New Jersey). The gas chromatograph was coupled with PeakSimple® Software (SRI Instruments, Torrance, California) to record each gas peak, which corresponded to a particular component percentage in the biogas. The GC was calibrated before each use with carefully-made gas mixes of CO_2 and CH_4 at concentrations of 5% & 95%, and 30% & 70% respectively and the resulting peak heights were recorded.

These values were above and below the typical methane and carbon dioxide concentrations, allowing for interpolation. Additional calibration mixes were prepared if the biogas concentrations were not between the calibration gas values. Air (as nitrogen and oxygen) and low (<5%) nitrogen calibration mixes were also prepared. The peak height of each biogas sample was measured by PeakSimple® and the biogas CO_2 and CH_4 concentrations were calculated by interpolation between the known calibration gas mix concentrations. Splits were conducted on each sample and gas mix. If split results were in error more than 10%, a triplicate test was performed.

A.2 Packed-bed Porosity and Sludge Accumulation Measurement

Porosity was measured as an indicator of sludge accumulation by determining the volume of void space within the walnut shell packed-bed. As walnut shells appear to be an untested medium for packed-bed digesters, the degree and rate of sludge accumulation was unknown. The porosity was measured on four occasions during digester operation.

Porosity was described as any void space in the packed-bed not comprised of walnut shells. To calculate initial porosity of the packed-bed in the digesters, a 4-L bucket was filled to 3.5-L with 1.27-cm sieved walnut shells and filled with tap water. The shells were well mixed in the water to ensure that no air bubbles had become trapped within the shells. The water was then carefully poured out and measured. The water volume divided by the total walnut shell volume resulted in the porosity. The procedure was replicated five times, resulting in porosities of 0.743, 0.702, 0.693, 0.692 and 0.689 with an average porosity of 0.702. For the pilot-scale tanks, the initial walnut shell porosity in the packed-bed was assumed to be 0.70. The packed-bed dimensions for each tank were identical, with diameter of 88-cm and height of 132-cm.

The porosity of the packed-beds was calculated four times, on September 13, 2012, November 1, 2012, November 7, 2012 and December 10, 2012. Because porosity information was desired during the main anaerobic experiments, it was not possible to open the tanks and drain all the liquid as was done with the initial bucket test. The "reciprocation" mode of each digester however made it easy to transfer flush water from one tank to the next while measuring the volume en route. The removed liquid was measured with either a flow meter (Great Plains Industries, Inc., Wichita, Kansas) or by repeatedly filling a drum to a measured 30-L mark. The liquid level in the sump was measured at the beginning and end of the flush water removal, accounting for any tank pressure. Flush water was only removed within a portion of the packed-beds and not the underdrain. The digesters were not exposed to oxygen during this procedure. With the measured volume of flush water, change in liquid height of the packed-bed and the known dimensions of the packed-bed, it was possible to calculate porosity.

$$Porosity = \frac{V_{flush\ water}}{\Delta H_{flush\ water} * A_{PB}}$$

Where:

$V_{flush\ water}$	Measured volume of flush water removed from the digesters
$\Delta H_{flush\ water}$	Measured difference in liquid height of flush water at beginning and end of flush water removal.
A_{PB}	Cross-sectional area of the packed-bed with 88-cm diameter.

Accumulation of sludge as a fraction of packed-bed volume was simply the difference of initial porosity minus the porosity estimated by later tests. Multiplication of the sludge accumulation fraction with the total packed-bed volume (88-cm diameter and 132-cm height) resulted in a sludge volume at a particular time. The daily changes in porosity were linearly interpolated between measurement dates.

$$V_{sludge-i} = (0.70 - P_i) * V_{PB}$$

Where:

$V_{sludge-i}$	Volume of sludge at a particular time
P_i	Porosity of walnut shells at a particular time
V_{PB}	Overall volume of packed-bed (88-cm diameter, 132-cm height)

A.3 Walnut Shell Degradation Methods

Walnut shell degradation rates were calculated by the mass lost over the course of the digester operation. Of particular interest were the rates of degradation and the chemical composition of walnut shells, including cellulose, hemicellulose and lignin. Cellulose and hemicellulose may be calculated with the following equations (Antal et al. 2000):

$$Cellulose = 0.9 * (\%\ glucose)$$

$$Hemicellulose = 0.9 * (\%\ galactose + \%\ mannose) + 0.88 * (\%\ xylose + \%\ arabinose)$$

Antal et al. presents the organic compositions of several biomass products. Walnut shells contain glucose (23.3%), xylose (18.9%), galactose (2.4%) and arabinose (0%) resulting in cellulose content of 21.0% and hemicellulose content of 18.8% (Antal et al. 2000).

