ENHANCING ENERGY RECOVERY FROM BIOMASS WASTE STREAMS – FROM MEGA-LANDFILLS AND BIOREFINERIES TO MICROBIAL COMMUNITIES

by

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and approved by

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ABSTRACT OF THE DISSERTATION

Enhancing Energy Recovery from Biomass Waste Streams – from Mega-Landfills and Biorefineries to Microbial Communities

By David Babson

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Donna E. Fennell, Ph.D.

In the United States, biomass waste streams are often disposed of without consideration for energy recovery. Energy-from-waste (EfW) systems that utilize organic wastes as biomass energy feedstocks could be designed. This dissertation consists of four studies intended to improve energy recovery from biomass waste streams.

In *Study I*, a system-wide energy balance model incorporating the major components of a New Jersey bioreactor-landfill waste management system was developed. The model compared several biogas energy recovery options, identified sensitive areas for optimization, and illuminated future design implications for waste management infrastructure.

In *Study II*, methane generation, predicted by kinetic modeling, and system capital costs were quantified for onsite-batch and regional continuous anaerobic digestion systems handling horse waste in New Jersey. A range of horse quantities, waste methane potentials, and batch reactor sizes, as well as various retention scenarios were compared among each system. Costs and benefits of utilizing smaller onsite digester systems versus larger regional systems to recover bioenergy from horse waste were determined.

During traditional anaerobic digestion of biomass, such as municipal solid waste (*Study* I) or equine waste (*Study* II), unwanted toxic byproducts, such as ammonia, are liberated as the organic matter degrades. If recovered, however, ammonia can be catalytically converted to generate hydrogen, an additional biofuel.

Therefore, in *Study III*, the effect of ammonia stripping on nitrogen species accumulation and associated energy recovery from laboratory-scale batch reactors was assessed. A simulated organic waste feedstock with various carbon to nitrogen (C:N) ratios was created by varying the fractions of laboratory grade rabbit food, casein and cellulose.

Finally, in *Study IV*, a theoretical design scheme for an integrated system to carry out anaerobic digestion, ammonia separation, and hydrogen recovery was established to determine system energy requirements and biofuel (methane and hydrogen) outputs. Energy demands such as heating, fluid pumping, reactor mixing and ammonia reforming were characterized, and compared to the potential biofuel outputs over a range of possible feedstock C:N ratios. The model was also used to identify significant process tradeoffs to be optimized such as the recycle flux and minimum liquid set point. The model provided a basis and justification for further research of such processes.

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List of Abbreviations

ADBH	Anaerobic Digestion – Bioammonia to Hydrogen
Anammox	Anaerobic ammonia oxidation
BCRRC	Burlington County Resource Recovery Complex
BMP	Biochemical methane potential
C	Elemental carbon
CH_4	Methane
C:N	Carbon to nitrogen ratio (g C/g N)
CNG	Compressed natural gas
CO_2	Carbon Dioxide
COD	Chemical oxygen demand
CSTR	Continuous stirred-tank reactor
EfW	Energy-from-waste
HPLC	High performance liquid chromatography
HTC	Heat transfer coefficient
H_2	Hydrogen
IC	Ion chromatography
kWh	Kilowatt hours
LFG	Landfill gas
LFGTE	Landfill gas-to-energy
MC	Moisture content
MRE	Minimum recovery efficiency
MSW	Municipal solid waste
N	Elemental nitrogen
N_2	Nitrogen gas
NH_3	Ammonia
NH_4^+	Ammonium ion
NO_2^-	Nitrite
NO_3^-	Nitrate
OFMSW	Organic fraction of municipal solid waste
OLR	Organic loading rate
T	Retention time
TJ	Tera-joule
STP	Standard temperature and pressure
TAN	Total ammonia nitrogen
TDS	Total dissolved solids
TS	Total solids
VFA	Volatile fatty acid
VS	Volatile solids
WTE	Waste-to-energy

Chapter 1

1. Introduction and Rationale

1.1 Energy, Climate and Environmental Policy

The United States energy demand was $1.073 \cdot 10^8$ TJ in 2007, and 85% was derived from fossil fuel sources [1] (Figure 1.1; *developed using data from the US Department of Energy* [1]). The continued use of fossil fuels is transferring carbon from the geosphere to the atmosphere and hydrosphere at an unsustainable rate [2-3]. The accumulation of carbon species from burning fossil fuels is associated with global warming and ocean acidification [2, 4]. Impacts from burning fossil fuels are fundamental to the current debate about energy policy, and have fused energy and environmental policy together. Development of carbon neutral renewable energy technologies [5] along with political structures that assess and implement viable options will decrease the amount of fossil fuel used in the future [6-9]. The route towards achieving renewable energy security will be directed by an increasing demand for localized, efficient and sustainable production [10-11].

Life-cycle-assessment (LCA), energy balance and carbon emission models can be used to analyze, optimize and direct planning and infrastructure development for new technologies [12-16]. The development of new strategic energy policies generally include implementing and enforcing renewable portfolio standards (RPS) that draw upon a combination of numerous renewable energy sources such as wind, solar, hydroelectric, geothermal, and biomass [17-20].

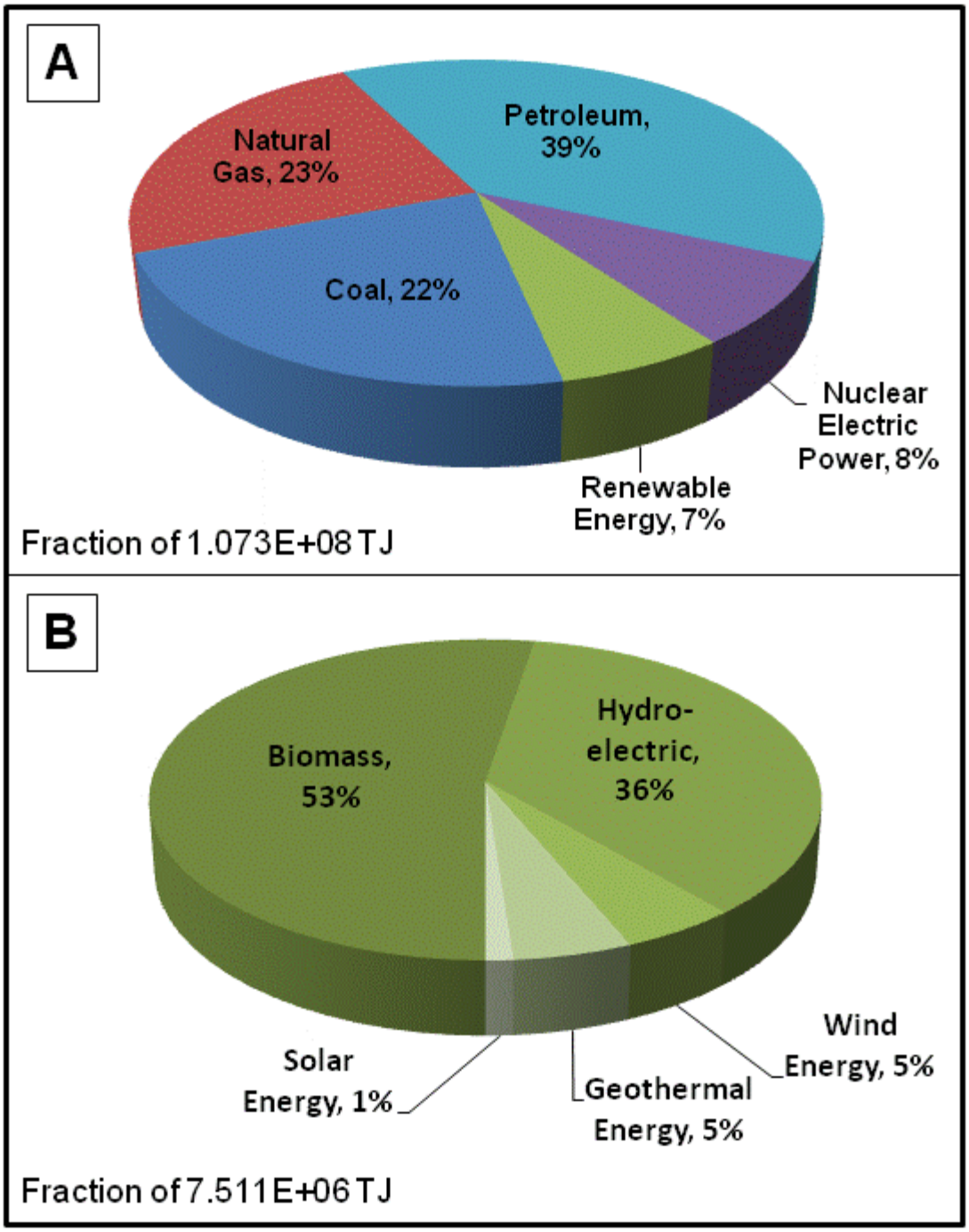

Figure 1.1 - U.S. energy sources (2007), fractions of total energy demand: (A) fractions of total, and (B) fractions of renewable energy

Greater awareness of global warming is catalyzing the development of new technologies and policies to shift energy consumption from fossil fuels to carbon neutral renewable energy sources. In the absence of federal leadership on energy policy, many states and localities have been moving independently to decrease their dependence on fossil fuels [21]. Nearly half of the states in the union have adopted RPS [1] (Figure 1.2, *developed using information from the US Department of Energy* [1]), designed to be a driver for increasing renewable energy capacity [20]. RPS require electricity suppliers to make available a certain fraction of a state's electricity from renewable energy sources [20]. Although the strengths and weaknesses of the state RPS have been debated [22-24], these requirements are being expanded [25] and could be followed by federal RPS [20, 26].

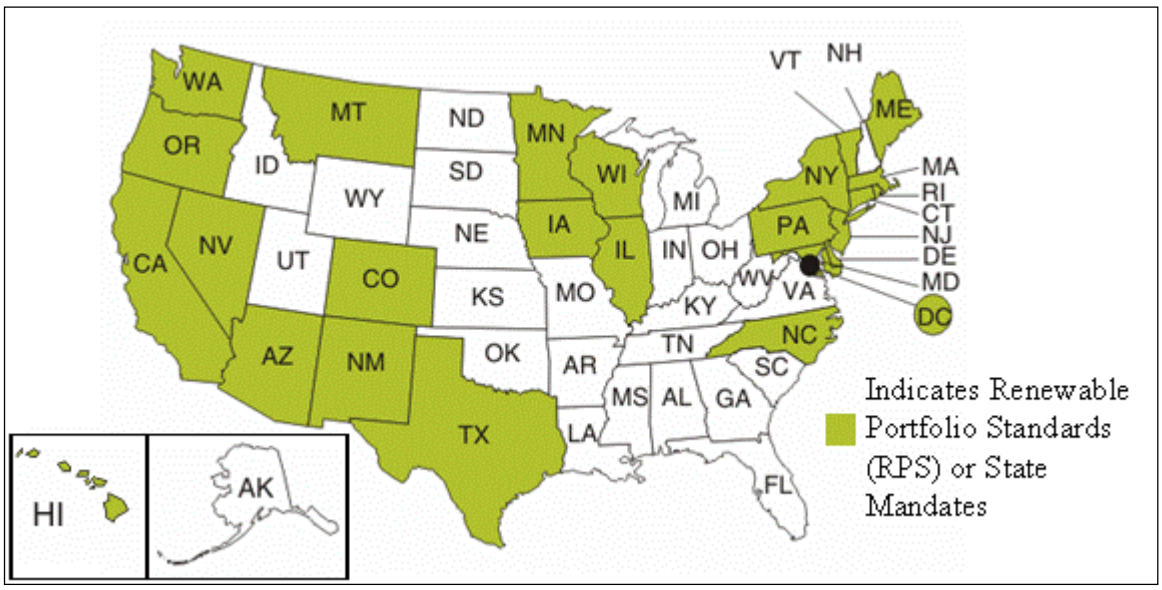

Figure 1.2 - Map of states with renewable portfolio standards or similar mandates

In recent years, major attitudinal shifts have occurred in the environmental engineering and science profession promoting wastes as resources rather than just

material requiring disposal [27]. Waste as a resource can be envisioned both as a means of reducing energy by eliminating the need for producing raw materials, and as an energy feedstock itself [28]. The attitudinal shift with respect to energy policy implies that future product, system and infrastructure design will be directed by environmental considerations to foster sustainable practices and lifestyles. In all respects, it will be desirable to minimize energy consumption, and maximize sustainable energy production from as many renewable sources as possible including biomass (organic) waste streams. One established technology, to be considered here, for extracting energy from waste is anaerobic digestion [29-30].

1.2 Beyond Waste Management: Waste Utilization

1.2.1 Waste Management in the United States

Two hundred and twenty-six million metric tons (tonnes) of municipal solid waste (MSW) was generated in the United States in 2008, and 54% or 122 million tonnes made its way into a landfill or bioreactor landfill that year [31]. There are 1,754 landfills in the United States, and although the number of active landfills and bioreactor landfills has decreased sharply over the past 20 years, these facilities are still an integral part of waste management systems in the United States [31-32]. The per capita MSW generation rate has remained relatively constant over the past 20 years, but the total MSW generation rate has increased as a function of the growing population (Figure 1.3; *developed using data from the USEPA* [31]).

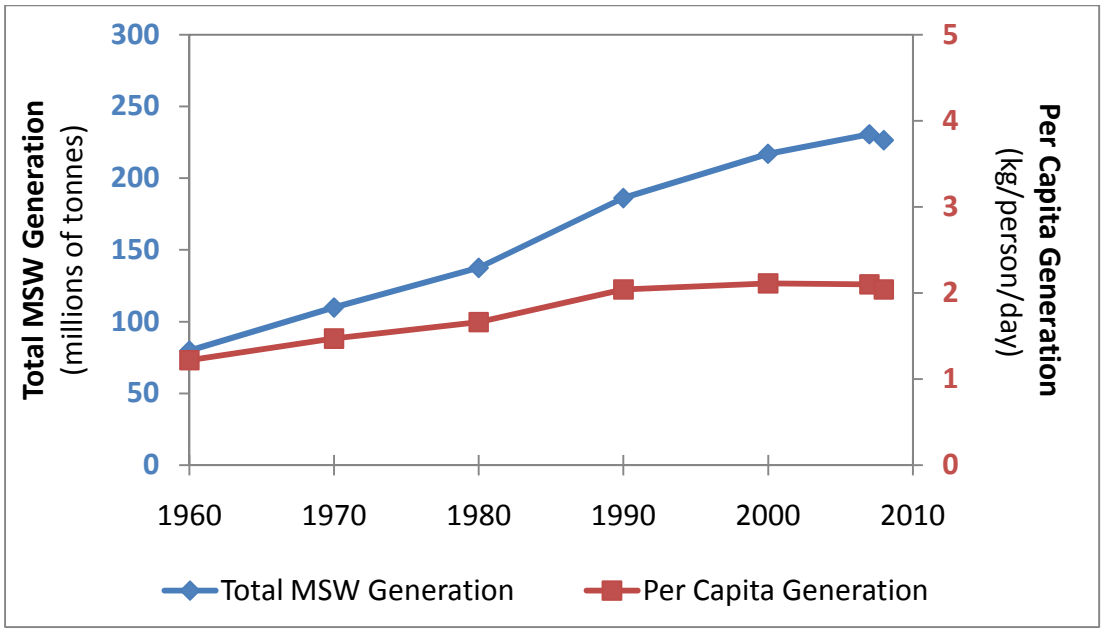

Figure 1.3 - Waste generation trends in the U.S. (1960-2008)

With the amount of MSW entering landfills increasing slightly year-to-year, the decrease in the number of landfills and bioreactor landfills has had the effect of creating larger more regional mega-landfills (Figure 1.4; *developed using data from the USEPA* [31]).

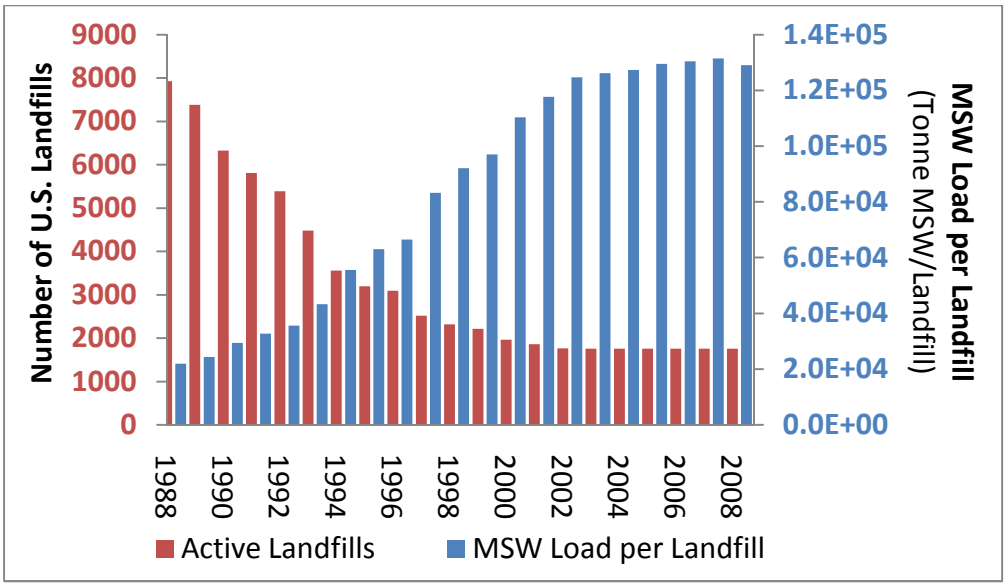

Figure 1.4 - Comparison of active landfills and annual MSW load delivered per landfill (1988-2008)

Further, greater recycling efforts that remove inert materials such as glass and metal has had the additional effect of concentrating the organic fraction of the MSW [31]. Thus, waste management trends in the United States have created an infrastructure that concentrates the MSW organic fraction and accumulates the material in fewer, larger landfills and bioreactor landfills. The organic fraction of the MSW, which degrades naturally via microbially mediated processes, can account for as much as 65 to 80% of the landfilled fraction [31, 33].

The major microbial processes of concern in landfills and bioreactor landfills are associated with organic carbon and inorganic nitrogen species such as ammonia [34]. With respect to organic carbon, the major gaseous products that are ultimately produced are methane (CH_4) and carbon dioxide (CO_2), while the dominant nitrogen species is inert nitrogen gas (N_2) [34]. Since landfill monitoring (gas emissions, leachate and groundwater testing) is costly, landfill space is valuable, and methane gas is a fuel,

strategies have been employed to enhance *in-situ* microbial processes [35-36] that maximize landfill space and methane production [36] while minimizing monitoring time [37].

Recirculation of landfill leachate is one method commonly employed to enhance in-situ microbial processes [36, 38-39]. Bioreactor landfills, where leachate recirculation is performed, are in this way distinct from traditional landfills that attempt to entomb waste and prevent moisture from entering [37]. Characterizing the effects of leachate recirculation on microbial dynamics, process kinetics, and product accumulation is of great importance for optimizing existing bioreactor landfill systems as well as for designing future systems [32, 36-37, 40]. Bioreactor landfill technology, while better than traditional landfill technology for producing and recovering biogas as well as stabilizing waste, is not a sustainable solution for handling MSW [41], and could be an intermediary between existing infrastructure and future, more sustainable waste management systems.

One concern of utilizing bioreactor landfill technology as a means to degrade waste and recover methane is the accumulation of aqueous nitrogen species in the generated leachate [34, 42-43]. As organic matter is degraded under anaerobic conditions in the landfill, nitrogen is released in the form of ammonia [44]. Containment and stabilization of reduced nitrogen is a dominant long-term monitoring concern for landfill and bioreactor systems [34, 37].

1.3 The future of waste management systems

The lack of control available to operators to direct *in situ* processes in bioreactor landfills by simply recirculating leachate limits the optimization potential of these systems [38]. Further, because of the variations in bioreactor design, function, waste

composition and optimization parameters from system-to-system, there is a lack of well established best-practice guidelines that can be employed to improve bioreactor efficiency [45]. Developing controllable, continuous, large-scale, and fully integrated organic waste handling systems that maximize desired fuel outputs while mitigating harmful pollutants is desirable.

Integrated in-vessel MSW digesters at pilot and full scales have been tested and employed, and are most prevalent in Europe [46-47]. The environmental advantages of developing, operating, and optimizing these systems include generating greater quantities of biogas capable of offsetting fossil fuels, producing digestate that can be used as a land amendment, and decreasing the environmental impacts associated with landfilling [46, 48].

Many of the same environmental concerns that dictate MSW handling practices, especially with regard to the fate of nutrients, apply to other waste streams including wastewater and agricultural wastes [49-50]. Incorporating numerous organic waste streams into a comprehensive waste management infrastructure has the potential to maximize energy recovery from readily available, and sustainable, organic matter while minimizing additional system-wide expenditures attributable to waste-hauling and other repetitive management practices.

Integrating waste streams for energy recovery, treatment and pollutant mitigation will present design tradeoffs at both the system and biochemical process level. These tradeoffs can be modeled and the impacts assessed using theoretical system-wide energy and carbon balances. Integrated waste handling systems have been previously proposed

[51], and some integrated waste management systems have been employed to digest organic wastes on a large scale [46-47, 52].

Energy-from-waste (EfW) refers to any number of technologies utilized to recover available energy from waste and digestion products. Applying the concept of a system-wide energy balance to this definition, a waste management system capable of generating more energy than it consumes could be considered an EfW system. Developing the energy balance and defining EfW in this way establishes energy as a control variable for all associated waste management system operations. Further, it allows more fuel sources from the system to be considered. For example, potential energy that could be recovered from nitrogen treatment processes such as recovery of the typically unwanted contaminant, ammonia, as a fuel.

1.3.1 Digestion Bioprocess Tradeoffs Effecting System Energy Optimization

Carbon and nitrogen cycling are critical factors for controlling anaerobic digester systems. The fate of each is controlled by different, and highly specific, bioprocesses that are not always compatible with each other. System performance is dictated by these specific bioprocesses. Of particular concern is the impact of ammonia release on methanogenesis, the microbial mediated process by which methane is generated. Developing a greater understanding of how to enhance these processes simultaneously or to the exclusion of one another, as well as characterizing the potential tradeoffs between them, could enable more emphasis to be placed on recovering energy from biomass wastes while mitigating the harms associated with nitrogen species accumulation in anaerobic systems.

The studies presented in this dissertation sought to establish the necessary fundamental knowledge to design waste management systems that handle greater varieties of biomass waste, improve energy recovery via anaerobic processes, and simultaneously avoid pollution from aqueous nitrogen species, by developing strategies to recover ammonia as a biofuel.

1.4 Overview of the Studies Conducted

To refine how waste management systems can be viewed, and to improve future design of such systems, four different studies were performed to examine scenarios important for improving energy recovery from waste management systems.

1.4.1 Study I – An Energy Balance of a Municipal Solid Waste Management System and its Applications to Burlington County, New Jersey

A system-wide energy balance and carbon emissions model incorporating the major components of the Burlington County (Florence, NJ, USA) waste management system was developed and is presented in Chapter 2. The Burlington County system operates a regional bioreactor landfill, and recovers landfill gas (LFG) for electricity generation. The model was used to compare several energy recovery options, identify sensitive areas for optimization, and illuminate implications for waste management considerations in Burlington County.