For the biological degradation of walnut shells, it was assumed that cellulose and hemicellulose is consumed much quicker than lignin. As all three of these components are organic and subject to combustion, a standard volatile solids test was performed on separate undigested walnut shells. The ash contents were measured and the total organic (volatile) fraction was calculated. The organic fraction was then divided into cellulose, hemicellulose and lignin. The fraction of more readily biodegradable cellulose and hemicellulose was considered "readily biodegradable" while the lignin portion remained "non-degradable." The total potential readily biodegradable fraction of walnut shell mass could then be calculated and compared to the actual lost mass.

After eight months of digestion, the walnut shells averaged a loss in mass of 31.4%. The average amount of readily biodegradable VS in a shell (cellulose and hemicellulose) was calculated as 38.4% of the total mass. It was not clear whether microbial, hydraulic, or physical action caused the loss in shell mass.

A.4 Methane Production from Digested Sludge Calculations

The endogenous decay of methane production from accumulated sludge in each of the digester packed-beds was gauged by a “starvation” test where the digesters were not fed. At that time, no influent was admitted to the digesters and all liquid in the packed-bed of one take was transferred via the reciprocation pumps to the other tank, leaving only the walnut shells and accumulated sludge. Biogas was measured from the empty tank and gas chromatography measured the methane concentration in the biogas. The resulting production of methane was then estimated based on the volume of sludge. The porosity and sludge accumulation experiments allowed for approximate measurement of the volume of accumulated sludge in each digester tank over time. With the known sludge degradation rates to methane as well as the accumulation rates of sludge, it was possible to estimate the rate of methane production each day from sludge degradation (**Table 7.1**). Calculated methane from sludge degradation was then subtracted from the total methane production of each digester tank. This was important as the methane production models were developed to predict the methane produced from the influent COD and VS substrate and not the accumulated sludge.

Table 7.1: Estimation of daily endogenous decay of sludge to methane. Shown with date of analysis.

Digester Tank	September 6-10, 2012			December 10, 2012			
	Total Methane (L)	Starvation Period (days)	Sludge Vol. (L)	Sludge VS (g/L)	Sludge COD (g/L)	Sludge to Methane L CH_4/g sludge COD-day	Sludge to Methane L CH_4/g sludge VS-day
D1B	140.4	3.89	68.0	67.09	93.4	0.0057	0.0079
D3B	216.5	3.89	28.0	86.69	123.0	0.0162	0.0229
Average	178.4	3.89	48.0	76.89	108.2	0.0109	0.0154

The measured gas and sludge volumes in September and the subsequent COD and VS sludge calculations in December 2012 allow for the following conversion of methane formed per gram of sludge COD or VS each day. Note that D2B was not included due to sampling error.

$$\frac{140.38\ L\ CH_4}{67.09\ \frac{g_{sludge}\ VS}{L_{sludge}} * 68\ L_{sludge} * 3.89\ days} = 0.0079\ \frac{L\ CH_4}{g_{sludge}\ VS - day}$$

With the given volume of methane produced each day per gram of sludge COD or VS, the methane production may be calculated daily based on the measured mass of sludge as COD or VS. The mass of sludge COD or VS was measured based on the concentration of sludge, measured in December 2012 and then matched on a daily basis with interpolated sludge volume calculations, estimated from porosity experiments which allowed for a daily calculation of the methane *produced* from sludge. The calculation follows:

$$0.0079\ \frac{L\ CH_4}{g_{sludge}\ VS - day} * \frac{g_{sludge} VS}{L_{sludge}} * \frac{L_{sludge}}{1135\ L_{Liquid}} = \frac{L\ CH_4}{L_{Liquid} - day}$$

The volume of sludge (L_{sludge}) was calculated on a daily basis by interpolation between the porosity and sludge accumulation points. For this calculation, digester liquid volume (L_{Liquid}) was held constant at 1135 L. The daily contribution of methane from sludge was then subtracted from the total methane production measured each day. The methane production as shown in the results was the total measured production of methane minus the contribution from sludge, which allowed for reporting the methane contribution from flush water only, as sludge accumulation was an unintended and undesirable consequence of the packed-bed digesters.