1.4.2 Study II – Comparative Energetic and Economic Analysis of Anaerobic Digestion of Equine Waste on Farms and at Regional Digesters

In Chapter 3, methane generation, predicted by kinetic modeling, and system capital costs were quantified for theoretical anaerobic digestion systems handling horse waste in New Jersey. Two scenarios were considered: an onsite batch reactor system and a regional continuous-flow system. A range of horse quantities, equine waste methane production potentials, and standard batch reactor sizes, as well as various retention scenarios, were compared for each system. The theoretical designs were used to identify potential costs and benefits of utilizing smaller onsite digester systems versus larger regional systems to recover bioenergy from equine waste.

1.4.3 Study III – Effect of Ammonia Removal, by Simulated Stripping or Aeration to Stimulate Nitrification, on Methane Production in Laboratory-Scale Anaerobic Batch Reactor

The effect of ammonia stripping and aeration on nitrogen species accumulation and potential energy recovery from laboratory-scale batch digesters was assessed and is presented in Chapter 4. A simulated organic waste feedstock with three nitrogen loadings was created by varying the ratios of laboratory grade rabbit food, casein and cellulose. Methane accumulation was normalized on a volatile solids (VS) basis so that the various feedstocks could be compared. The effect of ammonia stripping on overall energy generation as a function of the feedstock nitrogen-content was determined. The results were also used to assess whether anaerobic digestion systems using high-nitrogen feedstocks could benefit from separating hydrolysis and fermentation processes from acidogenesis and methanogenesis.

1.4.4 Study IV – Anaerobic Digestion for Methane Generation and Ammonia Reforming Hydrogen Production: Theoretical Analysis of a Model System

A theoretical design scheme for an integrated system to carry out anaerobic digestion, ammonia separation, and hydrogen recovery was established to determine system energy requirements and biofuel (methane and hydrogen) outputs and is presented in Chapter 5. Energy demands such as heating, fluid pumping, reactor mixing and ammonia reforming were characterized, and compared to the potential biofuel outputs over a range of possible feedstock carbon to nitrogen (C:N) ratios. The model was also use to identify important process tradeoffs to be optimized such as the recycle flux, and operating solids content of the digester. The model provided a basis and justification for further research of system design.

Chapter 2

2. An Energy Balance of a Municipal Solid Waste Management System and its Implications for Burlington County, New Jersey

[Babson, D., Fennell, D., Ravit, E., and Krogmann, U. to be submitted to Waste Management*]*

2.1 Abstract

Improving energy recovery from municipal solid waste (MSW) in New Jersey is constrained by poorly designed and inefficient waste management infrastructure that will ultimately be in place for many years to come. Although broad and comprehensive life cycle assessment (LCA) models have been used to assess and compare waste management options and system designs, they may be too complex or expensive to be developed and appropriately utilized for improving day-to-day management of existing systems. Models that assess waste management system efficiency and identify implementable options for improvement can be developed on a system-by-system basis using a simple energy balance.

Operating data from a bioreactor landfill in New Jersey (USA) were used to develop an energy balance for its associated waste management system. The model considered ongoing operations, and was used to assess management practices and system design, identify sensitive areas for optimization, and determine the effect of onsite anaerobic digestion on overall biogas and energy recovery.

The potential energy of the landfill gas (LFG) generated (2,057 $\pm$ 590 MJ/tonne MSW) was 96% greater than the energy consumed during waste collection, hauling and system maintenance (1,047 $\pm$ 182 MJ/tonne MSW), but the positive balance was diminished completely when the LFG electrical recovery efficiency ($f_{efficiency}$ = 0.212) was

considered, generating 58% less energy than it consumed over the same period (generated 436 ± 125 MJ-electricity/tonne and consumed 1,047 ± 182 MJ/tonne). Analyses of the bioreactor design, waste generation and LFG production and recovery capabilities showed that inaccuracies in predicting the waste delivery rate as a function of time during the design phase of the bioreactor substantially decreased the LFG recovery rate, and resulted in an average 80% (± 36%) difference between initially predicted and observed LFG generation quantities (2000 to 2009). The bioreactor landfill design has limited its ability to maximize LFG recovery, and has recovered between 31 and 57 cubic meters less LFG per tonne MSW than predicted (2000 to 2009). Onsite anaerobic digestion would have a substantial parasitic load (~40% for electricity; ~10% for heat; ~22% overall), but the technology could increase biogas recovery potential (as much as 66%), reduce variability in biogas production, minimize fugitive biogas emissions, and improve the overall energy generation rate (62% more energy generated over 18 years).

2.2 Introduction and Literature Review

2.2.1 Recovering Energy Municipal Solid Waste (MSW)

Recovering and optimizing available bioenergy resources from municipal solid waste (MSW) is becoming a more important objective for waste management system operators [53]. Numerous scenarios and tradeoffs for energy-from-waste (EfW) technologies have been considered including landfill gas recovery (LFGTE), in vessel anaerobic digestion of MSW, and incineration, also called waste-to-energy (WTE) [54-60].

In recent years bioreactor landfill technology has been extensively employed in the United States to enhance biodegradation and stabilization rates as a means to diminish environmental monitoring costs over the long-term [37, 61]. However, bioreactor landfills are typically designed and operated using empirical population and economic data that may not accurately reflect waste generation trends over time [62]. Further, these systems are imperfectly controlled by leachate recirculation and thus energy recovery is not optimized [45].

Increasing biogas recovery from landfills, bioreactor landfills, and the waste stream in general, is of particular interest in New Jersey where the state renewable portfolio standard (RPS) mandates that 22.5% of its electrical energy be derived from renewable sources by 2021 [20, 63]. A greater reliance on renewable energy establishes energy as a control variable to be optimized. Establishing energy as a waste management system optimization control variable emphasizes the need to increase the collection of biogas from existing New Jersey waste management infrastructure (landfills and bioreactor landfills) while providing the impetus to design organic waste management reactors (integrated digesters or biorefineries) that can be readily monitored, controlled, and optimized to maximize energy recovery. It is not clear how effective New Jersey's existing waste management infrastructure is at recovering available biogas from MSW or what impact specific changes to this infrastructure could have on biogas and energy recovery.

Although waste-to-energy (WTE) typically refers to waste combustion [64-65], energy-from-waste (EfW) can more broadly include any number of technologies that recover useful energy from waste or waste digestion products like biogas. Anaerobic

digestion based methods have been shown to be superior to combustion when considering environmental and economic parameters [54, 66-70]. Biogas recovery at landfills and bioreactor landfills takes advantage of the natural *in situ* anaerobic digestion processes by recovering LFG energy from MSW, but until recently the United States has not appropriately viewed MSW as a biomass feedstock [71], which has resulted in inefficient energy recovery from existing waste management infrastructure. If MSW is viewed as a biofuel feedstock, three distinct objectives for future waste management systems emerge, (1) safely dispose of MSW, (2) minimize waste management system energy consumption, and (3) maximize useable energy recovery.

2.2.2 Assessing Environmental Impacts of Waste Management Systems

The difficulty of simultaneously achieving the stated objectives requires melding energy science and technology with environmental policy and planning to be able to design and develop sustainable energy infrastructures [72-73]. Life-cycle assessment methods have been developed and adapted for waste management systems to estimate associated environmental impacts and to compare relative impacts among various system options [74]. Multiple criteria have been employed independently or simultaneously to assess the best options for waste management [41, 75-77], setting a precedent for models to direct future policies and infrastructure development [54, 78-83]. Several waste management options have been compared directly including: landfilling versus landfill gas to energy (LFGE) [84], landfilling versus incineration (WTE) [85], LFGE versus WTE [86], and in vessel anaerobic digestion versus WTE [70]. Numerous studies have used life cycle assessment (LCA) to compare various waste management or treatment options [75-77, 87-90].

A comprehensive review of life-cycle assessments (LCAs) of MSW management systems by Cleary (2009) showed variations in decision making during the goal and scope phase of the LCA, could limit the applicability of the results to the specific system considered [41]. However, the complexities of designing comprehensive studies, analyzing and comparing multiple tradeoffs and effecting changes to ongoing management practices can be challenging on a case-by-case basis [23]. Given the complexity and exacting standards prescribed by such organizations as the *International Society of Standardization* (ISO) and the *Society of Environmental Toxicology and Chemistry* (SETAC) [41], developing comprehensive LCAs can be difficult and unnecessarily for specific applications. Considering a single control variable, such as energy, can accurately identify major system inefficiencies, and provide a means to quantify the efficiency's sensitivity to a particular system parameter. Moreover an energy balance can be related to overall fossil carbon emissions, a major impact factor for LCAs [91-93], without being explicitly quantified. In fact, reducing system energy consumption that is typically fossil derived and increasing overall biogas energy generation can be viewed as a qualitative reduction in the overall system's global warming potential. The extent of this impact reduction is related to the overall system energy balance.

2.2.3 Rationale and Objectives

Developing simpler energy balance models that can be easily tailored to a specific waste management system could save costs and technical investments as compared to LCA analysis, and might still provide sufficient information for operators to adjust their operations to reduce system energy consumption and increase bioenergy production from

MSW. Using energy as the single model control variable eliminates many of the complications and costs of performing the more complex LCA while informing decision making for the specific waste management system.

The purpose of this study was to (1) develop an energy balance for the Burlington County Bioreactor Landfill (New Jersey) system, (2) develop an associated carbon dioxide emissions profile, and (3) use the resulting data as a decision making tool for efficiency considerations for the Burlington County waste management system.

2.3 Materials and Methods

This study used data from the Burlington County Resource Recovery Complex (BCRRC), located in the Florence and Mansfield Townships of New Jersey, to develop an energy balance and associated carbon dioxide emissions model. The model was constructed in a Microsoft Office Excel spreadsheet (Microsoft Corporation, Redmond, WA) and input variables' dependence was propagated throughout the model system (Appendix I).

2.3.1 Burlington County (New Jersey) MSW Management System

The bioreactor landfill started operation in 2000 and is currently projected to reach its capacity in 2018, at which point it will cover 28.3 hectares (ha), have a height of 44 meters (m) and a waste density of 980 kilograms (kg) of MSW per cubic meter (m^3). Data were obtained that summarized BCRRC operations from 2002 to 2009 (available data sets varied each year), and only considers the operation of the BCRRC's bioreactor landfill. The facility received an average of 307,600 tonnes of MSW per year through

2009. The yearly delivered MSW quantity has been as high as 354,200 tonnes (2004) and as low as 267,500 tonnes (2007), but was typically lower than the design MSW quantity of 335,600 tonne/yr. MSW was received from localities a weighted average distance of 24.47 km away. The average MSW truck load per delivery to the bioreactor landfill was 5.18 tonne per delivery. Excess (unrecycled) leachate from the bioreactor landfill is hauled off-site for subsequent treatment.

The energy balance and carbon dioxide emissions associated with the overall waste management system were broadly established to include the major operational components for the BCRRC system (Figure 2.1), but considers only ongoing operations including MSW collection from house-to-house and hauling to the bioreactor landfill, daily cover transportation, landfill construction, leachate and stormwater removal and treatment, and landfill gas collection (LFG) with electrical recovery via internal combustion.

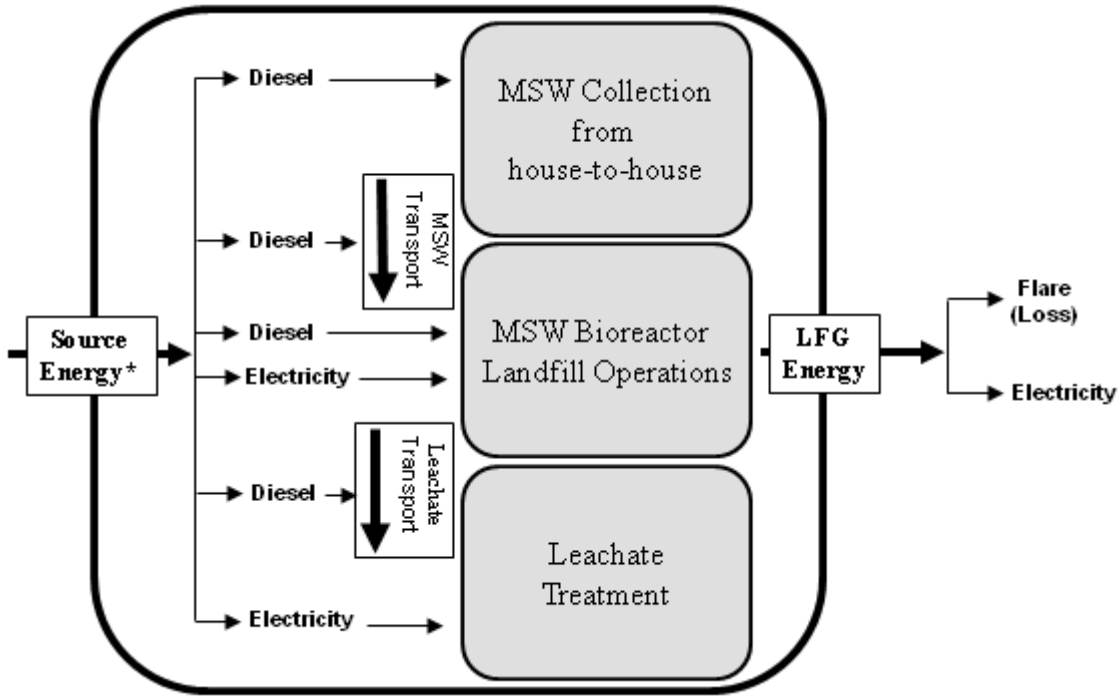

Figure 2.1 - Energy balance boundary for the Burlington County waste management system

*Figure 2.1: Source energy does not include provisional energy from upstream resource development (e.g. mining, refining, generation, transport, transmission).

2.3.2 Energy balance

The energy balance for the BCRRC accounted for all major operational components shown in Figure 1 (Equation 2.1).

$$\frac{dE_{Net}}{dt} = f_{efficiency} \cdot E_{LFG} - E_{Collection} - E_{Operation} \qquad \text{Equation 2.1}$$

where:

$\frac{dE_{Net}}{dt}$	Useable energy production rate (TJ/yr)
$f_{efficiency}$	Unit-less energy recovery efficiency factor specified for energy utilization
E_{LFG}	Energy content of recoverable LFG (TJ/yr)

$E_{Collection}$ Energy required for (1) MSW collection from house-to-house, (2) MSW hauling to landfill, (3) additional cover material transport (TJ/yr)

$E_{Operation}$ Energy used for (1) landfill operation, (2) leachate transport, (3) leachate treatment (TJ/yr)

All energy units (10^6J = 1MJ = 10^{-6}TJ) were normalized using conversion factors, 37.3 MJ/L-diesel [94], 947 BTU/MJ, and 0.278 kWh/MJ. A positive energy balance indicates that the amount of energy recovered from the system is greater than the energy required for MSW collection and facility operation. The energy balance from 2000 to 2009 was computed based on operating data while the energy balance for 2010 to 2030 was based on predicted values.

Input values for the components of the overall energy balance (Equation 2.1) were calculated independently. These independent calculation methods are described subsequently. Input variables and variances for these calculations were obtained from operational data, literature values or professional judgment (Table 2.1). All independent outputs are given in Table 2.2.

Table 2.1 - BCRRC energy balance input variable descriptions

Inputs				
Variable	**Description and Units**	**BCRRC Value (*Assumed value**)**	**Standard Deviation (σ)**	**Value and Variance Source**
L_1	Methane generation potential for open cells without recirculation (L/kg-MSW)	*138 L-LFG/kg-MSW**	± 15	Value: [95] Variance: [95]
R_i	Average annual MSW quantity (tonne-MSW/yr).	Time-dependent input	± 27,000	Available data from

	Value is calculated annually	*315,000 tonne-MSW/yr for future predictions*[*]		BCRRC
k_1	Methane generation rate constant for open cells assuming no leachate recirculation (yr^{-1})	*0.04 1/yr*[*]	± 0.01	Value: [95] Variance: [95]
t_i	Time since initial refuse placement into the cell (yr)	Time-dependent input	---	---
L_2	Methane generation potential for closed cells with recirculation	*185 L-LFG/kg-MSW*[*]	± 20	Value: [95] Variance: [95]
R_{Avg}	Average annual MSW quantity observed over the open duration of the given cell.	Time-dependent input *315,000 tonne-MSW/yr for future predictions*[*]	± 27,000	Available data from BCRRC
k_2	Methane generation rate constant for open cells assuming leachate recirculation (1/yr)	*0.26 1/yr*[*]	± 0.04	Value: [95] Variance: [95]
c_j	Time since cell closure (yr)	Time-dependent input	---	---
$E_{Density}$	Energy density of the LFG (J/L)	17,500 J/L	± 1,000	Available data from BCRRC
$d_{Transport}$	Weighted average distance from the waste origin municipality to the BCRRC (km/delivery)	24.47 km/delivery	± 0.23	Available data from BCRRC
$F_{Transport}$	Average truck fuel economy for hauling to landfill (km/L-diesel)	*2.13 km/L- diesel*[*]	± 0.11	Extrapolate from available data
$Load_{AVG}$	Average delivery mass (tonne-MSW/delivery)	5.19 tonne-MSW/delivery	± 0.49	Available data from BCRRC
$X_{CollAVG}$	Unit-less fractional contribution of MSW	0.595	± 0.054	Available data from

	collection to total truck travel distance			BCRRC
$F_{AccumAVG}$	Average fuel economy (2006 data) for MSW collection and hauling to landfill combined (km/L-diesel)	1.36 km/L-diesel	± 0.07	Available data for 2006
$F_{Collect}$	Average truck fuel economy (km/L-diesel) for collection from house-to-house	*0.85 km/L-diesel**	± 0.04	Extrapolate from available data
X_i	Unit-less fractional volumetric contribution to cover material for glass cullet, soil, and wood	0.33 Volumetric-fraction for each material	± 0.03	Available data from BCRRC
v_{Cover}	Combined volumetric cover material accumulation rate (m^3/yr)	Time-dependent input *113,000 m^3/yr for future predictions**	± 6,500	Available data from BCRRC
v_{Ct}	Cover material transport truck capacity (m^3)	*15 m^3**	*± 4*	*Estimate*
d_{Soil}	One-way cover soil transportation distance (km)	*48 km**	*± 16*	*Estimate*
d_{Glass}	One-way glass cullet transportation distance (km)	*72 km**	*± 24*	*Estimate*
$E_{Electricity}$	Electrical energy consumption at the BCRRC (MJ/yr)	Time-dependent input *2.65E+7 MJ/yr for future projections**	*± 19,000*	Available data for 2006-2007
E_{Fuel}	Fuel consumption during operation at the BCRRC (L-diesel/yr)	408,000 L-diesel/yr	*± 19,000*	Available data 2007
V_{Wt}	Volumetric water truck capacity per load (L-wastewater/trip)	*22,000 L-wastewater/trip**	*± 1,500*	*Estimate*

d_{Leach}	Distance from BCRRC to leachate treatment facility (km)	109 km	---	---
d_{Storm}	Distance from BCRRC to stormwater treatment facility (km)	26 km	---	---
v_{Leach}	Annual leachate quantity (L-leachate/yr)	Time-dependent input *49,000,000 L-leachate/yr for future predictions*[*]	± 29E+06	Available data from BCRRC
v_{Storm}	Annual stormwater quantity (L-stormwater/yr)	Time-dependent input *3,000,000 L-stormwater/yr for future predictions*[*]	± 15E+06	Available data from BCRRC
N_0	Mass of oxygen, O_2, transferred by the aerator at 20^0 C and zero dissolved oxygen, characterized by an associated energy (kg O_2/MJ)	*0.50 kg-O_2/MJ*[*]	± 0.17	Value: [96] Variance: [96]
β	Unitless salinity-surface tension correction factor	*0.9*[*]	---	---
C_{walt}	Oxygen saturation concentration for tap water at specified elevation and temperature (mg/L)	Calculated value based on average New Jersey temperature of 15° C and an elevation of 90 m *10 mg/L*[*]	---	---
C_L	Operating oxygen concentration (mg/L)	*3 mg/L*[*]	± 1	Value: [96] Variance: [96]
T	Operating temperature (^oC) for leachate treatment	*15° C*[*]	---	---
α	Unitless oxygen transfer correction factor	*0.85*[*]	± 0.16	Value: [96] Variance:

				[96]
Eq_{Oxygen}	Stoichiometric oxygen equivalent for balance chemical reaction	*4.5 parts O_2 per part NH_3 (mass basis)*[*]	---	---
$M_{Nitrogen}$	Mass of total ammonia nitrogen to be treated (kg/yr)	Time dependent input *Future predictions based on 920 mg-ammonium/L-leachate*[*]	± 30	Available data from BCRRC
$\rho_{CO2\text{-}diesel}$	Carbon dioxide released during combustion of a specified volume of diesel fuel (kg CO_2/L-diesel)	2.668 kg CO_2/L-diesel	---	Value: [97]
$\rho_{CO2\text{-}NJ\text{-}Elec}$	Carbon dioxide emissions attributed to New Jersey electrical generation (kg CO_2/MJ)	0.731 kg CO_2/MJ		Value: [98-100]
$f_{Elec.\text{-}fossil.}$	Unitless fraction of electrical energy obtained from fossil fuel sources	0.52	---	---
$f_{Trans.\text{-}fossil}$	Unitless fraction of transportation fuel energy obtained from fossil fuel sources	1	---	---
$f_{Elec.}$	Unitless fraction of net energy associated with electrical energy demands	0.05	---	---
$f_{Trans.}$	Unitless fraction of net energy associated with transportation fuel energy demands	0.95	---	---

Table 2.2 - BCRRC energy balance calculated outputs

Outputs		
Variable	**Description and Units**	**Output Dependence**

Q_1	Open cell LFG generation rate (m^3/yr)	Calculated time-dependent output
Q_2	Closed cell LFG generation rate	Calculated time-dependent output
Q_{LFG}	Total LFG generation rate for the bioreactor landfill predicted by the model	Calculated time-dependent output
$Fuel_{transport}$	Total fuel consumed during MSW transport as a function of the average annual delivered MSW quantity (L-diesel/yr)	MSW accumulation rate dependent output
$d_{Collection}$	Weighted average distance from the waste origin municipality to the BCRRC (km)	Estimated output based on transport distance and truck fuel economy
$Fuel_{Collection}$	Total fuel consumed during MSW collection as a function of the average annual delivered waste quantity (L-diesel/yr)	MSW accumulation rate dependent output
v_i	Volumetric fraction of cover material for glass cullet, soil, and wood (m^3/yr)	Fractional time-dependent output
$Fuel_{Cover}$	Fuel required to transport cover materials (soil and glass cullet) from respective origins to the BCRRC (L-diesel/yr)	Volumetric cover material accumulation rate dependent output
$E_{Operation}$	The sum of the electrical and fuel expenditures for all operations at the BCRRC normalized to a single energy equivalent (L-diesel/yr)	Calculated time-dependent output
$E_{transport(out)}$	The sum of the fuel consumed to transport leachate and stormwater to separate respective treatment facilities (L-diesel/yr)	Calculated time-dependent output
$f_{aerator}$	Aerator efficiency: mass of oxygen, O_2, transferred by the aerator under specified field conditions characterized by an associated amount of energy (kg O_2/MJ)	Calculated time-dependent output
$E_{treatment}$	Total estimated electrical energy utilized to treat BCRRC leachate using aeration	Calculated time-dependent output
M_{CO2}	Total mass of fossil fuel associated carbon emitted by the considered system (kg/yr)	Calculated time-dependent output

2.3.3 LFG generation, collection and loss

Numerous LFG generation models have been developed and reported [33, 101-102], and methane quantity is typically modeled with a first-order kinetic equation [102-104]. Kinetic parameters are a function of MSW composition, local climate, inhibitor concentrations, and other factors [102]. LFG quantity at the BCRRC was predicted based on the Scholl Canyon Gas Generation Model [33, 101] that differentiates between open (Equation 2.2) and closed (Equation 2.3) bioreactor landfill cells.

$$Q_1 = \sum_i L_1 \cdot R_{avg} \cdot \left[1 - \exp(-k_1 \cdot t_i)\right] \qquad \text{Equation 2.2}$$

$$Q_2 = \sum_{i,j} L_2 \cdot R_{avg} \cdot \left[\exp(-k_2 \cdot c_j) - \exp(-k_2 \cdot t_i)\right] \qquad \text{Equation 2.3}$$

The Scholl Canyon Gas Generation Model was selected for this system because it was used in the original bioreactor design and the parameters could be fitted to the operational data. This model is typically used to size landfill gas collection systems, and does not estimate the associated fugitive biogas emissions. Thus, biogas and energy losses corresponding to fugitive emissions are not formally included in the energy balance. However, since fugitive biogas is not recoverable, the inclusion of these values would not affect the overall energy balance even if they could be accurately measured.