Appendix B Detailed Methane Production Modeling Methods

Included in the following subsections are the detailed methods for the modeling of methane production from organic loading of COD and VS as well as temperature.

B.1 Minitab® Regression Procedure

The Nonlinear Regression Function was chosen in Minitab® to produce the models of organic loading and methane production. The closest functions resembling the graphed data of interest were selected and included: Monod-type saturation (Michaelis-Menten in Minitab®), power and linear (**Figure 7.1**). Once the model was chosen, the response (dependent variable, production of methane) was selected along with the independent variables (organic loading as COD or VS). Statistical values, including the S value and kinetic parameters and were calculated by the program with the iterative approach.

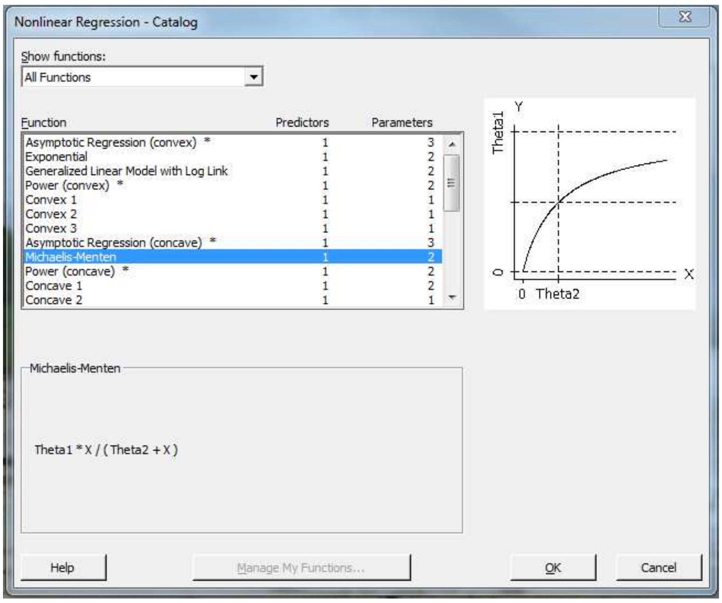


Figure 7.1: Catalog of available non-linear modeling functions in Minitab®.

The following pages include the Minitab® outputs for the various models of COD and VS organic loading and methane production. Bolded, underlined and enlarged values are of particular importance.

7/9/2014 2:29:25 PM

```
Welcome to Minitab, press F1 for help.
Retrieving project from file: 'C:\USERS\SEAN\DROPBOX\THESIS
SEAN\MINITAB\SUMMER 2014\FINAL MODELING BY EXP.MPJ'
```

Nonlinear Regression: P CH4 (L/Ld) = Theta1 * 'COD Load' / (Theta2 + ...

```
Method

Algorithm        Gauss-Newton
Max iterations            200
Tolerance             0.00001

Starting Values for Parameters

Parameter  Value
Theta1         1
Theta2         5

Constraints on Parameters

0 < Theta1 < 10
0 < Theta2 < 100

Equation
```

P CH4 (L/Ld) = 0.490223 * 'COD Load' / (9.07224 + 'COD Load')

```
Parameter Estimates

Parameter  Estimate  SE Estimate
Theta1      0.49022        0.055
Theta2      9.07224      374.833

P CH4 (L/Ld) = Theta1 * 'COD Load' / (Theta2 + 'COD Load')


Lack of Fit

There are no replicates.
Minitab cannot do the lack of fit test based on pure error.


Summary

Iterations         11
Final SSE   0.0045575
DFE                 7
MSE         0.0006511
```