The total LFG generation rate is the sum of the calculated rates corresponding to the gas being generated from both open and closed bioreactor landfill cells (Equation 2.4).

$$Q_{LFG} = Q_1 + Q_2 \qquad \text{Equation 2.4}$$

The associated energy of the LFG is calculated by relating an energy density to the generated LFG volume (Equation 2.5).

$$E_{LFG} = E_{density} \cdot Q_{LFG} \qquad \text{Equation 2.5}$$

The total potential LFG energy (E_{LFG}) generated by the system (Equation 2.5) comprises the energy generation in the overall balance (Equation 2.1). The actual energy output is dependent on the efficiency ($f_{efficiency}$) of the LFG energy utilization option.

2.3.4 Material accumulation: MSW collection, transportation, and additional cover

Fuel used to haul MSW (not including MSW collection) to the landfill was calculated directly from the BCRRC MSW quantity data from 2004 through 2007. The distance, total number of deliveries and mass of MSW from a given origin were used to calculate a weighted average distance and MSW truck load. The total transport fuel consumption was estimated using an average fuel economy ($F_{Transport}$) and the MSW quantity (Equation 2.6).

$$Fuel_{Transport} = \frac{R_i \cdot (2 \cdot d_{Transport})}{F_{Transport} \cdot Load_{AVG}} \qquad \text{Equation 2.6}$$

Fuel required for house-to-house collection of MSW was estimated using 2006 data that included total mileage and total fuel consumption. These data accounted for both MSW collection from house-to-house and hauling to the landfill. Thus, to calculate a fractional distance from each activity, an average fuel economy for each operation is specified, and the fractional distance traveled during MSW collection from house-to-house was obtained by difference (Equation 2.7). MSW truck fuel economy was assumed to be 0.85 km/L-diesel during MSW collection, and 2.13 km/L-diesel during MSW transport.

$$X_{CollAVG} = \frac{2.13\left(\frac{km}{L}\right) - F_{AccumAVG}}{2.13\left(\frac{km}{L}\right) - 0.85\left(\frac{km}{L}\right)} \qquad \text{Equation 2.7}$$

This calculation was performed for each month in 2006 and the average distance fraction obtained over the year was used to calculate the weighted average MSW collection distance (Equation 2.8).

$$d_{Collection} = 2 \cdot d_{transport}\left(\frac{1}{(1 - X_{CollAVG})} - 1\right) \qquad \text{Equation 2.8}$$

The average collection distance per delivery is used to calculate the fuel consumed as a function of the annual average MSW accumulation rate (Equation 2.9).

$$Fuel_{Collect} = \frac{R_i \cdot d_{Collection}}{F_{Collection} \cdot Load_{AVG}} \qquad \text{Equation 2.9}$$

The fraction of the deliveries that arrived from municipal routings (residential and commercial) requiring both collection and hauling (78.3 $\pm$ 6.7%) versus the fraction of the deliveries with direct routings (industrial and bulky waste) requiring only hauling (21.7 $\pm$ 6.7%) was considered.

The final component considered as part of the collection energy ($E_{Collection}$) was the fuel consumed during transport of cover material. The BCRRC uses a mixture of soil, glass cullet and shredded wood, in roughly equal parts by volume as cover. The wood is recovered from the MSW stream and therefore energy used to transport this material is accounted for as part of the MSW collection and hauling energy expenditure. The energy to shred the wood was included in facilities management operations. Specifying the volumetric cover quantity, v_{cover}, allowed the fractional cover material quantities to be estimated (Equation 2.10).

$$v_i = X_i \cdot v_{cover} \qquad \text{Equation 2.10}$$

The fuel required to transport soil and glass cullet was calculated (Equation 2.11).

$$Fuel_{Cover} = \frac{2}{V_{Ct} \cdot F_{transport}} \cdot \left(d_{soil} \cdot v_{soil} + d_{glass} \cdot v_{glass}\right) \qquad \text{Equation 2.11}$$

The total energy consumed accounting for MSW collection from house-to-house, MSW hauling to the landfill, and cover material transport can be calculated for a specified time interval (Equation 2.12).

$$E_{Collection} = Fuel_{Collect} + Fuel_{Transport} + Fuel_{Cover} \qquad \text{Equation 2.12}$$

The minimum recovery efficiency (MRE) was calculated by applying Equation 2.13.

$$MRE = \frac{\left(E_{Collection} + E_{Management}\right)}{E_{LFG}} \qquad \text{Equation 2.13}$$

Where $E_{Collection}$ is given by Equation 2.12, and $E_{Management}$ is given by Equation 2.18.

2.3.5 MSW Management: Operations and Leachate Treatment

Electricity consumption was converted to metric energy units (0.278 kWh/MJ). The sum of the onsite electrical and transportation fuel consumption gives the total system operating energy (Equation 2.14).

$$E_{operation} = (E_{electricity} + E_{fuel}) \qquad \text{Equation 2.14}$$

Leachate and stormwater that came in contact with waste are collected in different storage tanks and basins at the BCRRC and are transported to different wastewater treatment facilities. The fuel used to haul leachate and stormwater from the bioreactor landfill, is a function of the wastewater quantity, the fraction that is leachate versus stormwater, and the distance to the separate treatment facilities (Equation 2.15).

$$E_{transport(out)} = \frac{2}{F_{transport} \cdot V_{Wt}} \left(d_{Leach} \cdot v_{Leach} + d_{Storm} \cdot v_{Storm}\right) \qquad \text{Equation 2.15}$$

The leachate generated at the BCRRC exceeded the amount that could be recirculated. Excess leachate was hauled to a conventional wastewater treatment plant for treatment via aerobic processes. The energy attributed to transporting sufficient oxygen to convert associated nitrogen loads in the leachate stream was calculated using a design equation (Equation 2.16) [96].

$$f_{aerator} = N_0 \cdot \left(\frac{\beta \cdot C_{walt} - C_L}{9.17} \right) \cdot 1.024^{T-20} \alpha \qquad \text{Equation 2.16}$$

The energy required to treat the accumulated leachate was calculated using energy associated with the required oxygen transfer (Equation 2.17).

$$E_{treatment} = \frac{Eq_{Oxygen}}{f_{aerator}} \cdot M_{Nitrogen} \qquad \text{Equation 2.17}$$

The total energy consumed during system management ($E_{Operation}$) is the sum of the operating energy, the energy to transport the leachate to the wastewater treatment facility and the energy to treat the total ammonia nitrogen (TAN) in the leachate (Equation 2.18).

$$E_{Management} = E_{operation} + E_{transport(out)} + E_{treatment} \qquad \text{Equation 2.18}$$

2.3.6 Operation related carbon dioxide emissions assessment

All energy consumed by the modeled system that is not associated with the LFG is provided from external sources, a known fraction of which comes from fossil fuel sources. Fossil carbon emissions can be estimated by associating the energy value output from the model to the carbon dioxide released in the combustion of the corresponding mass or volume of the fossil fuel consumed (2.668 kg-CO_2/L-diesel [97], 0.731 kg-CO_2/MJ-NJ-electric [98-100]). The calculated carbon dioxide emissions are associated

only with additional energy needed from fossil fuel sources after accounting for system energy recovery. Thus, carbon dioxide emissions assessment does not include other carbon based greenhouse gasses (GHG) such as additional combustion products or unwanted methane emissions from the bioreactor itself. As will be discussed later, fugitive LFG emissions can be significant.

The system carbon dioxide equivalent is related to the calculated net energy (Equation 2.1), as well as a fraction of the energy consumed by the system that is derived from fossil fuel sources (Equation 2.18).

$$M_{CO2} = E_{Net}\left[\left(\rho_{CO2_diesel} \cdot f_{Trans} \cdot f_{Trans-fossil}\right) + \left(\rho_{CO2_NJ-Elec} \cdot f_{Elec}\right)\right] \qquad \text{Equation 2.18}$$

2.3.7 Scenario Analysis

The energy and carbon dioxide emissions model was developed to be a decision-making tool for testing modifications of the existing waste management system. Three scenarios were tested.

In the first scenario, the impact that more efficient trucks would have on system energy consumption was determined. The input variables affected in this scenario were the collection fuel economy and waste quantity per load. The new trucks were assumed to be hybrid diesel-electric vehicles with a collection fuel economy of 2.55 km/L, and an average waste delivery capacity of 6.35 tonnes. These values directly replaced the current operating values of 0.85 km/L and 5.19 tonnes respectively, and the changes in modeled outputs were calculated. Similarly, the effect of improving fuel economy alone was tested.

In the second scenario, the impact of varying the MSW transportation distance was examined. The transportation distance was varied from 0 to 100 km in 10 km increments.

In the third scenario, the impact of diverting the organic MSW fraction to onsite digesters in an effort to maximize recoverable biogas was analyzed. For this analysis the LFG generation model used at the BCRRC was considered for the original design specifications [95] as well as modified for observed operating conditions. These differences were then compared to a biogas generation output for a hypothetical anaerobic digestion system for the organic MSW fraction. The impact on energy recovery at the BCRRC is analyzed.

2.3.8 Model Sensitivity Analysis

The model sensitivity to each input variable was determined by calculating the percent difference in total system energy consumption ($E_{Consumption} = E_{Collection} + E_{Operation}$) for a 100% change of each input variable (Equation 2.19). Each input variable was assessed separately.

$$S = \frac{\left| E_{Consumption_1} - E_{Consumption_2} \right|}{\left((E_{Consumption_1} + E_{Consumption_2}) / 2 \right)} \qquad \text{Equation 2.19}$$

2.3.9 Calculated Error and Error Propagation

Standard deviation values and estimated ranges of the input variables were considered for most input variables (Table 2.1). The source of these input ranges was obtained by calculating the standard deviation from operational data when possible. In other cases, literature values or best estimations were used to specify appropriate ranges.

The percent error corresponding to the various outputs was calculated using propagation of uncertainty [105]. The uncertainties in sums and differences were measured by applying Equation 2.20.

$$\Delta q = \sqrt{(\Delta x)^2 + (\Delta y)^2 + ... + (\Delta z)^2} \qquad \text{Equation 2.20}$$

Where Δq, is the uncertainty in the sum or difference, and Δx, Δy and Δz are the uncertainty of the summed input variables. The uncertainty of products and quotients were measured by applying Equation 2.21.

$$\Delta q = (x \cdot y \cdot ... \cdot z)\sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2 + ... + \left(\frac{\Delta z}{z}\right)^2} \qquad \text{Equation 2.21}$$

Where, x, y and z are the best-specified value for the given input. Finally, the uncertainty associated with input variables of the anti-natural logarithm, e^x, was calculated using Equation 2.22.

$$\Delta q = q \cdot \Delta x \qquad \text{Equation 2.22}$$

Uncertainty in intermediate outputs was propagated throughout all subsequent calculations allowing final desired outputs to represent uncertainty ranges originating from all relevant inputs.

2.4 Results and Discussion

2.4.1 Energy balance without energy recovery losses

The energy balance for the BCRRC was calculated for a 30-year period from 2000 to 2030. The estimated duration of MSW landfilling was 18 years based on observed MSW production, compaction density and estimated final capacity. LFG recovery at the BCRRC was initiated in 2002, two years after landfilling started.

The energy consumed during MSW collection from house-to-house, hauling to the landfill and placement in the landfill, as well as the energy consumed for operation and leachate management was subtracted from the energy associated with the generated LFG to obtain the overall system energy balance (Equation 2.1) (Figure 2.2).

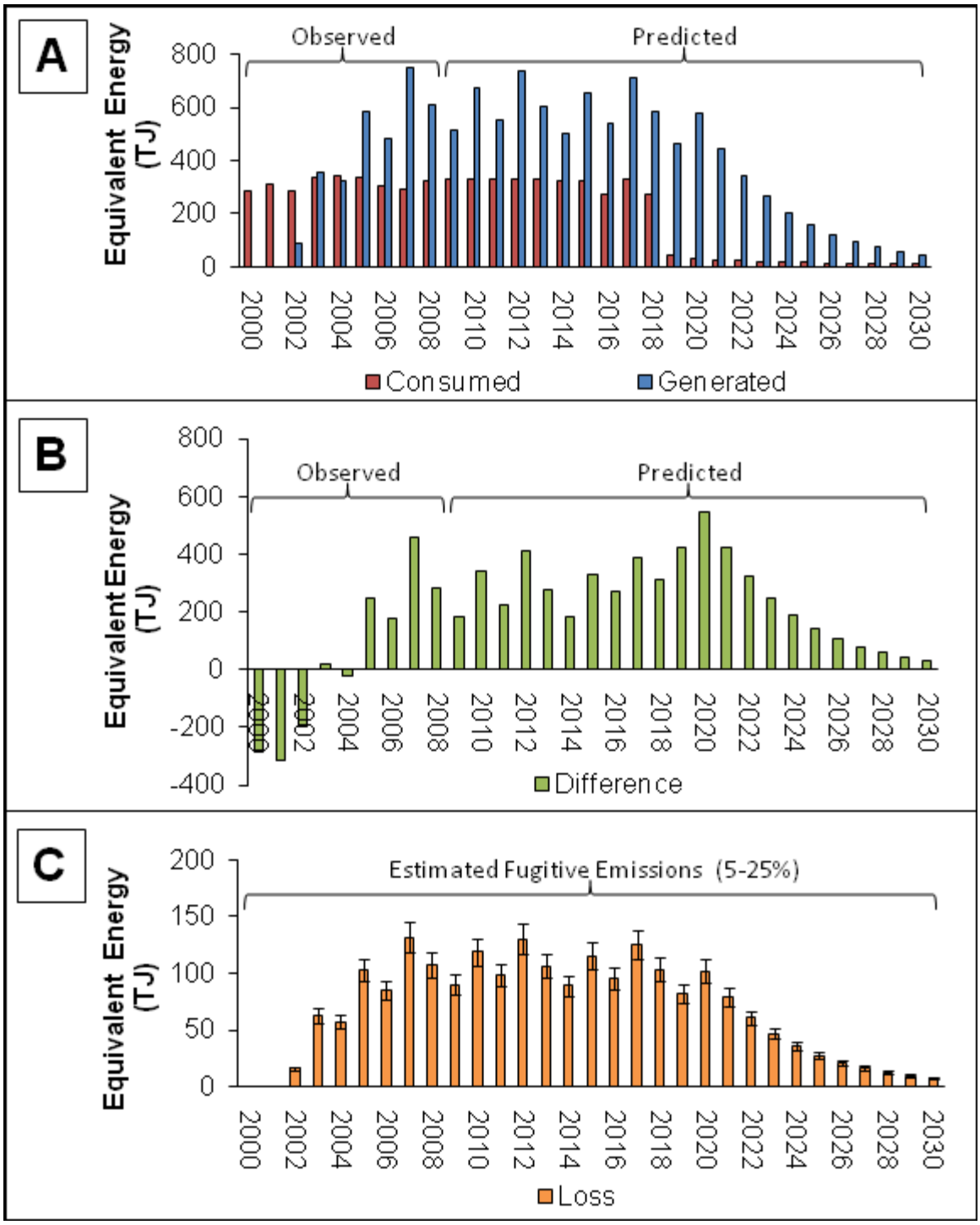

Figure 2.2 - Energy balance for the BCRRC without considering energy loss resulting from LFG conversion: (A) total energy consumed and generated, (B) recoverable difference, and (C) estimated fugitive LFG emissions

In Figure 2.2, the uncertainty associated with the energy consumed, generated and differences during predicted years are ± 17.4%, 28.7%, and 56.3%, respectively, where each individual year's uncertainty value would be a proportional fraction of the 30-year total. Fugitive emissions were estimated to be 5-25% of the total LFG generated. The cumulative energy balance over 30 years predicts the energy that the system is expected to consume and generate assuming 100% LFG utilization (6,227 ± 1,084 and 12,233 ± 3,511 TJ, respectively). The pattern of peak and decline of LFG generation is related to the start of LFG extraction in newly opened landfill cells (e.g., 2007, 2010, 2012, 2015, 2017, 2019, 2020). The energy consumption is expected to decrease continuously after 2020 because the landfill is projected to reach capacity and stop receiving waste by 2019. These projections do not consider expansion of the bioreactor landfill.

The LFG energy is greater than the energy consumed by the waste management system over the 30-year period considered. This indicates that the Burlington County waste management system can potentially offset all of its energy requirements and export energy. The minimum recovery efficiency (MRE) is the lowest necessary LFG energy recovery efficiency factor needed to offset the system energy consumption. The MRE is a function of the LFG energy generated, and the system energy consumption. The MRE of the BCRRC system is 0.49 meaning at least 49% of the available LFG energy must be recovered in a useable form to offset all system energy requirements. A recovery efficiency greater than 0.49 would enable additional energy to be contributed to a renewable portfolio. Although 0.49 would seem high for an EfW system, an energy balance assessment considering the life-cycle of biogas production from energy crops showed that 20-40% of the biogas energy generated was needed to offset system energy

requirements [89]. This is an important comparison because many of the impacts of utilizing energy crops such as the production and application of chemical fertilizers, land use, and combustion of fossil fuels during energy crop cultivation are avoided during biogas production from MSW [106]. Efficiency improvements in the EfW system could reduce its MRE and improve its energy contribution while avoiding the impacts associated with energy crop production and processing.

Assessment of energy consumption (Table 2.3) indicates that far more transportation fuel will be used over the lifetime of the bioreactor landfill than will be needed as electrical energy. The greatest percentage of the energy being consumed by the BCRRC is used during MSW collection (Table 2.3).

Table 2.3 - Total energy consumption for various landfill operations of the Burlington County Waste Management System

	Total Expected Consumption	
	[Tera-Joules (TJ)]	[% of Total]
Transportation Fuel	**5,853 ± 1,019**	**94 ± 16.4**
MSW House-to-house Collect.	3,985 ± 694	64 ± 11.0
MSW Hauling	965 ± 168	16 ± 2.8
Operation	355 ± 62	6 ± 1.0
Wastewater/Leachate Transport	311 ± 54	5 ± 0.9
Cover Material Transport	237 ± 41	4 ± 0.7
Electricity	**374 ± 65**	**6 ± 1.0**
Operation (Utilities)	343 ± 59	5.5 ± 0.9
Wastewater/Leachate Treatment	31 ± 6	0.5 ± 0.1

MSW collection from house-to-house and hauling to the landfill collectively account for 80% of the total energy consumption, but operators of the Burlington County waste management system have little control over collection or hauling. Figure 2.3 compares the relative contributions of various landfill operations, and further considers the relative

contributions of landfill operations with collection and hauling removed to better describe the sensitivity of aspects that can be controlled by system operators.

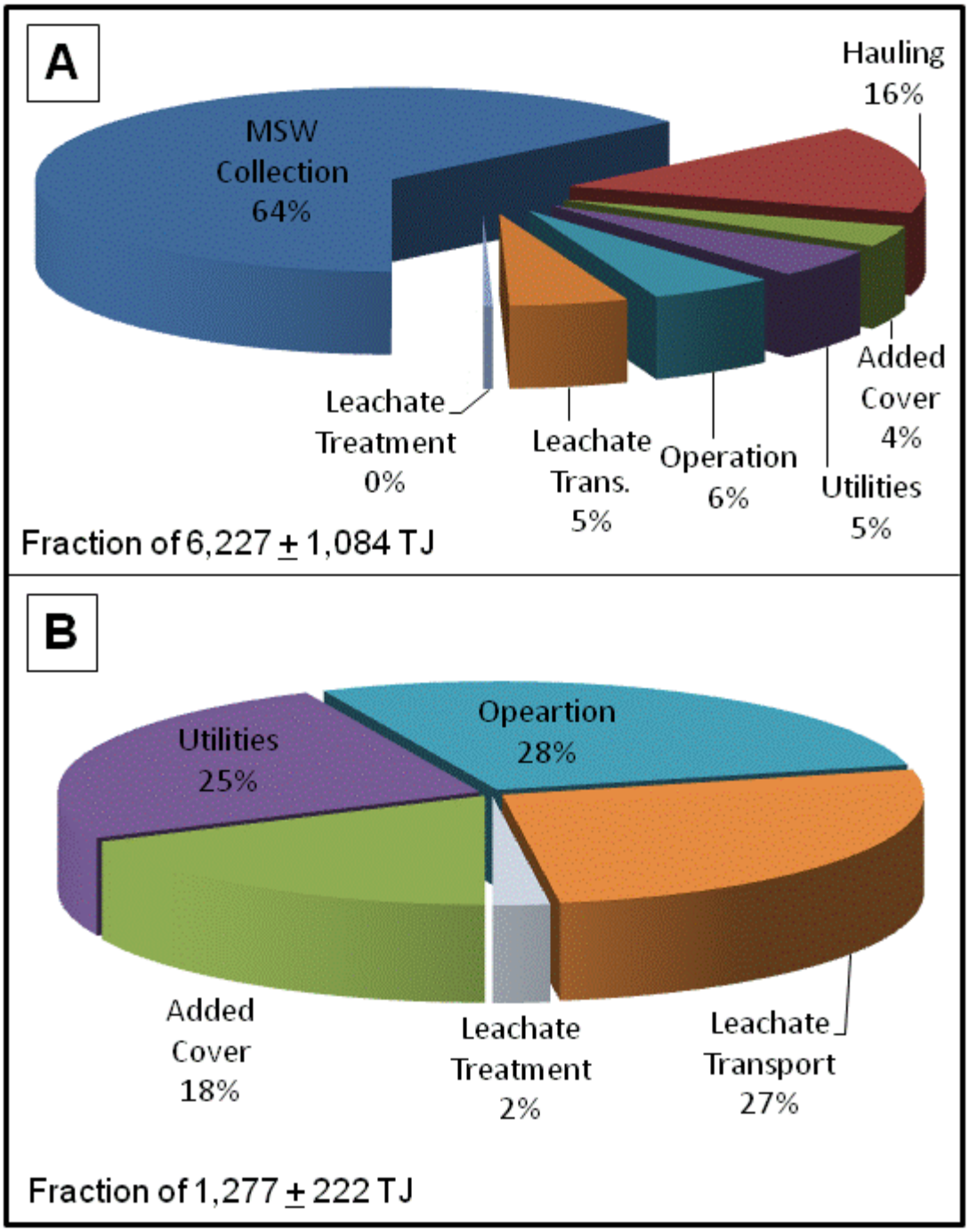

Figure 2.3 - Comparison of Burlington County system energy requirements: (A) fraction of total consumption, and (B) fractions of consumption when energy required for collection and hauling is removed from the balance

When the energy required for collection and hauling are removed from consideration, landfill operations (28%) and leachate transport (27%) become the most important system energy requirements. Leachate transport and added cover transport (18%) are important aspects to consider because Burlington County has direct control over these energy sinks. The decision to transport leachate to a closer facility for treatment or to obtain cover from a locality nearer the bioreactor landfill could be quantified by the model and used to predict savings in terms of transport fuel consumption.