S 0.0255160

Fitted Line: P CH4 (L/Ld) versus COD Load
Nonlinear Regression: P CH4 = Theta1 * 'COD Load' ^ Theta2

```
Method

Algorithm        Gauss-Newton
Max iterations            200
Tolerance             0.00001


Starting Values for Parameters

Parameter  Value
Theta1         1
Theta2         1


Constraints on Parameters

0 < Theta1 < 1000
0 < Theta2 < 1000


Equation
```

P CH4 = 0.0551849 * 'COD Load' ^ 0.671083

```
Parameter Estimates

Parameter  Estimate  SE Estimate
Theta1     0.055185    0.0000324
Theta2     0.671083    0.0003152

P CH4 = Theta1 * 'COD Load' ^ Theta2


Lack of Fit

There are no replicates.
Minitab cannot do the lack of fit test based on pure error.


Summary

Iterations         11
Final SSE   0.0031109
DFE                 7
MSE         0.0004444
```

S   0.0210813

Fitted Line: P CH4 versus COD Load

Regression Analysis: P CH4 versus COD Load

The regression equation is
P CH4 = 0.0366 + 0.0225 COD Load

Predictor	Coef	SE Coef	T	P
Constant	0.036551	0.008313	4.40	0.003
COD Load	0.022523	0.001628	13.84	0.000

S = 0.0180400   R-Sq = 96.5%   R-Sq(adj) = 96.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.062295	0.062295	191.42	0.000
Residual Error	7	0.002278	0.000325		
Total	8	0.064573			

Unusual Observations

Obs	COD Load	P CH4	Fit	SE Fit	Residual	St Resid
9	9.7	0.28855	0.25480	0.01170	0.03375	2.46R

R denotes an observation with a large standardized residual.

Regression Analysis: P CH4 versus COD Load

The regression equation is
P CH4 = 0.03655 + 0.02252 COD Load

S = 0.0180400   R-Sq = 96.5%   R-Sq(adj) = 96.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.0622950	0.0622950	191.42	0.000
Error	7	0.0022781	0.0003254		
Total	8	0.0645731			

Fitted Line: P CH4 versus COD Load

Nonlinear Regression: P CH4 = Theta1 * 'VS Load' / (Theta2 + 'VS Load')

Method

Algorithm	Gauss-Newton
Max iterations	200
Tolerance	0.00001

Starting Values for Parameters

Parameter	Value
Theta1	1
Theta2	3

Constraints on Parameters

0 < Theta1 < 100
0 < Theta2 < 100

Equation

P CH4 = 0.475829 * 'VS Load' / (5.56537 + 'VS Load')

Parameter Estimates

Parameter	Estimate	SE Estimate
Theta1	0.47583	0.00470
Theta2	5.56537	6.30580

P CH4 = Theta1 * 'VS Load' / (Theta2 + 'VS Load')

Lack of Fit

There are no replicates.
Minitab cannot do the lack of fit test based on pure error.

Summary

Iterations	11
Final SSE	0.0041036
DFE	7
MSE	0.0005862
S	**0.0242121**

Fitted Line: P CH4 versus VS Load

Nonlinear Regression: P CH4 = Theta1 * 'VS Load' ^ Theta2

```
Method
Algorithm        Gauss-Newton
Max iterations            200
Tolerance             0.00001

Starting Values for Parameters
Parameter  Value
Theta1         1
Theta2         1

Constraints on Parameters
0 < Theta1 < 100
0 < Theta2 < 100

Equation
```

P CH4 = 0.0748213 * 'VS Load' ^ 0.659757

```
Parameter Estimates
Parameter  Estimate  SE Estimate
Theta1     0.074821    0.0003190
Theta2     0.659757    0.0027966

P CH4 = Theta1 * 'VS Load' ^ Theta2

Lack of Fit
There are no replicates.
Minitab cannot do the lack of fit test based on pure error.

Summary
Iterations         11
Final SSE   0.0025975
DFE                 7
MSE         0.0003711
```

S 0.0192634

Fitted Line: P CH4 versus VS Load

Regression Analysis: P CH4 versus VS Load

```
The regression equation is
```
P CH4 = 0.03777 + 0.03410 VS Load

S = 0.0159344   R-Sq = 97.2%   R-Sq(adj) = 96.9%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.0627958	0.0627958	247.32	0.000
Error	7	0.0017773	0.0002539		
Total	8	0.0645731			

Fitted Line: P CH4 versus VS Load

B.2 ANOVA for Temperature Influence on Methane Production

Temperature influence on methane production was evaluated by two analyses of variance (ANOVA) tests as described in the methods section. Temperature data and the resulting methane production were separated as either above or below the mean digester temperature of 20.52°C, or stepwise by degree from 19°C to 22°C. The following information is the output of the one-way ANOVA presented in Minitab® and values of importance are bolded and underlined.

One-way ANOVA: P CH4 (L/L-d) versus Temperature Category

```
Source                 DF        SS        MS     F      P
Temperature Category    1  0.000492  0.000492  2.31  0.131
Error                 105  0.022348  0.000213
Total                 106  0.022840

S = 0.01459   R-Sq = 2.15%   R-Sq(adj) = 1.22%

                                      Individual 95% CIs For Mean Based on
                                      Pooled StDev
Level            N     Mean    StDev  ---+---------+---------+---------+------
Over 20.52° C   67  0.06397  0.01362                  (---------*---------)
Under 20.52° C  40  0.05954  0.01610  (------------*------------)
                                      ---+---------+---------+---------+------
                                       0.0560    0.0595    0.0630    0.0665

Pooled StDev = 0.01459
```

One-way ANOVA: P CH4 (L/Ld)_1 versus Temperature Category_2

```
Source                  DF        SS        MS     F       P
Temperature Category_2   2  0.000906  0.000453  2.15  0.122
Error                   90  0.018954  0.000211
Total                   92  0.019860

S = 0.01451   R-Sq = 4.56%   R-Sq(adj) = 2.44%


Level          N     Mean    StDev
19°C - 20°C  16  0.06249  0.01719
20°C - 21°C  41  0.05952  0.01444
21°C - 22°C  36  0.06640  0.01329

             Individual 95% CIs For Mean Based on Pooled StDev
Level          +---------+---------+---------+---------
19°C - 20°C     (-------------*-------------)
20°C - 21°C    (--------*--------)
21°C - 22°C                 (---------*--------)
               +---------+---------+---------+---------
             0.0550    0.0600    0.0650    0.0700
```

Appendix C Methane Output and Economic Calculations

Methane output (L CH_4/day) was calculated from the best fitting linear organic loading and methane production models as defined in the results section. Several organic loading and milking cow population scenarios were evaluated to provide a range of outcomes for methane production. The daily volume of methane was converted into energy equivalents as kilowatt-hours (kWh) based on the mass and energy density of methane at 1 atmosphere pressure and 20°C. Note that methane production was calculated from the two best linear equations from both COD and VS organic loadings and were then averaged. Several iterations of the economic calculation were performed to provide a range of economic outcomes (**Table 7.2**).

Commercial-scale capital costs for a packed-bed digester were divided among size requirements, equipment and services needed to complete the project. The calculation for digester size was based on the influent organic loading rates as described in methods with additional headspace and underdrain volumes added. The occupied space of walnut shells was also accounted for. Equipment costs were found in literature or assumed. Below is an example calculation of the cost breakdown (**Table 7.3**).

Table 7.2: Example methane prediction calculations. Based on the best developed models. Milking cow population was held at 1,510 and electrical rate at $0.20/kWh for this example.

Total Cows	2696	tHRT (days)	3.53	Digester Type
Milking Cow Population	1510	Liquid (L_{liquid}) Volume (m^3)	3,458	packed-bed covered lagoon
Organic Loading Rate (g/L_{liquid}-day)				
From COD		(gVS/L_{liquid}-day)	5.2	Average of this study
From VS		(gCOD/L_{liquid}-day)	4.8	Average of this study
Methane Production Models				
Model from COD	PCOD=0.02252(COD OLR)+0.03655			Best fit linear model
Model from VS	PVS=0.03410(VS OLR)+0.03777			Best fit linear model
Methane Production from Best Fit Linear Model				
CH_4 Production from COD Loading		L CH_4/L_{liquid}-day	0.215	At average loading
CH_4 Production from VS Loading		L CH_4/L_{liquid}-day	0.145	At average loading
Daily Methane from COD		L CH_4/day	747,778	
Daily Methane from VS		L CH_4/day	497,329	
Average Daily Methane from COD and VS			**622,554**	
Power Generation from Averaged Daily Methane (L CH_4/day)				
Total ekW (equivalent)		Average of COD and VS	72	Average continuous annual power
Annual Total kWh		Average of COD and VS	2,036,051	Theoretical maximum
Annual Generated kWh/cow		Average of COD and VS	256.3	
Annual Generated kWh		Average of COD and VS	**570,094**	At generator efficiency of 28%
Benefits from Retail Power Savings at $0.20/kWh				
Total Annual Benefits			$57,009	From retail power avoidance
Benefits After Maintenance			**$16,701**	After maintenance costs
Uncompressed Gas Storage Volume				
Biogas Volume Range for Generator and Storage Sizing		CH4 %	80%	This study (approx)
		CO2 %	20%	This study (approx)
		Biogas from VS (L CH_4/d)	934,723	
		Biogas from COD (L CH_4/d)	621,662	