2.4.2 Model sensitivity analysis

A sensitivity analysis was conducted to evaluate and identify factors having the greatest impact on the energy balance. The model was most sensitive to input factors (Table 2.4) that were related to the components responsible for the greatest energy consumption (MSW collection from house-to-house and hauling to the landfill) and the least sensitive input factors were those relating to components responsible for the smallest energy consumption (leachate treatment). The most sensitive inputs (> 0.040) are shown in Table 2.4.

Table 2.4 – Input parameters for Burlington County system to which the model is most sensitive

Model Component	Input Variable	S
MSW Collection and Hauling	Average hauling distance ($d_{transport}$)	0.521
	MSW delivery load ($Load_{AVG}$)	0.428
	MSW collection fuel economy ($F_{collection}$)	0.411
Leachate Transport	Leachate transport distance (d_{Leach})	0.042

The model was most sensitive to the average waste transport distance and the MSW delivery load size. Neither of these values were assumed, but rather determined from available data. The sensitivity to the MSW collection fuel economy was also relatively high, and is dependent on an assumed input value of 0.85 km/L-diesel. However, since the combined fuel economy of MSW hauling and collection from house-to-house can be obtained from available operating data, the potential variance in the assumption is thought to be small and known to be less than the 100% variance tested in the sensitivity analysis. The sensitivity analysis, overall, identifies the most vital system components for optimization as being the distance from the MSW collection site to the bioreactor landfill, the MSW delivery size, and the average fuel economy of the MSW collection and hauling trucks.

2.4.3 Selected LFG energy utilization options

The utilized energy is a function of the efficiency of the conversion technology and the LFG generation. Efficiency, as defined here ($f_{Efficiency}$, Equation 2.1), is the recoverable energy divided by the energy associated with the total collected (total flared) LFG (12,233 ± 3,511 TJ from 2000 to 2030). Although numerous LFG energy recovery technologies exist, LFG utilization in the U.S. largely involves only electricity generation and/or direct heating [107-108]. Three options are compared in Table 2.5. Liquefaction (LNG) and internal combustion (IC; currently employed at the BCRRC) are considered because specific operating and efficiency data were available for the Burlington County waste management system. Cogeneration is considered for comparison.

Table 2.5 - Recovery efficiencies for selected LFG utilization methods at BCRRC (observed efficiency in italics)

Recovery Method	$f_{efficiency}$	Recoverable Energy (TJ)
Liquefied Natural Gas (LNG)	0.305	3,731 ± 1,071
Internal Combustion (Electricity)	0.318 *0.212*	3,890 ± 1,116 *2,593 ± 774*
Cogeneration (Electricity, Heat)	0.73	8,930 ± 2,563

The recoverable energy is the associated useable (convertible to work) energy to be obtained from recovering otherwise flared LFG. Converting LFG to liquefied natural gas (LNG) produces the equivalent of 3,731 ± 1,071 TJ of transportation fuel. It is assumed that 2 liters of LNG are equivalent to 1 liter of diesel, and that 20% of the LFG is converted to electricity at an electrical efficiency of 0.35. These assumptions were

confirmed by data obtained onsite at the BCRRC by Acrion Technologies (Cleveland, OH, USA). Others [109-110] have observed higher LNG conversion efficiencies indicating that 1.33 liters of LNG are equivalent to 1 liter of diesel. If verified operationally, the efficiency of LNG recovery could be increased above 0.305.

Internal combustion engines (IC) produce electricity to be used onsite and/or sold to the grid, but do not recover heat. This technology has been employed at the BCRRC since late 2007, and the efficiency of this process is confirmed by operating data obtained from DCO Energy (Mays Landing, NJ, USA). Although the engine efficiency of 0.318 can potentially generate electricity equivalent to 3,890 $\pm$ 1,116 TJ (electrical transmission not considered), this result is not observed. Fluctuations in gas quality forces plant operators to divert unwanted LFG to a flare while shutting down some engines, and waiting for better biogas quality. Additionally, a utility company can control the utilization of electricity generated at the BCRRC. Because electricity is not a stored form of energy, it must be consumed as it is generated, and electricity demand can dictate the generation plant's electrical contribution to the grid. If electrical demand decreases, electrical production would decrease as well, and the excess LFG would be diverted to a flare where its associated energy would be wasted as heat. Accounting for the potential losses (difference between plant capacity and observed electrical generation) at the BCRRC decreases the observed efficiency from 0.318 to 0.212. By comparison, since LNG is a stored form of energy, the observed process efficiency can be realized independent of immediate demand and variable biogas quality.

Cogeneration would generate electricity equivalent to 3,661 $\pm$ 1,051 TJ and 5,269 $\pm$ 1,512 TJ as useable heat (transmission of electricity and heat not considered) based on

efficiency data and technology analysis findings from the USEPA [111-112]. Although cogeneration would seem to be the best of the three options for energy recovery (greatest recovery efficiency), cost, feasibility, and available infrastructure are major factors and do not always make cogeneration a viable option.

2.4.4 Operations related carbon dioxide emissions assessment

The amount of carbon dioxide released during the combustion of a liter of diesel fuel (2.668 kg-CO_2/L-diesel) served as the basis for the calculations, and was applied directly to the associated energy in liters of diesel equivalents obtained from the modeled output (Equation 2.18). As with the analysis of energy consumption and generation, the associated carbon dioxide emissions and neutral offsets can be assessed yearly or as the sum of the yearly outputs for a specified consideration length. The model allows for the carbon offsets of various LFG energy-recovery options to be compared (Figure 2.4).

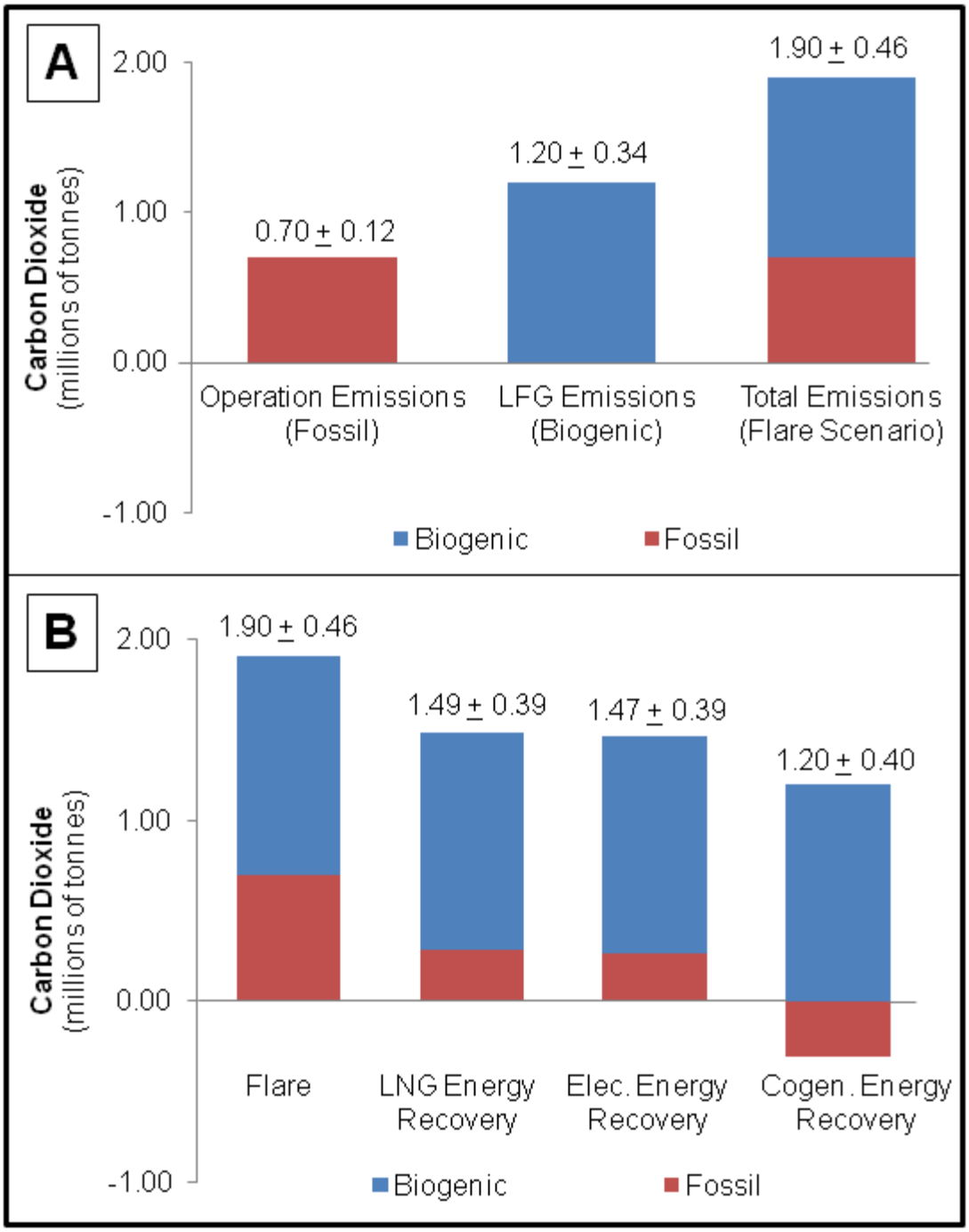

Figure 2.4 - Carbon dioxide emissions attributed to landfill operations (including waste collection, hauling, management and maintenance) over a 30-year period: (A) LFG emissions and the sum of these emissions, and (B) total carbon emissions with attributable fraction to fossil and biogenic sources for each considered energy recovery

Fugitive LFG emissions are not included in Figure 2.4, and could contribute 0.21 $\pm$ 0.02 million tonne-CO_2-eq. to total emissions. Based on the current system energy consumption of 6,227 $\pm$ 1,084 TJ, the system would contribute 1.90 $\pm$ 0.46 million tonnes of carbon dioxide equivalents to the atmosphere over the 30-year operation time of which 0.70 $\pm$ 0.12 million tonnes (36.8%) would be from fossil derived sources. Additionally, fugitive emissions could contribute an additional 0.21 $\pm$ 0.02 million tonnes of carbon dioxide equivalents to the atmosphere over the same period.

Only cogeneration has a great enough recovery efficiency to fully offset the required system energy and is the only option that would offset all associated fossil fuel carbon dioxide emissions (>100% offset). Achieving the theoretical cogeneration efficiency of 0.73 (Table 2.5) would allow an additional 0.30 $\pm$ 0.09 million tonnes of fossil fuel derived carbon dioxide to be offset by LFG (143.4% offset). By contrast the LNG and IC electricity recovery options would offset, respectively, only 59.8% and 62.5% of the fossil fuel derived carbon dioxide emissions associated with system energy consumption. The LNG and IC electricity energy recovery options considered, if employed, would require additional energy contributing, respectively, 0.28 $\pm$ 0.08 and 0.26 $\pm$ 0.07 million tonnes of fossil derived carbon dioxide.

Currently, the energy balance and carbon dioxide emissions model are directly and nearly exactly proportional because the supplemental system energy is almost entirely attributable to fossil fuel derived sources. As the supplemental sources become less dependent on fossil fuel sources, the system energy and carbon dioxide emission

balance for the modeled system will differ more significantly, and thus it is conceivable that carbon neutrality can be achieved before energy neutrality is achieved.

Since bioreactor landfills and digesters selectively recover the biogenic energy fraction from the MSW feedstock, there is not an associated anthropogenic carbon output associated with LFG combustion as there is with direct MSW combustion [54, 113]. The calculated carbon dioxide emissions associated with fossil fuel derived sources is contained within the model and can be updated in real time as the available electrical or transportation fuel mixtures for this system change. Transportation fuel (fossil derived diesel) for BCRRC operation and MSW collection is obtained exclusively from fossil fuel sources (94 $\pm$ 16.4% of total consumption), and electrical energy (6 $\pm$ 1.0% of total consumption) is obtained from the NJ electrical power grid (estimated carbon density is 0.731 kg-CO_2/MJ [98-100]).

2.4.5 Lower than Expected Waste Delivery Rate: Effect on LFG generation

Although the bioreactor landfill at the BCRRC was designed to more thoroughly degrade MSW to recover landfill space and available LFG, the layout, construction schedule, and operation protocols were also devised during the initial design, which hinders adequate LFG optimization in real-time. Deviations from assumed MSW accumulation rates, waste composition, LFG recovery efficiency, and leachate permeation impact long-term operation requirements without respect to the initial design. A profound effect on the expected LFG generation is being observed and predicted as a result of a lower than expected and decreasing MSW accumulation rate at the BCRRC (Figure 2.5).

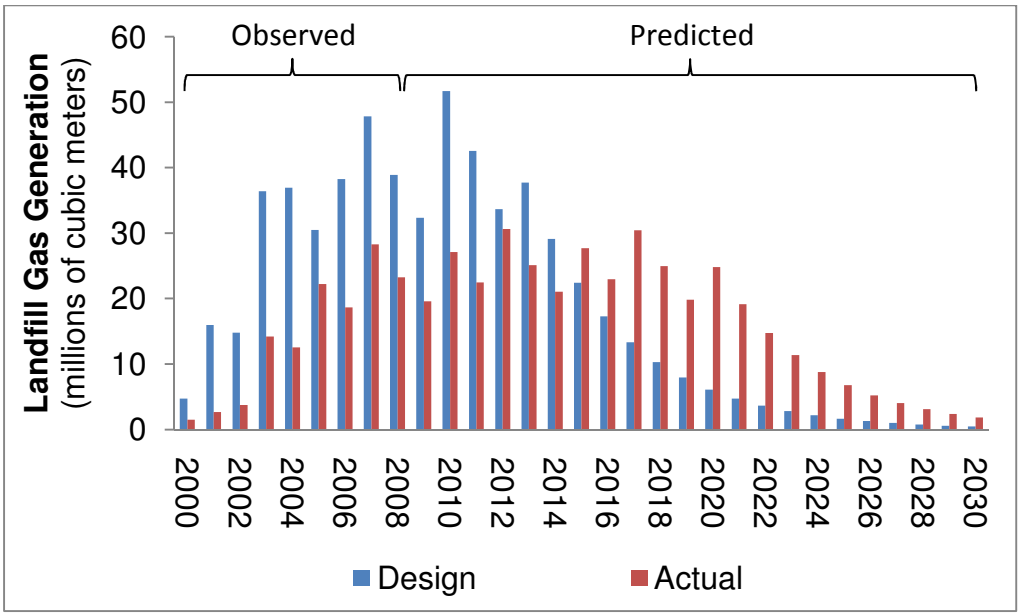

Figure 2.5 - Comparison of LFG generation volumes per year between original design projections assuming a higher than observed and currently projected MSW accumulation rate over a 30 year period at the BCRRC

The BCRRC bioreactor landfill was, in 1996 when it was designed, projected to receive 335,700 tonnes of waste per year, receive waste from 1999 to 2012 and then be capped. The leachate recirculation and LFG recovery systems were projected to come online in 8 stages (4 low and high phases) in-order-to more effectively increase waste stabilization and LFG recovery. The rate of phase completion is a function of the waste accumulation rate, and with a smaller accumulation rate comes a slower phase completion rate. The second stage of Phase 4 is now projected to take place in 2018. As a result the LFG generation is slowed down and extended over a greater period of time (Figure 2.5). Although the total LFG recovery currently projected is slightly less than that predicted in the original design (501 versus 590 million cubic meters of LFG), the model does not adequately account for additional fugitive LFG emissions resulting from the waste degradation occurring in open cells unaffected by LFG recovery infrastructure. Even if

the total potential LFG could be recovered by the system designed, the inflexibility of the system without redesign presents several infrastructure, operational and economic challenges: (1) the LFG recovery system was sized and designed to handle the original predicted LFG volumes, (2) fluctuations in LFG generation volumes from year-to-year requires recovery infrastructure to be sized to the largest expected yearly volume, (3) the LFG recovery system will have to be operated much longer than originally expected, (4) bioreactor operation and associated costs are extended into the future without the prospect of added revenue from additional waste, and (5) offset revenue from LFG energy recovery will likely be reduced as a result of losses due to fugitive LFG emissions.

2.4.6 Management Improvement Scenarios

The model allows entirely theoretical system designs to be tested or allows a few inputs for an established system to be tweaked to assess the impact of a specific operating change. The energy balance model was used to assess three scenarios (Table 2.6).

Table 2.6 – Comparison of selected improvement scenarios analyzed for Burlington County Waste Management System

Scenario	Description	Effect on Consumption	Effect on Generation
1a – Truck and collection efficiency	• Truck collection fuel economy increased from 0.85 to 2.55 km/L • Truck waste delivery capacity increased from 5.20 to 6.35 tonne/delivery	• Total consumption reduced 47.2% from 6,227 ± 1,084 to 3,290 ± 572.5 TJ • Reduction of transport fuel fraction from 94% to 90% • Reduced collection fractional demand from 64% to 33%	No effect
1b – Truck efficiency	• Truck collection fuel economy increased from 0.85 to 2.55 km/L	• Total consumption reduced 42.8% from 6,227 ± 1,083 to 3,561 ± 619.6 TJ • Reduction of transport fuel fraction from 94% to 90% • Reduced collection fractional demand from 64% to 37%.	No effect
2 – Hauling distance variation	• The hauling distance was varied as a function of the minimum recovery efficiency (MRE)	• Hauling distance was directly proportional to system consumption • System critical hauling distance (MRE basis) found to be 67 km	No effect
3 – Onsite in vessel anaerobic digestion	• Theoretical biogas generation from a high-solids AD system was compared to LFG generated	Not quantified	• Increased recoverable biogas by 66% over 18 year period

2.4.7 Effect of waste-truck efficiency

First, the model was used to show the impact that changing the type of MSW-collection truck to a hypothetical hybrid truck with a better collection fuel economy and greater payload has on the system-wide energy consumption. By assuming that the new trucks achieved a collection fuel economy of 2.55 km/L, and that the average waste delivery load was 6.35 tonnes, a 47.2% reduction in the system-wide energy consumption was observed (from 6,227 $\pm$ 1,084 TJ to 3,290 $\pm$ 572.5 TJ). The improvements tested in this scenario reduced the system's demand for transportation fuel allowing the energy fraction required as transport fuel to be diminished from 94% to 90%, and lowering the fractional fuel requirement for MSW collection from house-to-house from 64% to 33%. Under this scenario, all three energy recovery options considered would generate more useable energy than the system consumes (3,290 $\pm$ 572.5 TJ). However, operating data from the BCRRC indicates that the total number of deliveries does not directly correlate to the MSW accumulation rate (waste collection prevalence and routing is independent of the MSW generation rate). Considering only improvements in vehicle efficiency, a 42.8% reduction in the system-wide energy consumption can be observed (from 6,227 $\pm$ 1,083 TJ to 3,561 $\pm$ 619.6 TJ). This more modest improvement reduces the transport fuel requirement from 94% to 90%, and the fractional energy requirement for MSW collection from house-to-house from 64% to 37%.

Since the only available data for the BCRRC is an average fuel economy based on an aggregate of total miles traveled and fuel consumed, it is difficult to assess the efficiency of the system's vehicle routing. The energy balance model allows truck efficiency improvements to be assessed system-wide. For this model the best way to include truck routing would be to incorporate a fuel consumption reduction factor based

on routing schemes. This information is not available at this time. Recall, however, the fraction of the deliveries that arrived from municipal routings (residential and commercial) requiring both collection and hauling (78.3 ± 6.7%) versus the fraction of the deliveries with direct routings (industrial and bulky waste) requiring only hauling (21.7 ± 6.7%) was considered. The fraction requiring collection steadily increased from 70.8% in 2004 to 86.6% in 2007 (Figure 2.6).

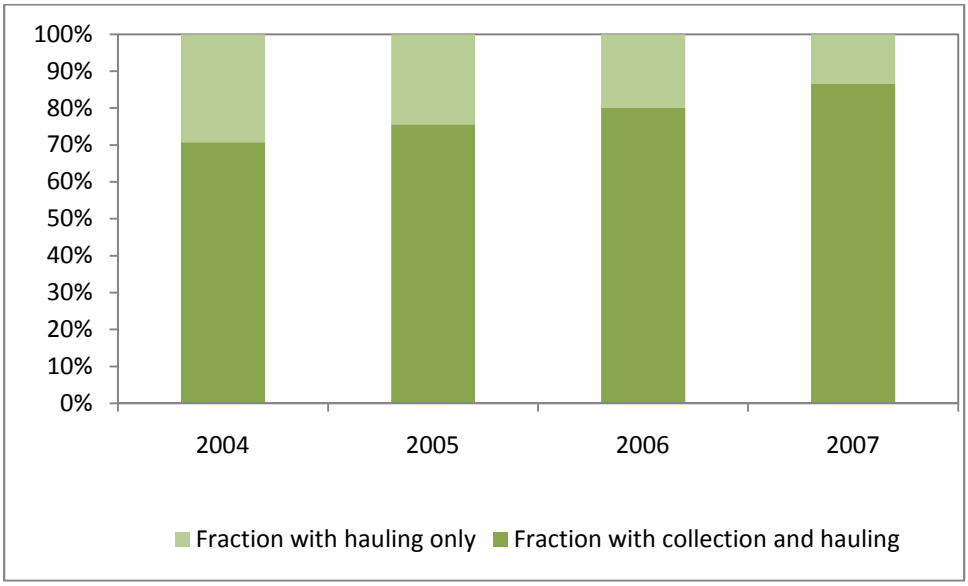

Figure 2.6 – Fraction of MSW delivered from direct hauling versus MSW collection from house-to-house and hauling.

Perhaps as a function of the declining economy, the number of bulky waste and industrial deliveries with direct hauling, but without house-to-house collection, declined. If this trend continued or did not reverse, the calculated average fraction of MSW requiring collection and hauling (78.3 ± 6.7%) would be less than the actual fraction. Thus, using the average fraction over a number of years would skew the observed consumption for the system down.

2.4.8 Effect of hauling distance

In the second scenario, the impact of varying the MSW transportation distance was correlated to the minimum recovery efficiency (MRE). The system generates more energy than it consumes when the energy balance is positive. Varying only the transport distance, it is possible for the system energy balance to remain positive as long as the average transport distance from collection location to the management facility is limited to 67 km, because increasing the average transport distance also increases the MRE. Beyond 67 km, regardless of the energy recovery efficiency, it is not possible for the waste management system to produce more energy than it consumes. This scenario does not account for increasing the MSW accumulation rate, which could be associated with expanding the waste management system, and increasing the average distance. This caveat could be incorporated into the model, and indicates a need to assess the MSW volume as a function of the waste management system's size in area. The tradeoff in system size as a function of transport distance and MSW accumulation rate would be an important factor in system design.