Table 7.3: Example commercial-scale digester sizing and costs worksheet. Milking cow population held at 1,510 for this model and subsidies shown are 50% of capital.

Total Cow Population 2,696	Milking Cows 1,510	HRT 3.53	Digester Type packed-bed covered lagoon
Packed-Bed Lagoon Digester Sizing			
Liquid Volume (m^3)		3,458	
Total Lagoon Depth (m)		7.32	
Freeboard (m)		0.61	
Headspace (%)		5%	Assumption
Underdrain (%)		10%	Assumption
Total Digester Vol (m^3)		4,996	Plus headspace/underdrain
Total Digester Vol (ft^3)		176,296	Plus headspace/underdrain
Square Length (m)		8.32	
Covered Area (m^2)		69.2	
Covered Area (hectare)		0.007	
Size Based Costs ($USD 2013)			
Excavation (incl freeboard)	@ $2/CY	$26,730	Spierling 2009
Liner	@ $3.50/SF	$62,580	Williams 2005
Walnut Shells	@ $30/ton	$50,455	Southam 2011
Underdrains	@ $2.89/SF	$25,837	ADS Pipe
Land Cost	@ $10,000/acre	$4,105	Assumption
Size Based Subtotal		**$169,706**	
Equipment Costs ($USD 2013)			
Separator Screen		$38,400	Spierling 2009
Screen Supply Pump		$13,400	Spierling 2009
Pit Agitator		$9,900	Spierling 2009
Engine & Generator		$306,600	Spierling 2009
H2S Removal		$65,300	Spierling 2009
Catalytic Reduction		$39,000	Spierling 2009
Flare		$117,000	Spierling 2009
Sumps		$30,000	Assumption
Electrical		$60,000	Assumption
Equipment Subtotal		**$679,600**	
Subtotal (of Size Based & Equipment Costs)		$849,306	
Sitework (10%)		$84,931	Spierling 2009
Subtotal		$934,237	
Services (26%)		$242,902	Spierling 2009
Capital Subsidies	50%	$588,569	
Total Capital Costs		**$588,569**	
Walnut Shell Removal	@ $2/CY	$6,529	Bi annually
New Walnut Shells	@ $30/ton	$25,227	Southam 2010
Maintenance @ $0.015/kWh		$8,551	Martin 2008
Total Annual Maintenance		**$40,308**	
Annual Benefits		$57,009	From methane production
Loss from Maintenance		-$40,308	
Annual Benefits		**$16,701**	

Internal rate of return (IRR) was calculated to understand the economic outlook of an investment for packed-bed digesters operating at commercial dairies. A 10 year investment was evaluated at various retail electric rates, capital cost subsidy fractions and milking cow populations. An example of the IRR setup in the spreadsheet is shown below with a milking cow population of 1,510 at a retail electrical rate of $0.20/kWh (**Table 7.4**).

Table 7.4: Example economic summary. Includes simple payback and the 10 year investment internal rate of return. This procedure was done several times for the high and low economic outlook scenarios as described in the methods section.