2.4.9 Effect of onsite in vessel anaerobic digestion of MSW relative to bioreactor landfilling

In the third scenario, onsite anaerobic digestion in a controlled reactor is considered because there are several substantial problems with using bioreactor landfill technology to facilitate the degradation processes needed to recover biogas for energy production. First, because these systems are merely an extension of landfill technology, never intended to be digesters, landfill bioreactors are largely uncontrollable, and not optimized to produce and recover biogas. The design and construction of bioreactor

landfills, which are effectively a collection of individual cells, can, at best, be modeled as a set of independent batch reactors. Steady-state biogas generation is not observed for such systems, making optimization and energy recovery infrastructure design difficult. Further, more than 25% of the LFG generated in bioreactor landfill systems, even with comprehensive wellfields, may not be captured by the LFG recovery system [103, 114], and far greater loss of methane as a fraction of LFG generated has been reported (65.6% loss) [107]. At the BCRRC, a 25% LFG loss corresponds to a loss of potential biogas energy equivalent to 5,843 TJ (note that the carbon dioxide balance does not include fugitive LFG emissions). Utilizing onsite digester technology could substantially reduce unwanted fugitive biogas emission losses.

The model predicts that the BCRRC will landfill 5.64 million tonnes of waste from 2000-2018 and recover 671.1 million cubic meters of biogas. Typically, 67.2% of the waste stream entering the bioreactor landfill at the BCRRC is considered MSW (Class 10: Residential, Commercial, and Industrial Waste). Generously assuming that 79% is considered dry weight with a volatile solids (VS) content of 88%, the BCRRC can expect to recover about 127.4 cubic meters of methane per tonne MSW (normalized on VS basis). This is somewhat lower than reported theoretical MSW methane potentials commonly between 190 and 330 cubic meters of methane per tonne of MSW_{VS} [107, 115-116]. An average value of 245 cubic meters of methane per tonne MSW_{VS} can be an assumed potential for landfill type systems [107]. Achieving the expected methane potential from MSW at the BCRRC (245 m^3 CH_4/tonne-MSW_{VS}) would reduce the MRE from 0.49 to 0.27 making all recovery options neutral with respect to system energy.

Although some differences in MSW composition between the BCRRC and the assumed composition used to obtain the theoretical methane potential of MSW per tonne may exist, it may not be great enough to substantially narrow the gap between 127.4 and 245 cubic meters of methane per tonne of MSW_{VS}. This difference thus, could perhaps be attributed to poor system optimization, inefficient gas recovery, and incomplete waste conversion. These problems could be avoided or mitigated by developing more controlled digester systems to recover energy-from-waste. Engineered in vessel systems would maximize the potential biogas production and recovery while allowing for reaction-system optimization and integration. Thus, the energy balance model was used to consider a third scenario in which the degradable organic fraction of the MSW stream is stabilized using anaerobic digestion.

Laboratory, pilot and large-scale anaerobic digesters have been designed and operated to optimize biomass conversion and methane recovery [117]. A controlled digester system would avoid the infrastructure, operational and economic challenges of a bioreactor landfill by lending itself to external dynamic controls capable of responding to observed deviations in waste characteristics, accumulation rate, and LFG generation. Moreover, the system could be operated at steady-state with continuous and relatively consistent biogas generation. Steady-state operation would be able to achieve the highest possible biochemical methane potential during the reaction period, and would allow for better planning and utilization of generated LFG energy. Digester infrastructure could also be used to process more waste than the bioreactor landfill can accumulate, and only needs to be modeled while receiving waste, avoiding greater uncertainty associated with long-term projections.

The impact on equivalent biogas and energy generation resulting from onsite MSW digestion was considered for the BCRRC (Figure 2.6). Operating an onsite digester would require MSW sorting, reactor heating, and residual treatment (dewatering) followed by solids residual landfilling. To reduce the hypothetical digester energy consumption, a "high-solids" anaerobic digestion scheme was considered. High solids (25 to 40%) anaerobic digestion processes minimize heating, pumping and pre- and post-treatment energy demands [66, 117-118], and parasitic loads have been reported [66]. Typically between 30% and 40% of the generated electricity and 10% of the generated heat is diverted to maintain the process [66]. Similar parasitic energy requirements have been used in estimations for "slurry" type anaerobic digestion systems [75, 89-90].

The digester biogas volumes generated are a function of the observed (2000-2009) and predicted (2010-2018) waste characteristics and waste delivery rate. It was estimated that 62% of the landfilled material at the BCRRC is MSW of which 47% is degradable organic material. The methane yield was assumed to be 160 cubic meters per tonne of degradable organic [117-118], and methane was assumed to account for 55% of total biogas generated [75].

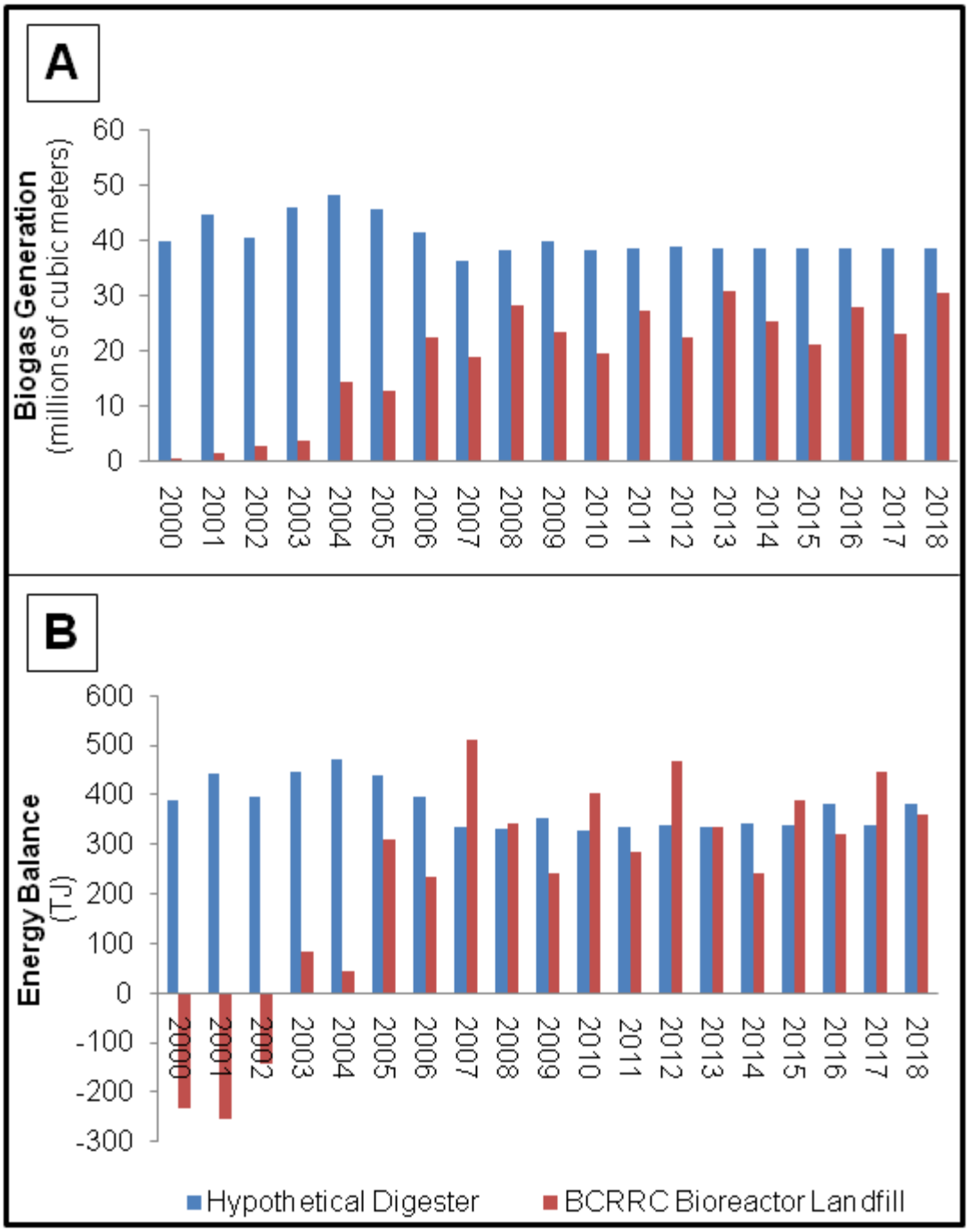

Figure 2.6 - Comparison of biogas/LFG (A) and equivalent energy (B) generated by employing onsite digester versus landfill bioreactor technology over the 18-year waste production period

The simulated biogas/LFG output (Figure 2.6A) shows that biogas volumes from the digester are greater and more consistent from year-to-year compared to LFG generated by the bioreactor landfill. As a result, the total recoverable energy (not considering system energy consumption), over the 18-year span, is greater when employing the considered digester technology (2,731 $\pm$ 756 MJ/tonne versus 1,645 $\pm$ 467 MJ/tonne). Accounting for parasitic losses (~22% of total generated biogas energy), the digester technology is capable of recovering more energy than the bioreactor landfill (1,263 $\pm$ 362 versus 778 $\pm$ 223 MJ/tonne) over the 18-year period considered.

Since the energy balance shows that more energy can be recovered from onsite anaerobic digestions, there is a case to be made for further developing this analysis in terms of energy and economics, and potentially for developing this technology at the Burlington County Resource Recovery Complex. In terms of reducing greenhouse gas emissions, and maximizing energy recovery from waste, more highly engineered systems such as WTE and anaerobic digestion systems have been shown to be more desirable as compared to bioreactor landfill technology with LFG recovery [41, 70, 86]. Further, as compared to WTE, anaerobic digestion has been shown to be advantageous in several cases [41, 66, 70].

2.5 Summary and Conclusions

The model results showed that the Burlington County waste management system is capable of generating more energy than it consumes, but only if its utilization capacity improved to 0.49 or its consumption decreased by 79% could it recover more useable energy than it consumes. Under either of these scenarios, the BCRRC would offset all of

its energy requirements, and indirectly all of its demand for fossil fuel, while contributing energy to a renewable portfolio.

The sensitivity analysis identified the most vital system components for optimization, as being the distance from the MSW collection site to the bioreactor, the MSW delivery size (truck load), and the average fuel economy of the MSW collection and hauling vehicles.

Among the potential recovery options considered for the BCRRC, electricity generation from an internal combustion engine produces the greatest amount of readily useable energy since using LNG cannot currently be achieved in large measure because there is currently no consumer of this fuel.

Three scenarios were considered to show how the model allows a few inputs for an established system to be tweaked to assess the impact of a specific operating change, or allows theoretical system designs to be tested. Results from the first scenario showed that MSW transport truck efficiency improvements could be realized system-wide, and that relatively modest efficiency enhancements in specific areas could have large impacts on the overall energy balance. Results from the second scenario established that the model can be used to consider tradeoffs in infrastructure design, identifying the tradeoff between MSW transport distance and required MRE as well as the dependence between necessary transport distance and waste volume. The third scenario considered the impact that developing in-vessel anaerobic digester infrastructure at the BCRRC could have on biogas and potential energy recovery. These results suggest that more gas could be reliably and consistently recovered for energy generation as compared to the existing bioreactor landfill technology, and more energy could be recovered as well.

The research conducted for this model has illuminated that existing waste management infrastructures, even those employing bioreactor technology such as the BCRRC, are difficult to optimize with respect to energy because existing system technology extends from landfill technology. The energy balance model identified the relative energy balance improvements to be expected from modifying particular operating practices or treatment options.

Chapter 3

3. Comparative Energetic and Economic Analysis of Anaerobic Digestion of Equine Waste on Farms and at Regional Digesters

[Babson, D., Sullivan, K., Zebib, T., Both, A.J., Brennan, M., and Fennell, D. to be submitted to Bioresource Technology]

3.1 Abstract

The relative energetic and economic advantages of onsite batch dry digestion versus regional continuous digestion of horse waste in New Jersey were investigated. Energy production from waste generated by a range of horse quantities (10, 50, 500 and 5,000 animals) and methane production potentials for the waste feedstock (100 to 300 L CH_4/kg VS) were compared. Theoretical systems utilizing either different standard off-the-shelf batch reactor sizes (10, 20 and 40 cubic yards, CY, equivalent to 7.6, 15.3 and 30.6 m^3) with various filling and retention scenarios, or a centralized continuous flow complete mix digester, were considered. The batch reactor system predicated on a dry fermentation, fill-digest-haul scenario was considered for on-farm applications. As the number of horses per facility increased, either the size and/or the number of batch reactors increased, or the solids retention time (SRT) decreased. For the centralized, continuous system, an upright digester was considered and its size increased as the number of horses served increased.

Not surprisingly, the methane production potential of the waste had a substantial impact on recoverable methane for both systems and thus established the type and quantity of stall bedding material—i.e., scarcely biodegradable softwood chips versus highly biodegradable straw—as an important control variable. The maximum methane potential considered for comparison, 277 L CH_4/kg volatile solids (VS), corresponded to

values that have been previously reported for waste mixtures containing horse manure mixed with straw bedding and or horse manure alone.

The centralized continuous system was consistently more efficient at methane generation than the multiple-vessel batch system given a comparable solids retention time of 28 days. The continuous system recovered between 22% and 30% more methane per horse and had a capital investment of between 13% and 68% less per kWh of electricity produced than the batch system. Doubling the retention time of the 10- and 20-cubic yard (56 d 10-CY and 56 d 20-CY) batch systems from 28 days to 56 days increased the recoverable methane by as much as 77% and 79%, respectively, which also reduced the required capital investment per kWh of electricity by as much as 27% and 26%, respectively. However, the 56 d 10-CY batch system, even with its retention time doubled (56 versus 28 days), required a greater capital investment per kWh of electricity when compared to a system with 40-CY batch reactors or to the continuous systems. The 56 d 20-CY batch system had the greatest energy output per capital investment among all batch systems considered for horse quantities up to approximately 25. The 40-CY batch system was found to cost less to construct per horse over a broad range of horse quantities (up to 700), but the cost per kWh of electricity produced was greater among batch systems for horse quantities above about 80, than for continuous systems. The largest capital cost for the batch system was an insulated structure to house and maintain a temperature of 35°C for the reactors. When the cost of the structure was subtracted, the capital investment per kWh of electricity produced by the batch system was less than that of the continuous system over the considered range of horse quantities, but the outsized footprint (land area) required to house multiple filling or digesting vessels for

batch systems could make large multi-reactor batch systems unrealistic. If horse waste management strategies include eventual removal of the material, the regional continuous digester system appears to be more advantageous when compared to onsite batch systems; especially for larger farms (greater than 50 horses) without preexisting infrastructure to house the batch reactors.

3.2 Introduction and Literature Review

As a result of different nitrogen to phosphorus (N:P) ratios present in manures and required by crops, not all manure produced on horse farms can be applied to fields in an environmentally acceptable manner. This is in part because phosphorus builds up in the soil and is eventually deposited into waterways, resulting in eutrophication of fresh water ecosystems [119]. Most animal feeding operations fall under the jurisdiction of Federal water quality regulations, such as the National Pollution Discharge Elimination Systems (NPDES) permit program and Section 319 of the 1987 Amendments to the Clean Water Act [120]. State programs may also regulate equine facilities. In New Jersey for example, equine facilities with greater than eight horses must have a waste management plan and operations with 300 or more horses must develop and implement a Comprehensive Nutrient Management Plan [121]. Further, large facilities may fall under the Department of Environmental Protection (DEP) stormwater permitting program for concentrated animal feeding operations (CAFOs) and designated animal feeding operations (AFOs) [122]. The aforementioned regulations, to be implemented in New Jersey beginning in 2010, could further regulate onsite animal waste handling. This increased regulation of waste handling practices on equine farms could increase the need for offsite removal, and present an additional economic burden for affected facilities.

Anaerobic digestion, which produces the fuel gas methane, is a potentially profitable means of defraying operating costs associated with waste handling regulations. Recovery of methane from equine waste could also allow horse owners to take advantage of emerging economic benefits from renewable energy credits or greenhouse gas mitigation credits [123-125] as described in Section 3.2.2.

3.2.1 Anaerobic Digestion of Horse Waste

Numerous guides for best horse and animal waste management practices have been developed to minimize environmental impacts and maximize the utility of the manure [126-130]. In contrast to dairy or swine manure, which are recovered as liquid slurries of 2.6 to 18.4% total solids (TS) [131], horse manure and horse stall waste, which contains bedding, have higher solids contents of 25 to 40% TS [132]. Further, the presence of stall bedding such as wood chips provides a bulking agent. Therefore, horse waste stabilization has usually been achieved by aerobic composting [126]. Several studies have reported investigations of composting of horse waste and have provided nutrient control parameters for this process [133-135]. On-site horse waste composting has several advantages as a management practice because is simple to implement, cheap to operate and produces a valuable compost product [126, 130]. However, the benefit of the compost product, typically used as a soil amendment, cannot be realized without either sale or free distribution of the composted material. Excessive onsite application of composted equine waste would confer many of the same environmental harms as direct manure application because nutrients such as phosphorus are not removed during composting. Thus, horse waste removal from the site of generation may be necessary in one form or another, if there is not adequate land area to handle the nutrient loading.

In contrast to aerobic composting, there are only a few published studies related to anaerobic digestion of horse waste [132, 136-141]. This lack of information may reflect the fact that equine waste is a less abundant waste than cattle and swine manures and/or that the material is considered highly suitable for composting rather than digestion. The primary advantage of employing anaerobic digestion in the treatment of horse manure is that it has the potential to recover methane, an energy source. Further, as compared to composting, Murphy and Power (2006) concluded that anaerobic digestion is favorable from an environmental standpoint because it reduces greenhouse gas emissions by displacing fossil fuels [142]. Residual material (digester effluent) could subsequently be composted to generate the desirable compost product as well.

The study by Mandel and Mandel (1998) used horse waste as one of many local substrates in investigation of improving methane production by addition of magnesium catalyst [140], while the study by Zuru et al. (2004) included horse waste as one of several substrates in a study examining model development for anaerobic digestion [137]. Kusch et al. however, published an extensive investigation of methane production from stable waste as a single substrate [138]. The stable waste used by Kusch et al. was characterized as follows: "Horse dung was collected from a typical horse stable with straw bedding. The proportion of straw in the manure was high." The study examined methane yields in mesophilic (35°C) solid state batch reactors. Because the horse gut is not a highly methanogenic system like the bovine rumen, it may not be as efficient at self-inoculation for anaerobic digestion. Thus, the batch reactors were operated with variations that included use of different ratios of inoculation with previously digested material to ensure rapid start of methanogenesis, percolation of recycled process leachate

as inoculum, or flooding with tap water to investigate self-starting of methanogenesis. Kusch et al. (2008) also investigated the effect of aerobic pre-composting and particle size reduction on methane yield [138]. The total methane production potential of the stable waste used by Kusch et al. (2008) was 277 L CH_4/kg VS added and recovery of that methane potential was 52% in four weeks, 62% in six weeks and 74% in 74 days. Percolating or flooding the reactor as well as chopping the feedstock improved the effective conversion. Percolation required larger reactor volumes than flooding, and did not show any greater effective conversion [138].

Wartell (2009) and Wartell et al. (2008 and 2010) reported methane production potentials for horse manure and horse manure mixed with softwood chip stall bedding or straw bedding. These values are reported in Table 3.1 along with the data from other studies of methane production potential [132, 141, 143]. From the information available it appears that horse manure alone or horse manure with straw bedding would have an upper methane production potential of 200 to 300 L CH_4/ kg VS. Horse manure mixed with the wood chip bedding had a lower methane production potential, depending upon the ratio of bedding to manure. This is because the wood bedding is scarcely degradable on its own, with a methane production potential of approximately 15 L CH_4/ kg VS. Thus, on the basis of total VS loaded (manure plus bedding) into digesters, the methane production potential could be greatly diminished by the presence of the softwood bedding, which on its own, is scarcely convertible to methane (Table 3.1).

Table 3.1 - G_{pot}, methane production potential, as $t \rightarrow \infty$ for horse manure, stall waste mixtures and bedding types expressed on the basis of the total (horse manure, stall waste or bedding only) VS added. *NA = not applicable

Waste	Ratio Bedding VS: Manure VS	G_{pot} (L CH_4/kg VS)	Reference
Horse Manure	NA	206 ± 45 277 ± 29	Wartell et al. 2010 [143]
Horse Manure + Wood Chip Bedding	0.25 0.5 1 2 4	167 ± 43 138 ± 34 113 ± 35 124 ± 23 119 ± 17	Wartell et al. 2010 [143]
Horse Manure + Straw Bedding	Unknown	277	Kusch et al. 2008 [138]
Straw	Fresh	333 195	Tong et al. (1990) [144] Møller et al. (2004) [145]
Softwood Chips	Fresh	~15	Wartell et al. 2010 [143]

The use of horse waste in an "as generated" state leads to the approach outlined by Kusch et al. (2008 and 2009) for so-called "dry digestion" or "dry fermentation" where the reactor operational solids content is >20% TS. This approach has been described previously for other agricultural biomass [146-147], and has been proposed in recent years as a promising system for on-farm conversion of many different high solids agricultural wastes to biogas [148]. The application of batch reactors for on-farm conversion requires a multiple reactor configuration to equalize temporal biogas output

and may require some type of leachate recirculation to encourage microbial activity [139].

Batch digestion also lends itself to onsite application better than continuous digestion because it is a simpler method to employ [149], an important aspect of successful on-farm application. However, there are numerous conditions resulting from batch operation that limit methane yields as compared to continuous operation. In batch systems, microbially mediated processes may be limited by inadequate access to substrates as a result of reduced moisture mass-transfer [150-151]. Convective transport mechanisms can be added to improve overall mass-transfer in the batch digester by employing liquid recirculation [152], but initiating recirculation too early in the batch process can disrupt the establishment of the methanogenic microbial community [151, 153]. Enhanced acidogenesis as a result of recirculation can inhibit methanogenesis as well [154]. Without the establishment of a sufficient methanogenic community in the initial phases of the batch process, digester failure can occur [155]. This makes not only recirculation an important parameter for controlling methanogenic community establishment, but also the quantity [138, 156-157] and quality [158] of the inoculum utilized. Thus, the dynamic nature of the batch system makes the inoculum selection and addition, as well as the timing and extent of recirculation critical, and increases the complexity of batch operation. Another concern for batch operation is potential methane loss during reactor filling. Batch reactor size and manure volume as a function of time, control the length of time needed to fill a batch reactor. As the fill time increases, the amount of organic matter that can be degraded (either aerobically or anaerobically) without methane capture increases. This could decrease the overall methane yield from

the batch digester system. For example, Kusch et al. (2008) reported that 11% of the methane production potential was lost from horse waste that was pre-aerated prior to high solids batch digestion, compared to fresh material [138]. Further, Wartell (2008) observed that stall waste that had been stored in outdoor piles for several weeks, that was subsequently minimally inoculated and digested in high solids batch reactors, yielded only approximately 30% of the expected methane potential when compared to freshly collected waste digested in slurries -[132].

Continuous digester systems have several advantages when compared to batch systems. By operating at a steady-state, higher moisture content, and with constant mixing, continuous systems decrease the challenges of microbial community dynamics and mass-transfer limitations observed in batch systems. These advantages typically correspond to greater methane yields on a VS and reaction time basis. However, the cost and complexity of continuous operation often lends the technology to larger systems, and can make onsite development and operation of continuous systems difficult for individual farms.

Single (combined hydrolysis-acidogenesis and methanogenesis) and double-phase (segregated hydrolysis-acidogenesis and methanogenesis) continuous digester systems have been employed to react organic wastes, but singe-phase systems are most common [159]. Although single-phase systems require fewer initial investments and operating costs [160], optimized two-phase systems have been shown to be more stable and kinetically robust compared to the single-phase system [161]. Besides costing more, two-phase systems are complicated to operate because maintaining the separation

between hydrolysis-acidification and methanogenesis is difficult [160, 162-163]. In many cases, the benefit of two-phase operation is offset by cost and complexity [161].

In the study described here, batch and single-phase continuous digester configurations were considered for onsite and regional horse manure digestion systems, respectively. Onsite batch digester designs originate from the desire to develop anaerobic digestion infrastructure that could easily recover available biogas from horse waste while being readily incorporated into existing or future waste management systems. Typical waste management scenarios at horse farms include daily removal of waste from stalls, storage of waste for weeks in static piles or in containers, and eventual haul away for local or remote land application or other disposal via off-site composting or landfilling.

A typical 455 kilogram stabled horse will generate 16 to 23 kilograms of waste and 4 to 7 kilograms of bedding per day producing between 0.057 and 0.085 cubic meters of waste each day [164]. Horse waste has a high solids content (25 to 35% TS) [141] and is handled with shovels and wheel-barrels at small facilities or with front-end loaders and conveyor belts at large facilities. Horse waste contains stall bedding such as woodchips, and thus, producing a pumpable mixture (desirable for continuous flow reactor processes) of 5 to 15% total solids would require addition of substantial liquid and mixing to keep solids in suspension. Such manipulation would require more resources, machinery and system controls along with a skilled operator, and might not be practical for small operations.

3.2.2 Economic Assessment of Anaerobic Digestion of Manures

Much of the information contained in Section 3.2.2 *was provided by Kevin Sullivan and Margaret Brennan of the New Jersey Agricultural Experiment Station.*

Several studies have been undertaken to assess the economic feasibility of manure anaerobic digestion. Most of the studies have looked at dairy or swine wastes exclusively, and have taken a wide range of approaches to determine the economic feasibility of manure anaerobic digestion. Using survey and census data from Iowa livestock production facilities, as well as the AgSTAR methane recovery models and various electricity and propane prices, Garrison and Richard (2005) assessed the economic feasibility of complete mix and plug flow digestion of dairy waste [165]. Loan rates and producer down payment rates also varied between 0% and 10%, and 5% and 20%, respectively [165]. The most pertinent results from Garrison and Richard are listed in Table 3.2 [165].

Table 3.2 - Comparison of break-even point depending on number of cows for two scenarios

Number of Cows Necessary to Reach Economic Break-Even Point				
Conditions	Tie Stall Plug Flow	Tie Stall Complete Mix	Free Stall Plug Flow	Free Stall Complete Mix
$0.12/kWh retail electricity price, 10% loan rate, 20% down payment, no propane sale	222	148	234	148
Same scenario with sale of excess electricity for $0.025/kWh	155	119	155	118

The results in Table 3.2 could provide expected ranges for comparison of horse quantities if the waste volume and energy content could be related to dairy cows. Retail electricity prices were shown to be a critical factor in controlling the breakeven point. Cow quantities over 5,000 were necessary as electricity prices fell below $0.08 per kWh. Retail electricity prices in New Jersey, however, were $0.1369/kWh in December 2008 and $0.1402/kWh in December 2009 [166], and wholesale electricity prices in PJM were an average of $0.08466/kWh in 2008 and $0.0637/kWh in 2009 [167].

A 2007 study by Lazarus and Rudstrom focused on the capital cost investment necessary for a highly specific system (heated plug-flow digester with a 130 kW engine/generator), but assessed the effects grants, loans and subsidies have on the profitability of this specific anaerobic digestion operation [168]. The total cost of the system was $355,000 ($444/cow), of which 36% was covered by grants or other external assistance [168]. With this level of assistance (36% of total capital cost), and with cows generating 1,253 kWh per cow per yr, the investment could be recouped in 4 years with an average electricity sale price of $0.06 per kWh. Under this condition, the internal rates of return on assets and equity were 8% and 21%, respectively. If loans, grants and subsidies comprised 0% of total capital costs, it was projected to take over ten years to recoup the investment and both rates of return would be negative (assuming also that the wholesale price of electricity dropped to $0.031 per kWh) [168].

Another study (AgSTAR), focused exclusively on the capital costs of dairy digestion operations throughout the United States by performing regression analyses on system capital costs and the number of cows used in the various operations [169]. Equation 3.1 gives the relationship between capital costs and number of cows for a

complete mix digester, assuming the number of cows falls within the range of 700-2,300 [169].

$$C_{System} = 615 \cdot n_{Cows} + 354{,}866 \qquad \text{Equation 3.1}$$

Where, C_{System} is the system capital cost and, n_{Cows} is the number of cows contributing waste to the system. The capital cost per dairy cow is given by Equation 3.2 [169].

$$C_{Cow} = 12{,}331 \cdot (n_{Cows})^{-0.362} \qquad \text{Equation 3.2}$$

Where, C_{Cow} is the capital cost per cow.

The most extensive analysis was conducted by Bishop and Shumway (2009), who assessed the net present value (NPV) of sixteen different scenarios, many of which included the sale of co-products such as fiber (as a soil amendment), and carbon credits, as well as the acceptance of food waste (with and without tipping fees) and manure transported from one mile away [170]. The depreciation period of the project was also varied (20 to 40 years), as was the discount rate (3% to 5%) [170]. The baseline scenario, which had a negative NPV of $644,556, was a 500 cow operation with the price of electricity at $0.05/kWh plus a $0.02/kWh tax credit [170]. The fiber produced was utilized for bedding and a 4% discount rate and 40 year depreciation period were applied. The total capital cost of the anaerobic digester system (hardtop plug-flow digester) was $924,000 [170]. The total cost of the project was $1,136,000 including engineering and administrative costs, as well as, feasibility studies [170]. Transporting manure from 250 cows one mile to be digested, even with 38% of the digester cost covered by grants, caused the NPV to fall to negative $727,607 using a 30 year depreciation period [170]. For this reason, Bishop and Shumway asserted that “the cost to the digester owner of transporting the manure is much greater than the value of the additional electricity

generated [170]." The most lucrative option was collecting tipping fees for the disposal of food waste. In the model, food waste comprised just 17% of the total digester influent, while 37% of the generated biogas came from food waste, due to its higher energy content [170]. Even without tipping fees, the inclusion of food waste increased the NPV by $325,000 indicating the strong dependence of economic feasibility on feedstock energy content [170]. Once tipping fees were included, the NPV increased by almost $1.5 million, but on-farm nutrient loading costs from food waste were not considered [170].

With the establishment of cap and trade legislation, not currently in place in the United States, carbon dioxide offsets would be accrued as a result of methane emission reductions associated with manure digestion generating additional revenue for digester operators [123]. Appropriately priced carbon credits, have been shown to increase the NPV of digester systems [125]. Comparing methane yield, energy utilization and economic profitability of onsite or regional digester systems allows the value of digestion and the associated carbon credits to be assessed.

It is worth noting that all operations were conducted on existing farm land, and that the cost of an anaerobic digestion project will be too great to make it economical if the dairy operator does not own the land or hold a lease in excess of the expected project lifetime [171]. However, the economic assessment of such systems can be used to measure the extent to which external subsidies, grants, tax incentives or credits need to be provided to make anaerobic digestion systems viable. Currently, there are numerous federal and state incentives for anaerobic digestion systems (Table 3.3) [172-173].

Table 3.3 - Federal and New Jersey State incentives for anaerobic digestion systems

Incentives for Anaerobic Digestion Systems	
Federal Incentives for Anaerobic Digestion [172]	
Incentive	Affected Sectors
1. Modified Accelerated Cost-Recovery System (MACRS)	Business may recover investment in certain property through depreciation deductions
2. Renewable Energy Production Tax Credit	Commercial, industrial
3. U.S. Department of Treasury-Renewable Energy Grants	Commercial, industrial
4. USDA Rural Energy for America Program (REAP Grants)	Commercial, rural electricity cooperative, agriculture, public power utilities – up to 25% of the project cost
5. Clean Renewable Energy bonds	Rural electricity cooperative
6. Qualified Energy Conservation Bonds (QECBs)	Local government, state government
7. USDA Rural Energy for America Program loan guarantees	Commercial, agricultural
8. Renewable Energy Production Incentive	Rural electricity cooperative
9. Interconnection Standards for Small Generators	Commercial, agricultural (for systems less than 20 MW)
New Jersey State Incentives for Anaerobic Digestion [173]	
Incentive	Affected Sectors
1. Edison Innovation Clean Energy Manufacturing Fund	Commercial, industrial
2. Grid-Connected Renewables Program	Commercial, industrial
3. Clean Energy Solutions Capital Investment Loan/Grant Program	Commercial, industrial
4. NJ Customer-sited Renewable	Commercial, industrial, residential

Energy Rebates	
5. Interconnection Standards	Commercial, industrial, residential
6. NJ New Metering	All sectors (system capacity limit of 2 MW AC)
7. Social Benefits Charge	All sectors
8. Renewable Portfolio Standard	Investor owned utility, retail supplier

3.2.3 Rationale and Objectives

New Jersey has over 42,500 horses, and its equestrian industry is valued at more than a billion dollars annually [174]. Eighty-nine percent of NJ's horse farms have fewer than 20 horses, and 93% of NJ farms are less than 50 acres [174]. A large number of horse farms, limited space, and strict environmental regulations, make horse waste management in New Jersey an important challenge for both policy makers and individual farm owners. Horse farm owners may be interested in developing onsite energy-from-waste technology to minimize waste and offset energy demands; however, little economic or technical information is available regarding anaerobic digestion of horse waste.

Bioenergy recovery from horse waste may not be economical for all New Jersey horse farms. Farm sizes, specifically, the ratio between the number of horses and farm acreage may be a critical concern for assessing economic incentives for developing private onsite waste-to-energy infrastructure. Models linking farm size, local farm and horse density and potential available energy from horse waste, are needed to develop public or private facilities that recover bioenergy from horse waste on the farm or in a facility that digests waste collected from smaller farms.

As described at the beginning of Section 3.2, New Jersey regulations require horse farms to develop specific horse waste handling plans designed to limit excessive nutrient application to land. These regulations could result in mandates for removal of horse waste from the source location, and would create additional operating costs for the horse farms in the form of greater onsite waste management and offsite hauling costs. Under this scenario, anaerobic digestion could provide a means to defray some of these additional costs. The main goal of this study was to develop guidelines and models to describe theoretical production of energy from horse waste via anaerobic digestion. The specific objectives of the study were to:

1. Use known horse waste characteristics and methane production potentials to develop a theoretical design for a high solids horse waste digestion and methane recovery system for on-farm application,
2. Develop a mass and energy balance and economic comparisons for on-farm anaerobic digestion of horse waste based on the theoretical system that includes consideration of (i.) recovery efficiency, and (ii.) horse farm size, horse density (horse/acre) and energy recovery efficiency for various recovery options as a function of farm size,
3. Develop a mass and energy balance and economic comparisons for cooperative anaerobic digestion of horse waste in a theoretical high-rate (methane generated equals half of the feedstock methane potential after 14 days) continuous system that includes consideration of (i.) recovery efficiency, and (ii.) horse waste volume/mass “densities” and travel distances for hauling.

3.3 Model Systems and Scope

Three horse quantity scales were considered for each digester type. Onsite batch digestion schemes considered farm sizes of 10, 50, and 500 horses, and the regional digester considered 50, 500 and 5,000 horses. However, direct comparisons, on a per horse basis, were made over a large range of horse quantities. The rationale for considering these specific sizes and digestion schemes was to allow the viability of simple onsite biogas recovery from small, medium and large horse farming operations to be compared to regional digestion that would accept waste from numerous facilities. For all scenarios, the ultimate disposal of the horse waste was assumed to be by removal from the site of waste generation. With anaerobic digestion as the waste treatment method, waste or digested waste residue removal from the property for final disposal was considered to be the only means for limiting local eutrophication from land application.

The model was constructed in a Microsoft Office Excel spreadsheet (Microsoft Corporation, Redmond, WA) and input variables and flow stream dependence were propagated throughout the model system (Appendix II).

3.3.1 Onsite Batch Digestion with Residual Removal

The digestion system considered for on-farm applications utilizes individual batch reactors that can be filled with waste in its "as-collected" form. The batch reactors were fixed at typical off-the shelf U.S. commercial waste container sizes of 10-, 20- and 40-CY (cubic yards; equivalent to 7.6, 15.3 and 30.6 m^3), and the number of reactors employed for a given farm size became a primary system control variable. These vessels are standardized and can be picked up and dropped off by truck. In a batch digestion

scenario, these standard vessels could be modified as needed to allow gas collection, leachate collection and percolation, and even physical mixing.

In the operational scenario once the vessels have been filled, they are sealed and allowed to digest for a set solids retention time (*SRT*) before being hauled offsite for finishing treatment and final disposal. The operational process is timed such that an empty container arrives to begin filling as a full container begins digesting, and a container that has finished digesting is to be removed (Figure 3.1). Similar batch schemes had been proposed previously and are currently employed in farm applications [139, 175].

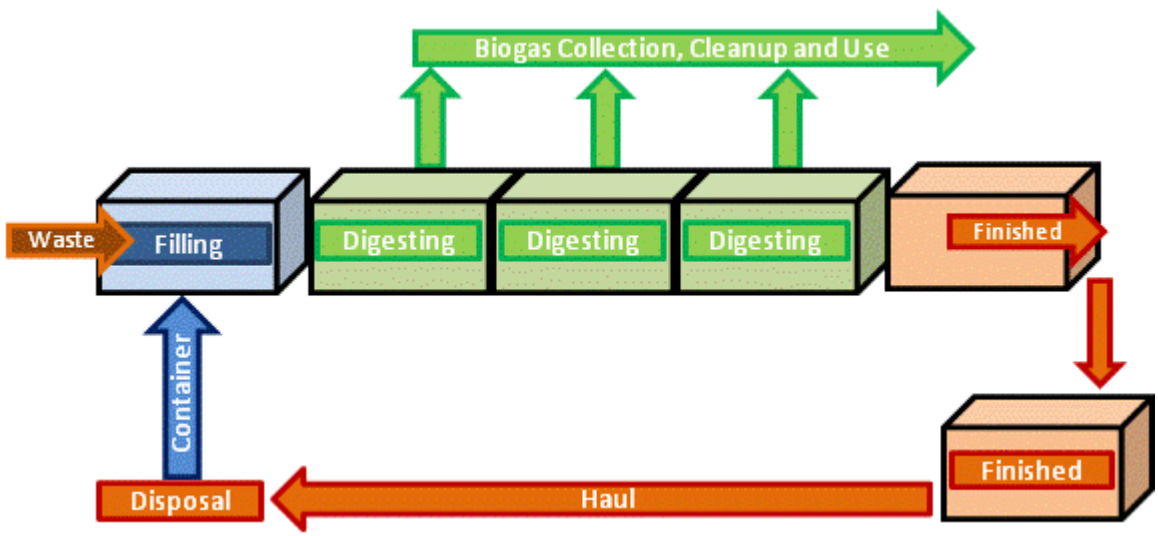

Figure 3.1 - Process schematic for high solids batch fill-digest-haul operational scenario for on-farm anaerobic digestion of equine waste

The number of reactors employed (*N*) controls the effective solids retention time (Equation 3.3) and influences overall biogas and methane accumulation by controlling biogas production kinetics (Equation 3.4).

$$SRT = \frac{V \cdot (N-1)}{Q} \qquad \text{Equation 3.3}$$

Where, *SRT*, is the solids retention time, *V*, is the reactor volume (40 m^3), *N*, is the number of reactors, and *Q*, is the volumetric waste flow rate (typically 5.62E-02 m^3/day per horse) [126], which can be varied to accommodate numerous waste to bedding ratios. To compare various farm sizes, Equation 3.3 can be rearranged to solve for the minimum number of reactors (*N*) for a given effective retention time (*SRT*).

The Gompertz equation (Equation 3.4) has been used to model batch kinetics for the anaerobic digestion of MSW [176] and cattle manure [177].

$$G_{CH4} = G_{pot} \cdot exp\left\{-exp\left[\frac{R_{max} \cdot e^1}{G_{pot}} \cdot (\lambda - SRT)\right]\right\} \qquad \text{Equation 3.4}$$

Where, G_{CH4}, is the methane gas generated (L CH_4/kg VS added per reactor), G_{pot}, is the maximum potential methane yield (L CH_4/kg VS added), R_{max}, is the maximum methane generation rate (L CH_4/kg VS per day), and λ, is the lag period (minimum time to produce biogas). For all model runs, R_{max} was 5.5 L CH_4/kg VS per day and λ was 2 days (values selected to fit conversion observed by Kusch (2008) [138]), and to assess the impact of the waste methane potential, G_{pot} was varied from 100 to 300 L CH_4/kg VS reflective of the range of previously reported outputs for various horse manure-stall bedding mixtures [138, 143] (Table 3.1). For system comparison, G_{pot} was fixed at 277 L CH_4/kg VS, which was an observed methane potential for horse waste consisting of a mixture of manure and straw bedding [138] and for horse manure alone [143] (Table 3.1). As the solids retention time (SRT) approaches infinity G_{CH4} approaches G_{pot} (Equation 3.4). Since the number of reactors (N; Equation 3.3) controls the SRT, there is a tradeoff between the number of reactors and the total amount of methane that can be generated by the system.

Energy losses are the sum of the methane loss during reactor filling, prior to sealing the reactor, and the amount of methane energy used to provide heat to maintain the reactor system operating temperature. The cumulative methane generated for any given system with this configuration is calculated by multiplying Equation 3.4 by both the number of reactors and the volatile solids (VS) input per reactor and subtracting total methane losses. Methane losses during filling were calculated using Equation 3.4 by substituting the SRT for the fill time and scaling down the total VS input per reactor to the total amount loaded between the lag period (λ) and the fill period.

For this systems analysis it was assumed that reactors would be housed in an insulated structure and heated to 35°C. Heat loss across the boundary of the system is the sum of losses from the sides, top, and bottom of the insulated system structure, and is computed using Equation 3.5.

$$Q_{loss} = \sum U_i \cdot A_i \cdot \Delta T_i \qquad \text{Equation 3.5}$$

Where, U is the overall heat transfer coefficient [$J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$], A is the surface area across which heat loss is occurring, and ΔT is the temperature drop across the surface. The cross-section of the structure walls and ceiling were assumed to consist of 25 mm softwood sheet panels ($U_{softwood}$ = 4.000 $J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$ [178]) and 25 mm fiberglass insulation ($U_{fiber\text{-}glass}$ = 1.538 $J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$ [179]). The floor is plain concrete, 150 mm thick, in contact with dry earth (U_{floor} = 0.85 $J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$) [180]). The average difference in temperature between inside of the insulated structure and the ambient temperature (ΔT) is assumed to be 20 °C. The heat transfer area (A) is a function of the number of reactors to be contained within the structure and the dimensions of the rectangular reactors. Standard container dimensions vary somewhat from company-to-

company among the height and length, but the width was typically 2.44 m (8 ft.) [181-183]. A comparison of several companies, however, revealed that the ratio between the length and height of the container for 10-, 20- and 40-CY containers was 3 to 1 [181-183]. The dimensions used for analysis are presented in Table 3.4.

Table 3.4 - Standard batch vessel dimensions

Vessel Dimensions			
	10-CY ($7.6\ m^3$)	20-CY ($15.3\ m^3$)	40-CY ($30.6\ m^3$)
Length (meters)	3.07	4.34	6.13
Width (meters)	2.44	2.44	2.44
Height (meters)	1.02	1.45	2.04

The total heat transfer area of the insulated structure includes an additional meter along its length, 2 meters along its width, and 0.2 meters along its height. Functionally, both ends of the insulated structure would open allowing the filled and reacted digester to be picked-up for hauling and replaced on the other end with an empty digester to begin filling and reacting.

The solids flow rate controls the reactor fill time and is a function of farm size (number of horses, N). Since the reactor volume (V) is standard, the number of required waste collections per month ($X_{transfers}$) is a function of the number of horses because the volumetric flow rate (5.62E-02 m^3/day per horse), Q is a function of the number of horses served (Equation 3.6).

$$X_{Transfers} = \frac{365 \cdot days}{12 \cdot months} \cdot \frac{Q}{V} \qquad \text{Equation 3.6}$$

Capital costs for these onsite batch reactor systems are a function of the number of needed reactors for a desired solid retention time. Itemized capital costs [provided by

Mr. Tarik Zebib] are given in (Appendix II – A.2.1.). Continued operating costs will be a function of the number of reactors to be maintained and the number of required waste transfers.

3.3.2 Regional Continuous Digestion

The regional continuous digester was considered to be an upright, single-phase, digester operated as a completely mixed stirred tank reactor (CSTR) with liquid addition and leachate recycle. In contrast to the onsite batch system, the regional system could acquire equine waste from a number of sources (Figure 3.2)

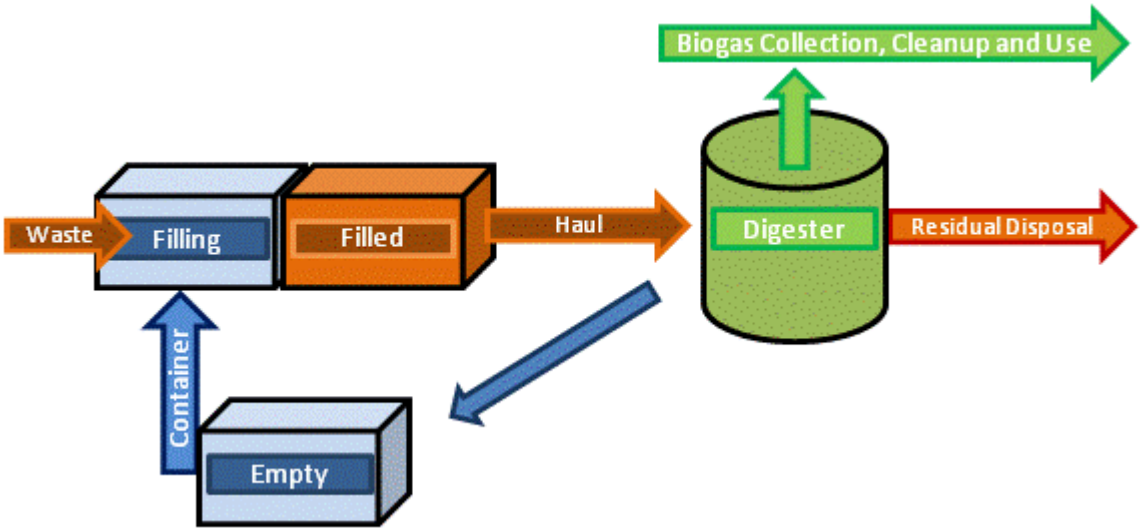

Figure 3.2 - Process schematic for fill-haul-digest operational scenario for regional anaerobic digestion of equine waste

The size of the regional continuous digester is a function of the number of horses that the facility services. In addition to the volume of equine stall waste to be reacted, the digester will also need to be sufficiently large to handle additional liquid and recirculated leachate required to establish and maintain the designated moisture content to facilitate pumping and other handling operations, and to provide inoculation. A system volume was

considered that could handle waste and bedding material for a range of horse quantities. Liquid addition was varied to maintain an influent total solids content of 15%. The volume of leachate to be recirculated, based on the waste characteristics of horse manure, was computed from Equation 3.7, assuming that the solids content of the recirculated liquid was negligible.

$$Q_{water} = -M_{waste}\left(\frac{f_{water}-f_{TS}}{f_{water}-f_{TS}-1}\right) \qquad \text{Equation 3.7}$$

Where, Q_{water}, is the total volumetric flow rate of the fresh water and recirculated liquid, M_{waste}, is the mass flow rate of manure, f_{water}, is the weight fraction of water in the digester and f_{TS}, is the solid weight fraction of the fresh waste.