	Low Analysis	High Analysis
# Milking Cows	1510	1510
COD Organic Loading	4.8	4.8
VS Organic Loading	5.2	5.2
Retail Electricity Rate ($/kWh)	$0.10	$0.20
Capital Subsidy	0%	50%
Total Capital Costs	$1,177,139	$588,569
Annual Benefits	$16,701	$73,710
Investment Year	Balance	Balance
0	-$1,177,139	-$588,569
1	$16,701	$73,710
2	$16,701	$73,710
3	$16,701	$73,710
4	$16,701	$73,710
5	$16,701	$73,710
6	$16,701	$73,710
7	$16,701	$73,710
8	$16,701	$73,710
9	$16,701	$73,710
10	$16,701	$73,710
Simple Payback (years)	70.48	7.98
Internal Rate of Return (IRR)	**-18.96%**	**9.52%**

Calculations for benefits of annual generated power from methane production, full scale digester capital costs and IRR are as follows using the methane production and organic loading modeled equations. The following example is for methane predicted from volatile solids (VS) organic loading. The procedure for methane production from chemical oxygen demand (COD) organic loading was not included but is identical to the VS procedure. The calculation begins with the linear VS organic loading (VS OLR) and methane production (P_{CH4}) model as shown in the results (**Figure 4.9**):

$$P_{CH4} = (0.0341 * VS\ OLR) + 0.03777$$

Where P_{CH4} is in units of L CH_4/L_{liquid}-day. Daily flow rate (L/d) of methane may be calculated by multiplying the production of methane (P_{CH4}) by the reactor vessel size (L_{liquid}) in liters. The calculation of L_{liquid} is described in **Section 3.11** based on the organic loading rate (OLR).

$$Methane\ Flow = P_{CH4} * L_{liquid}$$

With methane flow rate, the total theoretical annual kilowatt-hours (kWh) may be calculated:

$$Annual\ kWh = Methane\ Flow * \rho_{CH4} * E_{CH4}$$

Where ρ_{CH4} is the density of methane and E_{CH4} is the energy density of methane at 1 atm pressure and 20°C. Actual generated kWh of energy, accounting for heat losses and equipment down-time:

$$Annual\ Generated\ kWh = Annual\ kWh * n * t$$

Where n is efficiency of the generator (28%) and t is the run time of the generator (accounting for maintenance, etc.), set at 90% (**Table 7.3**).

Gross annual benefits in dollars from the generated electricity may be calculated as:

$$Gross\ Annual\ Benefits = Annual\ Generated\ kWh * Retail\ Rate$$

Where retail rate is the cost of electricity per kilowatt-hour (i.e. \$0.20/kWh).

Total annual benefits were adjusted by subtracting maintenance costs (including biannual walnut shell removal and replacement):

$$Total\ Annual\ Benefits = Gross\ Annual\ Benefits - Maintenance$$

Capital costs were calculated using parameters from **Table 7.2** and **Table 7.3**:

$$Capital\ Cost = Subtotal + Services - Subsidies$$

Where Subtotal refers to the costs of all equipment, land and materials plus site work at 10% and services (engineering and consulting fees), set at 26%. Subsidies could be adjusted in the model from 0% to 50% of capital costs.

Internal rate of return (IRR) was calculated from the total annual benefits and the capital cost of the full scale packed-bed digester over a ten year investment period. The IRR was determined with an iterative process in Microsoft Excel® using the "=IRR()" function. The basis for the IRR calculation in Excel® follows:

$$\sum_{n=10}^{N} \frac{-Capital\ Cost}{(1+r)^0} + \frac{Total\ Annual\ Benefits}{(1+r)^1} + \cdots + \frac{Total\ Annual\ Benefits}{(1+r)^{10}} = 0$$

The IRR in the economic model was adjusted with parameters described in **Table 3.3** of the methods section which allowed for the theoretical high and low economic outputs as described in the results.

Appendix D Additional Methods

Detailed descriptions of water quality tests, specific laboratory methods and equipment including: chemical oxygen demand (COD), total and volatile solids (TS & VS), total and volatile suspended solids (TSS & VSS), alkalinity and pH and total ammonia nitrogen (TAN) conducted over the study period are explained in the methods section as well as in greater detail in the companion research thesis (Adler 2013). That paper also describes a tracer study performed to better understand the hydraulic performance of the packed-bed digesters, a water quality analysis of re-circulated flush water, digester influent carbon to nitrogen (C:N) ratio and a comparison of the grab samples to automatic composite samples.