The required digester volume is a function of the residence time and volumetric flow (Equation 3.8).

$$V = T \cdot Q \qquad \text{Equation 3.8}$$

Where, T is the hydraulic residence time in the continuously mixed reactor and Q is the total volumetric flow (m^3/day), which is the sum of the volumetric waste, additional liquid and recirculated leachate flows. For this reaction configuration the residence time (T) is equal to the solids retention time (SRT), since the solids content of recirculated leachate was assumed to be negligible.

The CSTR is operated at steady-state with a constant SRT of 28 days, but the volatile solids loading rate (VSLR) is variable to accommodate a range of horse quantities. A number of continuous culture models have been developed and applied to anaerobic systems (Table 3.5).

Table 3.5 - Continuous-culture kinetic models used in anaerobic treatment

Name	Expression	Reference
First-order	$\mu = \frac{kS}{S_o - S} - b$	Moser (1959) [184]
Grau	$\mu = \frac{\mu_h S}{S_o} - b$	Grau et al. (1975) [185]
Monod	$\mu = \frac{\mu_h S}{K_s + S} - b$	Monod (1949) [186]
Contois	$\mu = \frac{u_m S}{BX + S} - b$	Contois (1959) [187]
Chen and Hashimoto	$\mu = \frac{\mu_h S}{KS_o + (1 - K)S} - b$	Chen and Hashimoto (1978) [188]

Where, μ, is the specific growth rate (time^{-1}), k, μ_h, and u_m are maximum specific growth rates (time^{-1}), S is the substrate concentration (mol/L), S_o is the initial substrate concentration, K_s is the half velocity coefficient (mol/L), K is a dimensionless constant and b is the decay rate (time^{-1}).

These models are applicable if the substrate (feedstock) is well characterized, and the model parameters can be quantified for the given substrate [189]. For comparison here, the feedstock methane potential (G_{pot}), and recoverable fraction for a specific SRT (28 days) in a batch system is available.

In order to relate the same input variables from the batch model (G_{pot}, SRT, and kinetic parameters R_{max} and λ) to a steady-state continuous model, the forms of the equations presented in Table 3.5 are used to establish a steady-state kinetic equation using G_{pot} and SRT (Equation 3.9). Methane generation is a function of the available volatile solids (VS), the maximum methane production potential of the VS, the solids

retention time, and a steady-state constant (C_s) that can be varied to achieve realistic yields.

$$G_{CH4} = \frac{G_{pot} \cdot SRT}{C_s + SRT} \qquad \text{Equation 3.9}$$

Where, G_{CH4} is the methane gas generated (L CH_4/kg VS added), G_{pot} is the maximum potential methane yield (L CH_4/kg VS added) as the solid retention time approaches infinity, and C_s (14 days) is the steady-state constant. The steady-state constant (C_s) was selected to be 14 days to achieve a conservative methane yield (67% with SRT = 28 days) [190]. The total number of required transfers – or deliveries in this case – is calculated using Equation 3.6.

The digester is assumed to be mechanically mixed. The power required to continuously mix the slurry contained is a function of the digester volume and is obtained by Equation 3.10 [180].

$$P_{digester} = UP_{digester} \cdot V_{digester} \qquad \text{Equation 3.10}$$

Where, $P_{digester}$ is the required mixing power [kJ/hr], $UP_{digester}$ is the unit power for a typical CSTR digester (0.0065 kW/m^3 [180]), and $V_{digester}$ is the digester volume (variable depending on specified operating flows and retention time).

Capital costs for the continuous reactor system were estimated using an established model for CSTR systems for dairy farm digesters [169], where the corresponding horse model was modified to account for differences in both average waste volume per animal and associated volatile solids content of the animal manure (Equation 3.11); see *Section 3.2.2*.

$$C_{horse} = -355 \cdot \ln(H) + 3597 \qquad \text{Equation 3.11}$$

Where, C_{horse}, is the normalized digester cost per horse, and H is the number of horses. Continued operating costs were considered to be a function of the required maintenance and the number of required waste deliveries.

3.3.3 System Comparison and Analysis

To compare the on-farm and centralized digester systems directly, normalized outputs were calculated for a range of potential horse quantities. In many cases, energy values were compared in various forms, and Table 3.6 provides the relationship between energy values used in the model.

Table 3.6 - Equivalent energy values and conversion factors used to normalize outputs for direct comparison

Equivalent Energy Values and Conversion Factors			
Storage Type	Energy Density by Mass (MJ/kg)	Energy Density by Volume (MJ/L)	Source
Methane	55.6	0.0378	[191-192]
Methane Lower Heating Value (LHV)	50	0.0339	[193]
Automotive Diesel Fuel	47.8	38.6	[194]
Energy Type	Energy Density by Mass (MJ/kWh)		
Electricity	3.6		[195]

In most cases the outputs were normalized on a per-horse basis, but the methane potential was normalized on a volatile solids added basis (kg VS). The assessment of the 1-year investment versus energy was normalized to electrical energy recovery in kilowatt hours (kWh). For purposes of comparison, the electrical energy recovery potential from methane combustion using an onsite generator was assumed to be 20% efficient and 33% efficient at an optimized regional power plant [196].

System inputs are compared in Table 3.7.

Table 3.7 - Comparison of system inputs for onsite batch and continuous regional digester systems. *N/A = not applicable; HTC = heat transfer coefficient

Waste Characteristics			
	Units	Batch	Continuous
Waste Production	$kg \cdot horse^{-1} \cdot day^{-1}$	22.7	22.7
Waste Density	kg/m^3	403.7	403.7
Total Solids (TS)	Dimensionless	0.4133	0.4133
Volatile Solids (VS)	Dimensionless	0.8204	0.8204
Kinetic Parameters			
	Units	Batch	Continuous
Methane Potential (G_{pot})	L/kg	Variable (277)	Variable (277)
Max Rate (R_{max})	$L \cdot kg^{-1} \cdot day^{-1}$	5.5	N/A
Lag (λ)	Day	1	N/A
Steady-state Const. (C_s)	Day	N/A	14
System Parameters			
	Units	Batch	Continuous
HTC Sides	$J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$	1.11	0.80
HTC Top	$J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$	1.11	0.12
HTC Floor	$J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$	0.85	0.17
Temperature Difference	°C	15	40
Insulated Structure Cost	$/m^2	915	N/A
Generator Efficiency	Dimensionless	0.20	0.33
Mixing Energy	kW/m^3	N/A	0.0065

The fractional difference (f_{diff}) between two values obtained for certain model outputs were compared and calculated as shown in (Equation 3.12).

$$f_{diff} = \frac{|X_2 - X_1|}{\left(\frac{X_2 + X_1}{2}\right)} \qquad \text{Equation 3.12}$$

Where X_1 and X_2 are the output values being compared.

The maximum transport distance is the distance (from the waste generation site to the subsequent waste handling site) at which the fuel energy consumed equals the potential electrical energy produced by the anaerobic digester system (Equation 3.13). Transporting waste a distance greater than the maximum transport distance would correspond to a system that consumes more useable energy than it produces.

$$d_{max} = \frac{E_{Elec} \cdot F_{truck}}{2 \cdot X_{Transfers}} \qquad \text{Equation 3.13}$$

Where, E_{Elec}, is the system electrical output (kWh/month), F_{truck}, is the fuel efficiency of the transport vehicle (km/kWh), and $X_{Transfers}$, is the number of required transfers (Equation 3.6).

3.4 Results and Discussion

3.4.1 Batch Systems

For a finite batch reactor size (10-, 20-, and 40-CY), the observed retention time (SRT) varies as a function of the volumetric waste flow (Equation 3.3). The volumetric waste flow is controlled by the number of horses, and the effective SRT will decrease as the number of horses per reactor increases (Figure 3.3).

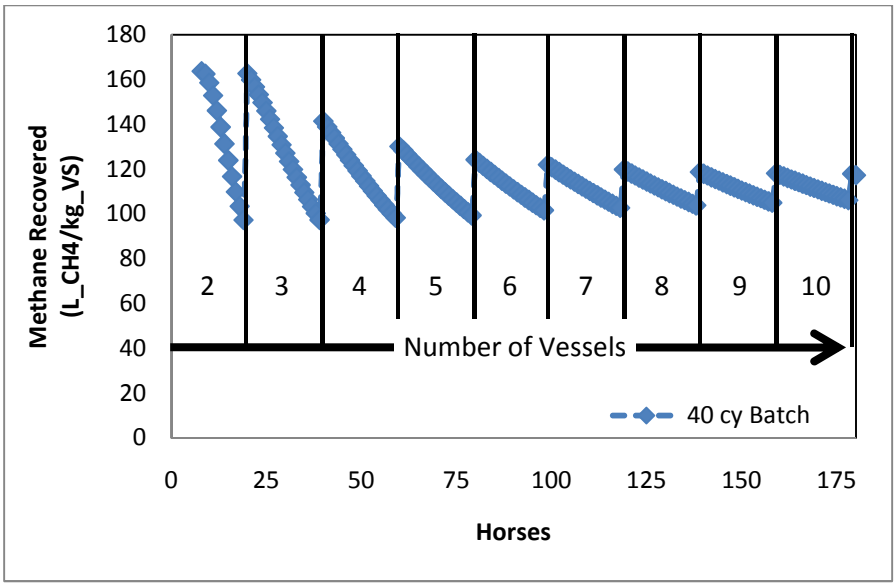

Figure 3.3 - Liters of methane recovered per kilogram of volatile solids (VS) added as a function of horse quantity and number of reactors (minimum SRT designated as 28 days)

For this analysis (Figure 3.3) a minimum of 10 horses and a maximum of 175 horses were considered and the input parameters shown in Table 3.7 were utilized. As the number of horses served by the specified number of reactors increases, the amount of methane recovered per mass of waste VS loaded decreases since each vessel fills at a faster rate and less time is allowed for digestion (Figure 3.3). A minimum retention time of 28 days, based on the batch-system SRT utilized by Kusch et al. (2008) was specified [138], and thus, an additional reactor is added to the system when the calculated SRT falls below 28 days. Each time an additional vessel is added, the SRT thus increases accordingly allowing a longer time for the in vessel waste to be converted to methane and producing a corresponding spike in recoverable methane per mass of waste VS loaded (Figure 3.3). The magnitude of the spike diminishes as the total number of horses increases because the volumetric waste-flow (Q; Equation 3.3) increases relative to the

finite vessel size (*V*; Equation 3.3). Thus, the variability in the observed methane recovery can be reduced by decreasing the vessel size (Figure 3.4).

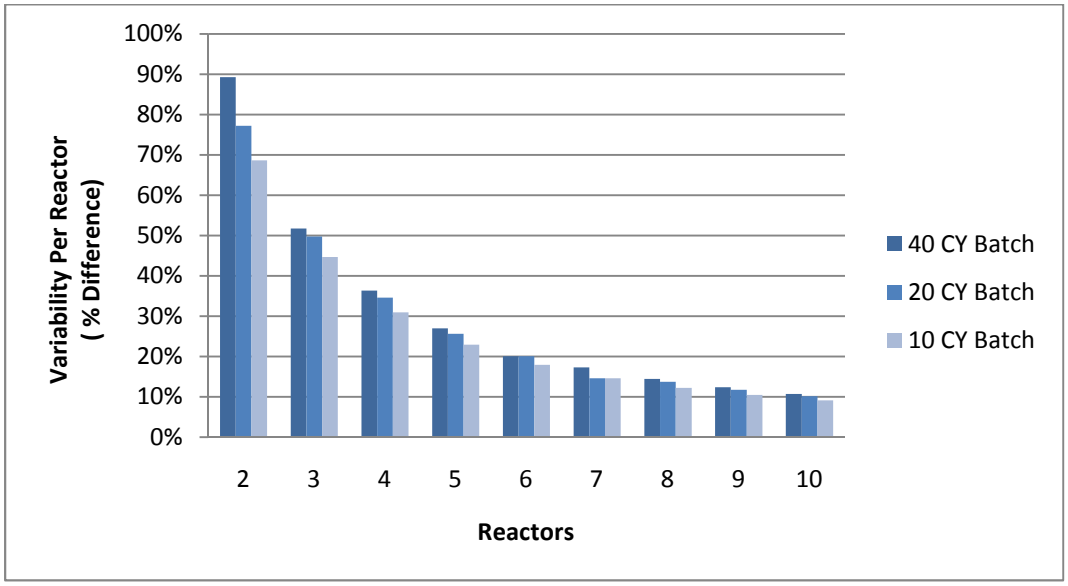

Figure 3.4 - Variability of recoverable methane as a function of the number of reactors; note: the number of reactors required depends on the minimum SRT, the vessel size and the number of horses (19 horses/40 CY vessel, 9 horses/20 CY vessel, and 5 horses/ 10 CY vessel)

Note that a relatively constant energy output from the digester system is desirable to allow predictive use of the energy and to avoid over- or under-sizing downstream processes in methane utilization. The variability in the methane output for the different scenarios of reactor number and SRT is thus an important aspect of system operation. The variability in recoverable methane as measured by the percent difference (Equation 3.12 × 100%) between the maximum and minimum daily methane generation outputs decreases as the number of reaction vessels increases (Figure 3.4). When the number of vessels is greater than five, the variability per reactor decreases to less than a 20% difference for all vessel sizes, but the recoverable methane variability decreases much faster for smaller vessels on a per horse basis. For example, horse quantities of as few as

20 would require 6 of the 10-CY vessels while 6 of the 40-CY vessels would correspond to 80 horses. Thus, more methane generation with less variability can be achieved by operating with more, smaller vessels, than with a few larger vessels.

In order for the batch system to operate there must be at least two reaction vessels, one being filled and one reacting. In a two reactor system, the fill time is equal to the reaction time. For a specified SRT, obtaining the smallest capital cost per horse is achieved by selecting a system configuration that minimizes the overall system size and number of reactors (Figure 3.5).

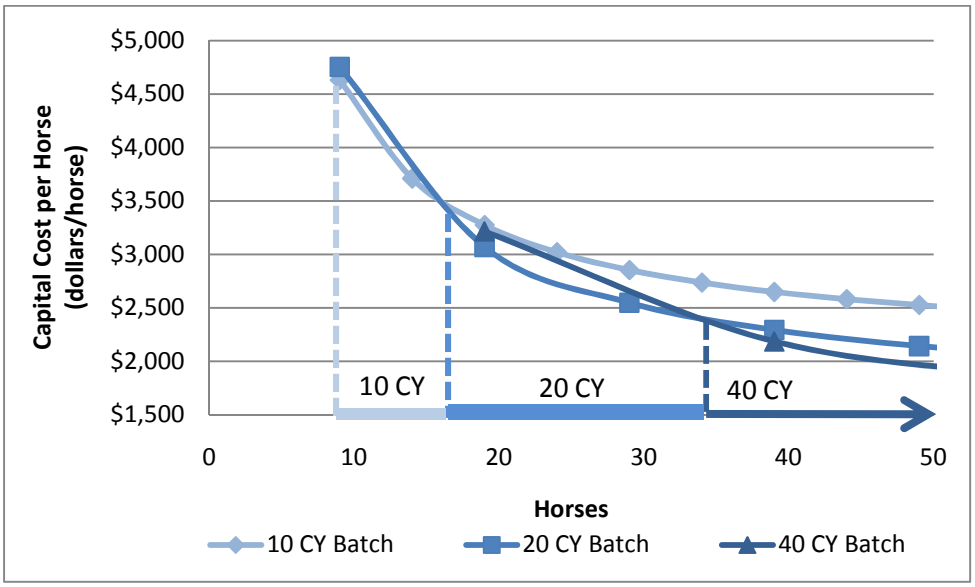

Figure 3.5 - Comparison of the capital costs per horse for 10-CY, 20-CY and 40-CY batch vessel sizes as a function of horse quantity

Based on the specified SRT, each vessel size corresponds to a different maximum horse quantity per vessel: e.g., 19 horses per 40-CY vessel, 9 horses per 20-CY vessel, and 5 horses per 10-CY vessel for an 28 day SRT. The trends in Figure 3.5 indicate that the selection of a larger size vessel would decrease the capital cost per horse and thus a larger vessel should be considered as the number of horses approaches twice the maximum

horses per vessel (i.e. select 10-CY for 10-17 horses, 20-CY for 18-37 horses, and 40-CY for horse quantities greater than 37).

Increasing the vessel size for a given volumetric waste flow (given number of horses) would increase the fill time and SRT, therefore increasing the fraction of the potential methane (G_{pot}) recovered. However, there is a cost trade-off between the SRT and the system size. To determine if the increased methane generation observed by selecting a larger vessel is sufficient to offset the additional capital costs, the energy investment is calculated (Figure 3.6).

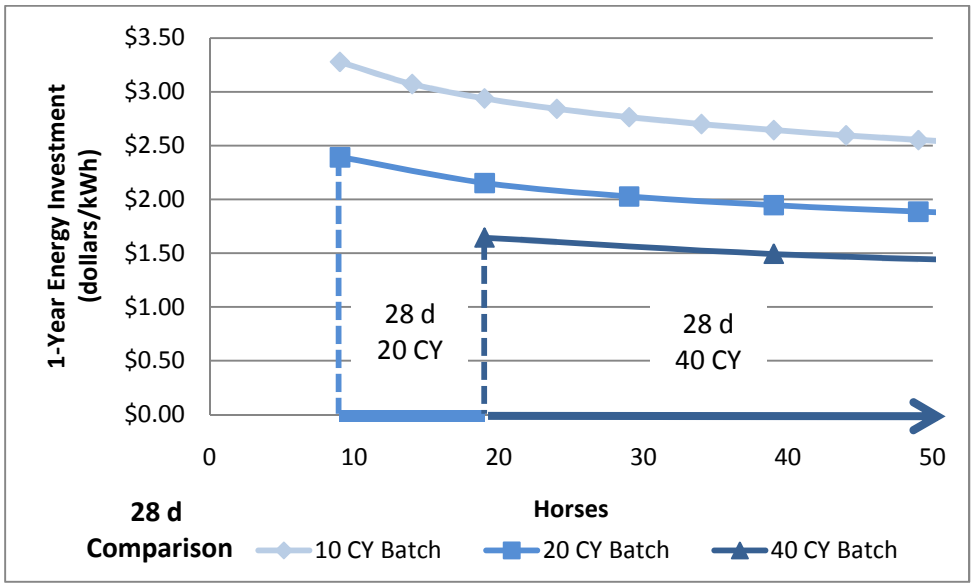

Figure 3.6 - Comparison of capital investment per kWh generated (over 1-year of operation) for 10-CY, 20-CY and 40-CY batch vessel sizes as a function of horse quantity

The energy investment normalizes the outputs for comparison among all standard vessel sizes by relating the total capital investment (dollars) to the total potential electrical generation for one year of operation (kWh/year). Increasing the methane recovery by selecting a larger vessel and lengthening the SRT increases the system

capital cost, but the additional methane recovered is sufficient to reduce the capital investment per unit of energy generated. Based on the energy investment, a 10-CY batch system should not be selected for horse quantities between 10 and 17 as suggested by assessing the capital costs alone. Rather, the 20-CY batch system should be employed for horse quantities between 10 and 17 and the 40-CY batch should be selected for horse quantities greater than 17.

The energy investment assessment relates the total capital costs to the potential methane recovery, but its sensitivity to the variability observed in methane recovery as a function of the selected reactor size is not shown. The energy investment assessment is effectively showing that increasing the retention time, independent of the vessel size, improves system economics. Therefore, doubling the retention time of the 10-CY and 20-CY batch systems, designated 56 d 10-CY and 56 d 20-CY reactors, respectively, can further improve system economics by increasing the recoverable methane and reducing methane recovery variability (Figure 3.7).

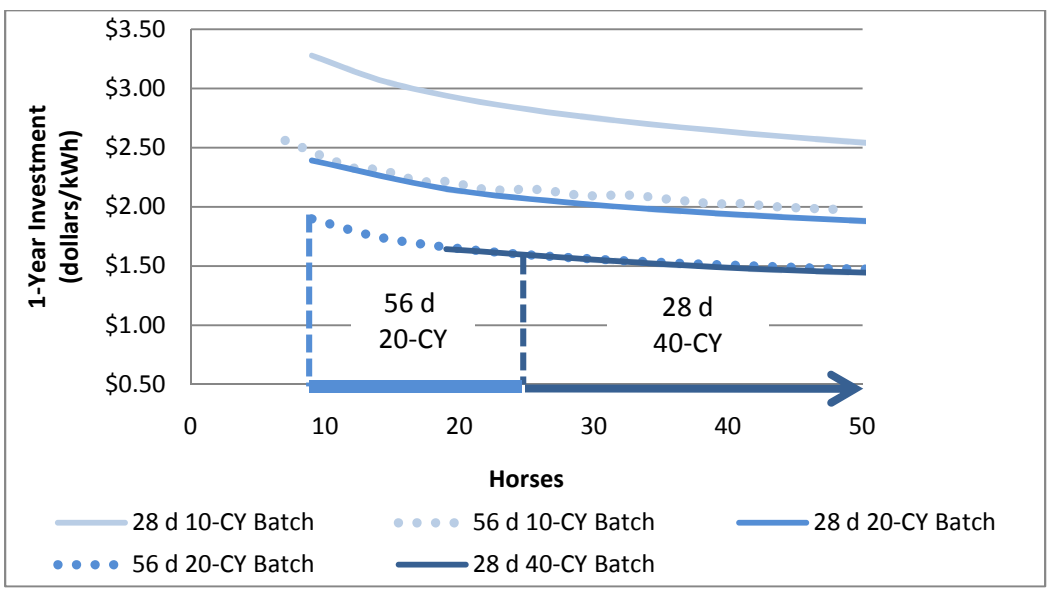

Figure 3.7 - Comparison of capital investment per kWh generated (over 1-year of operation) for 28-day 10-CY, 20-CY and 40-CY batch vessel sizes and 56-day 10-CY

and 20-CY batch systems where the SRT has been doubled (from 28 to 56 days), as a function of horse quantity

Doubling the SRT of the 10-CY and 20-CY batch systems from 28 to 56 days increases the VS normalized methane recovery by as much as 77% and 79% (118 to 209 L CH_4/kg VS and 112 to 200 L CH_4/kg VS), respectively. The 20-CY batch system with a SRT of 56 days requires the smallest 1-year energy investment (capital dollars per kWh energy for 1 year) of all vessel sizes and SRTs considered up to 25 horses (Figure 3.7). For horse quantities above 25, the 40-CY batch system with a SRT of 28 days has a slightly smaller required energy investment.

Between 48% and 87% of the batch system capital costs can be attributed to the insulated structure needed to hold the reactors at 35°C. Subtracting the cost of the structure substantially improves the energy investment for batch systems and presents additional considerations (Figure 3.8).

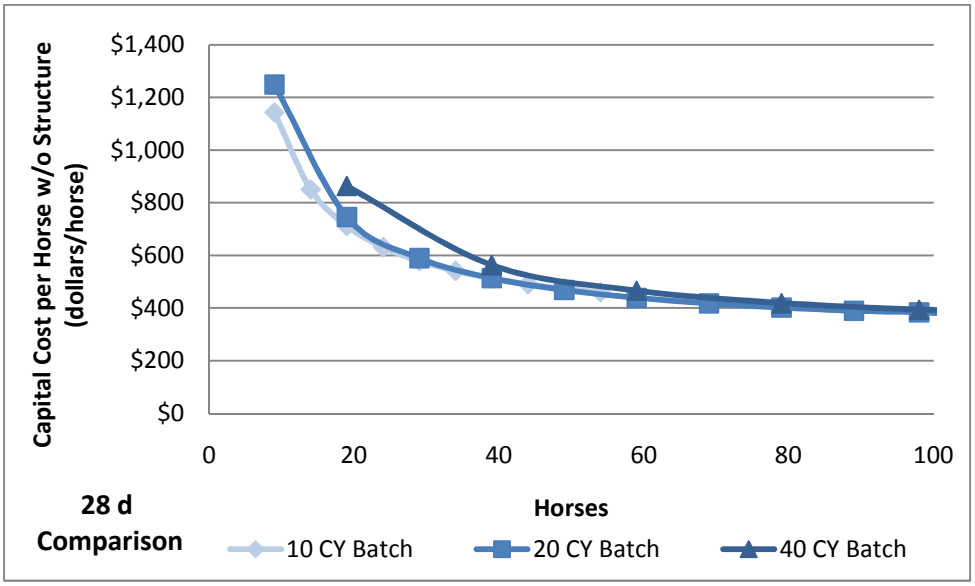

Figure 3.8 - Comparison of capital investment minus structure cost per kWh generated (over 1-year of operation) for 28-day 10-CY, 20-CY and 40-CY batch vessel sizes as a function of horse quantity

Disregarding the cost of building a structure to house the batch reactor system could be useful for assessing the batch system viability at a location with preexisting infrastructure. Relatively small differences in the 1-year energy investment are observed between the 10-, 20-, and 40-CY batch systems, and the vessel size selection could thus depend on other factors such as the system footprint (area) required.

The system space (or area) footprint has a linear dependency on horse quantity, and the larger vessels have a smaller per horse space footprint. The 10-, 20- and 40-CY vessels require 2.91, 1.93 and 1.20 m^2 per horse, respectively. The considerations for selecting a batch system would include whether vessel housing is available, if vessel housing is needed, the size of the available housing or land, the expected methane variability and the total energy investment. Since the batch systems require a relatively large footprint, making the structure capital important, the viability of batch systems is likely limited to smaller facilities with available vessel housing. Another option would be to devise a means to cheaply and effectively attach a heating unit to each vessel during the digestion phase of the process (Figure 3.1).

3.4.2 Batch and Continuous System Comparison

Comparisons among methane and energy generation (Table 3.8), system characteristics (Table 3.9), and capital costs (Table 3.10) were made for all batch and continuous systems for horse quantities of 10, 50, 500 and 5,000 and using the input parameters shown in Table 3.7.

Table 3.8 - Comparison of methane and energy generation for on-farm batch and centralized continuous-flow reactors for 10, 50, 500 and 5000 horses

Methane and Energy Generation							
	Horses	10CY (28-day)	10CY (56-day)	20 CY (28-day)	20CY (56-day)	40 CY (28-day)	Continuous (28-day)
Recoverable Methane (L CH_4/SRT)	10	3.72E+05	1.10E+06	4.73E+05	1.26E+06	3.50E+05	2.95E+05
	50	1.61E+06	5.01E+06	1.74E+06	5.18E+06	1.86E+06	1.63E+06
	500	1.42E+07	4.75E+07	1.40E+07	4.70E+07	1.37E+07	1.75E+07
	5000	1.39E+08	4.74E+08	1.36E+08	4.62E+08	1.33E+08	1.81E+08
Normalized Output (L CH_4/kg VS)	10	118	209	112	200	42	137
	50	128	218	119	206	111	152
	500	131	221	129	216	125	163
	5000	131	221	129	216	125	168
Electrcial Recovery per Horse (kWh/horse per mo.)	10	126	185	160	213	106	110
	50	102	165	119	173	127	122
	500	96	161	96	160	93	131
	5000	95	161	94	157	91	135

Table 3.9 - Comparison of system characteristics for on-farm batch and centralized continuous-flow reactors for 10, 50, 500 and 5000 horses

System Characteristics							
	Horses	10CY (28-day)	10CY (56-day)	20 CY (28-day)	20CY (56-day)	40 CY (28-day)	Continuous (28-day)
Reactors	10	3	5	2	3	2	1
	50	12	22	7	12	4	1
	500	103	205	52	104	26	1
	5000	1,012	2,045	507	1,021	254	1
System Footprint (m^2)	10	34	68	25	51	20	15
	50	149	299	101	202	66	45
	500	1,448	2,896	955	1,911	587	209
	5000	14,436	28,871	9,497	18,994	5,801	969
Footprint biofuel capacity (L CH_4 /m^2)	10	11,000	16,100	18,700	24,900	17,700	19,200
	50	10,800	16,800	17,200	25,600	28,200	36,300
	500	9,770	16,400	14,700	24,600	23,200	84,000
	5000	9,620	16,400	14,400	24,300	23,000	187,000
Required Transfers (per month)	10	2	2	1	1	1	1
	50	12	11	7	6	3	3
	500	113	112	56	56	28	28
	5000	1118	1120	559	559	280	279
Critical Transport Distance (km)	10	43	64	109	146	75	164
	50	34	55	68	109	144	182
	500	32	54	64	106	127	195
	5000	32	54	63	105	123	201

Table 3.10 - Comparison of capital cost assessments for on-farm batch and centralized continuous-flow reactors for 10, 50, 500 and 5000 horses

Capital Cost Assessments							
	Horses	10CY (28-day)	10CY (56-day)	20 CY (28-day)	20CY (56-day)	40 CY (28-day)	Continuous (28-day)
Cost per Horse ($/horse)	10	$4,985	$5,286	$4,626	$4,606	$3,166	$2,780
	50	$3,061	$3,916	$2,216	$2,893	$1,824	$2,208
	500	$2,663	$3,583	$1,785	$2,494	$1,275	$1,391
	5000	$2,619	$3,552	$1,733	$2,456	$1,207	$573
Cost per Horse w/o Structure ($/horse)	10	$1,029	$1,353	$1,124	$1,417	$1,641	N/A
	50	$498	$822	$518	$811	$551	N/A
	500	$345	$676	$316	$620	$300	N/A
	5000	$329	$664	$298	$600	$283	N/A
Energy Investment ($/kWh)	10	$3.30	$2.38	$2.42	$1.80	$2.50	$2.10
	50	$2.33	$1.94	$1.56	$1.40	$1.20	$1.51
	500	$2.29	$1.85	$1.55	$1.30	$1.14	$0.89
	5000	$2.29	$1.84	$1.54	$1.31	$1.10	$0.35
Energy Investment w/o Structure ($/kWh)	10	$0.68	$0.61	$0.59	$0.55	$1.30	N/A
	50	$0.38	$0.41	$0.36	$0.39	$0.36	N/A
	500	$0.30	$0.35	$0.27	$0.32	$0.27	N/A
	5000	$0.29	$0.34	$0.27	$0.32	$0.26	N/A

The capital cost per horse for both batch and continuous digester systems were compared for a range of horse quantities between 10 and 5,000. The 40-CY batch reactor system capital cost per horse was less than that of the continuous system over a range of horse quantities up to approximately 700 horses (Figure 3.9).

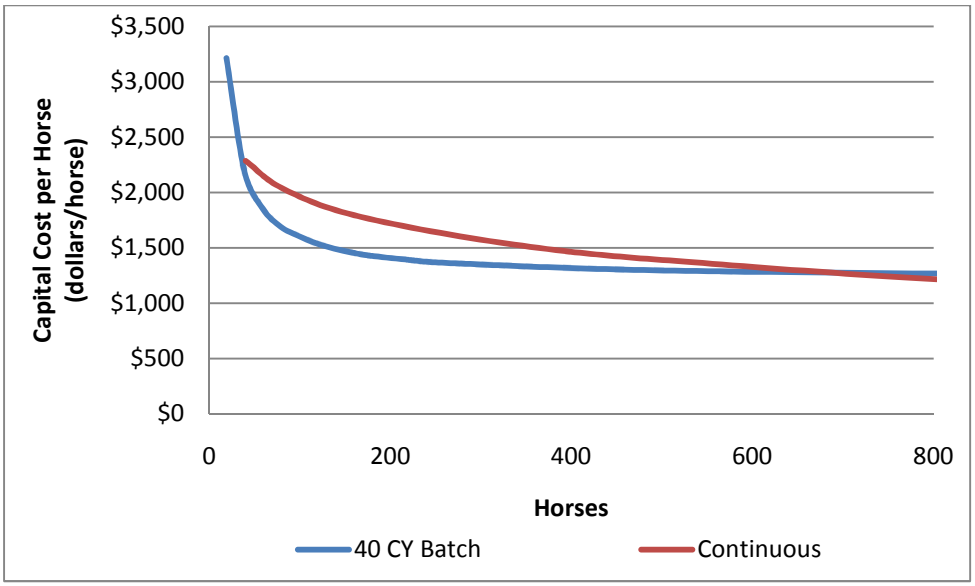

Figure 3.9 - Digester system capital cost per horse as a function of horse quantity

It is assumed that onsite batch systems utilize land that is already available at the horse farm, and thus, the cost of the land is not considered in the capital costs. One major disadvantage of the batch system is that its footprint is between 47% (66 versus 45 m^2 at 50 horses) and 500% (5,054 versus 969 m^2 at 5,000 horses) greater than the footprint of the continuous system. The continuous system capital costs have been extrapolated to smaller horse quantity systems for comparison (original model looked at dairy farm sizes between 700 and 2,300 animals) and the accuracy of the estimation for capital costs as a function of horse quantity may be less reliable for smaller horse quantities. A lower capital cost per horse can be expected by developing 40-CY vessel size batch systems as compared to continuous systems if the system footprint is not a concern.

The amount of energy that the various systems can expect to recover is a function of the system type and size (Figure 3.10).

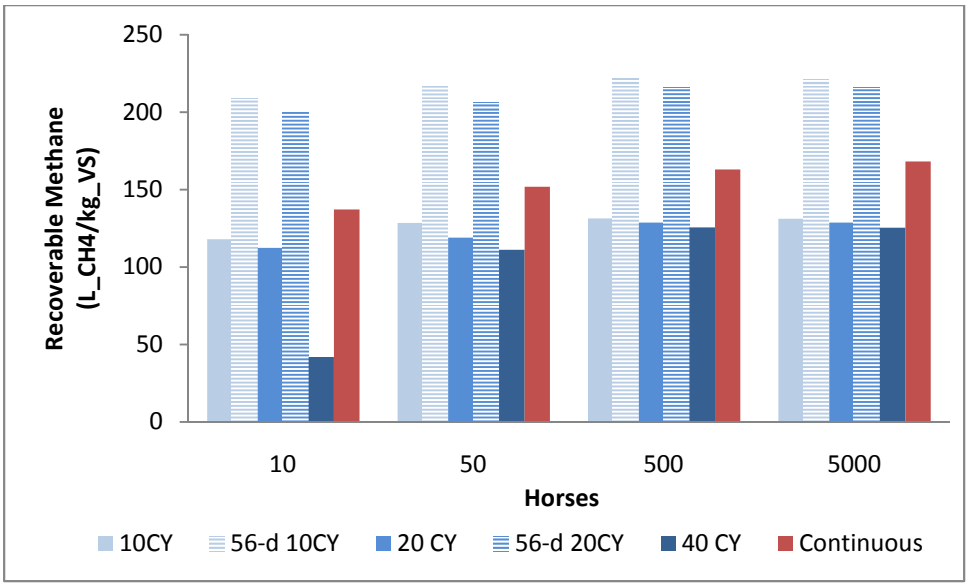

Figure 3.10 - Recoverable methane potential per kilogram of volatile solids added (VS) as for 10, 50, 500 and 5,000 horses

The methane potential increases as the system size (number of horses) increases for both the batch and continuous systems, but the increase of the continuous system is more pronounced. The theoretical methane potential used for comparison was 277 L CH_4/kg VS [138, 143]. Based on a 28 day retention time, the continuous system produces between 16% (10 horses) and 28% (5,000 horses) more methane per kilogram of VS added than the most productive batch system (10-CY). The batch system reaches a maximum recoverable methane potential of 135 L CH_4/kg VS while the continuous system reaches 168 L CH_4/kg VS. Doubling the retention time by doubling the number of 10- and 20-CY vessels improved methane recovery per kilogram of VS as much as 79% (20-CY with 10 horses). The improvement decreased marginally as the horse quantity increased.

Although the capital costs per horse of the continuous system are greater than those of the batch system, it will produce more methane than the batch system, regardless

of horse quantity. Calculating the capital investment per unit energy generated identified the benefit of recovering the greater quantities of methane relative to the system capital costs (Figure 3.11).

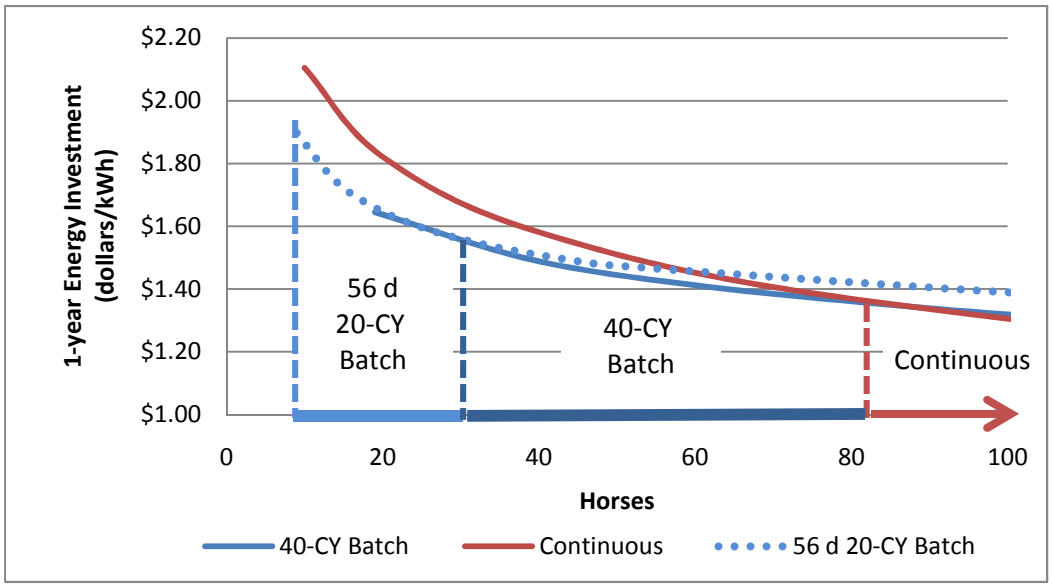

Figure 3.11 - Comparison of capital investment per kWh generated (over 1-year of operation) for 40-CY batch and continuous system as well as the 20-CY batch system where the SRT has been doubled (to 56 days) as a function of horse quantity

Based on the 1-year energy investment, which considers electricity recovery, the continuous system is expected to be a better investment for horse quantities approximately 80.

Onsite systems could recover heat as well as electricity, which would improve the energy investment assessment of the batch systems relative to the continuous system. Improving the system efficiency from 0.28 (assumed efficiency of onsite electricity generation) to 0.75 (possible electricity and heat efficiency) would substantially improve the energy investment. Assuming that the capital costs remained unchanged by including

onsite heat recovery, the improved efficiency would make the batch system economically favorable compared to the continuous system over a broad range of horse quantities.

The capital costs associated with the batch system housing structure are calculated explicitly. Subtracting the cost of the structure substantially improves the energy investment for batch systems (Figure 3.8), and reduces the cost per unit energy below that of the continuous system (Figure 3.12).

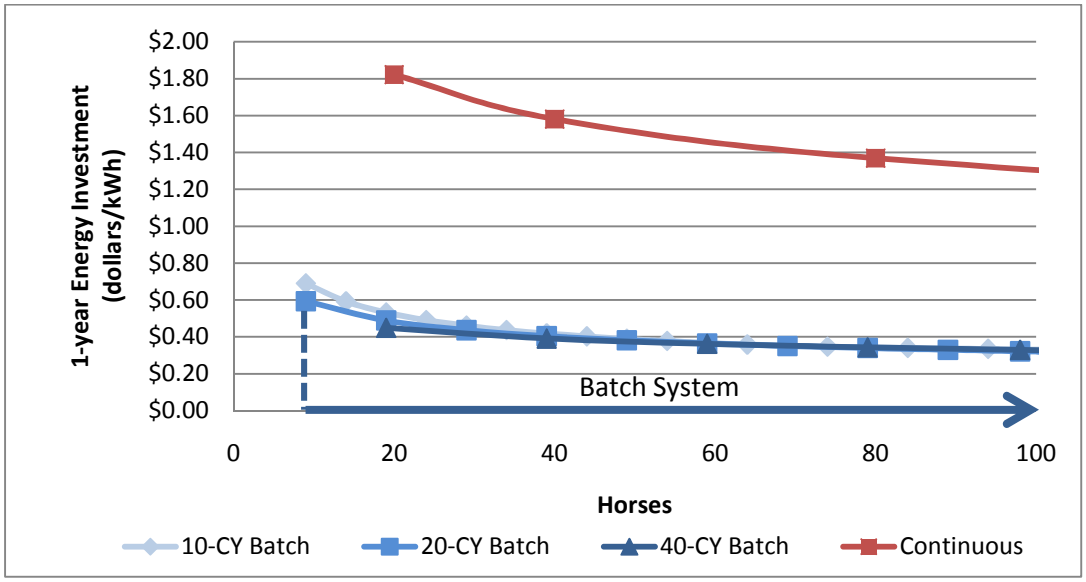

Figure 3.12 - Comparison of capital investment per kWh generated (over 1-year of operation) for 10-CY, 20-CY and 40-CY batch vessel sizes as well as continuous system

The energy investment assessment does not account for differences in the associated system footprint, where the batch system requires a substantially larger footprint on a per horse basis, than the continuous system.

Altering the batch system configuration to eliminate the need for the insulated vessel housing structure could reduce the system capital costs while maintaining the same functional objectives. Insulating each reactor separately and modifying the vessel

configuration to allow centralized leachate heating and distribution as well as biogas recovery (Figure 3.13) has been analyzed [197].

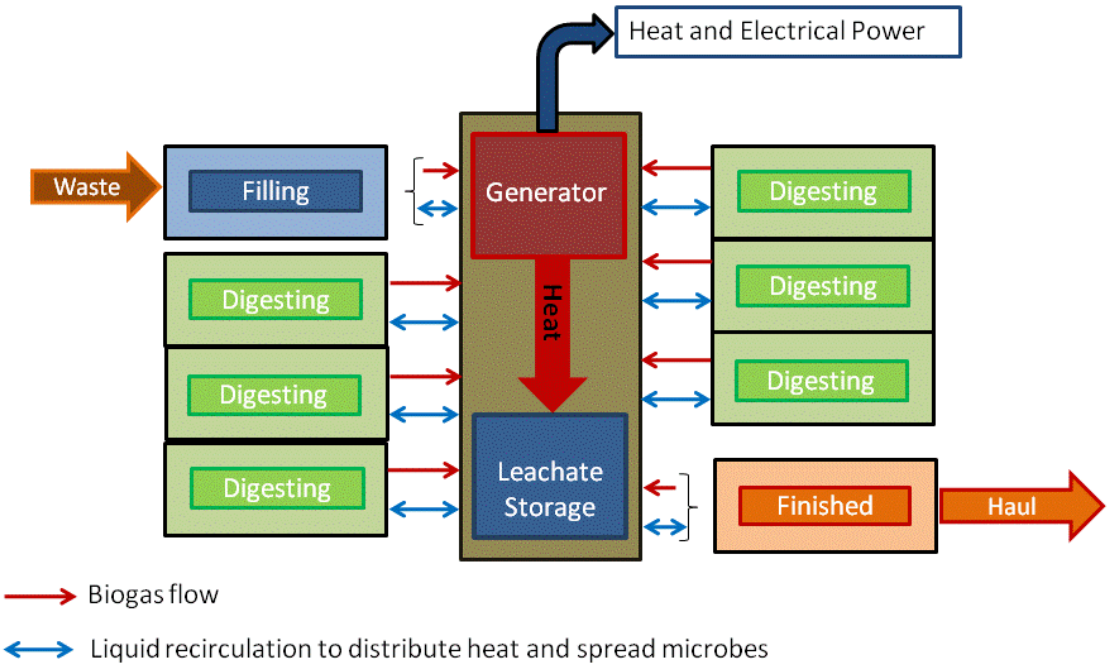

Figure 3.13 – Symmetrical batch system configuration were adjacent digesting vessels are in contact and heat transferred between them is not lost from the system

It is likely that this configuration could increase heating demands as compared to the single structure design, but the vessels could be configured such that heat transfer between adjacent vessels would not be counted as heat loss from the system. The effect of this configuration on overall batch system viability was not considered in this analysis.

3.4.3 System Footprint, Energy Balance and Operation Considerations

The footprint biofuel capacity (L CH_4/m^2 land) normalizes the expected methane production to the system footprint requirements, and identifies which system

configuration more adequately maximizes methane production per unit area (Figure 3.14).

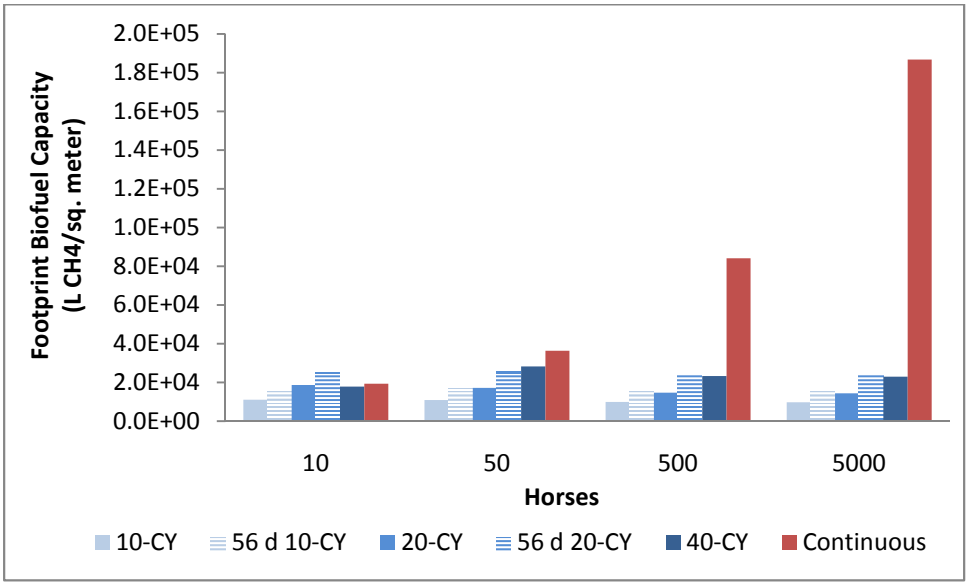

Figure 3.14 - Comparison of production footprints, liters of methane generated per square meter of land required, for all considered batch and continuous systems at10, 50, 500, and 5,000 horse quantities

A larger footprint biofuel capacity is favorable as it indicates that a greater volume of methane fuel gas can be accumulated per unit area that the system covers. For 10 horses, the footprint biofuel capacity of the batch systems is typically greater as compared to the continuous system (56 d 20-CY most favorable). For 50 horses, the continuous system footprint biofuel capacity becomes marginally more favorable compared to the batch system, and above 50 horses it is substantially more favorable. The results indicate that batch systems, particularly the 20-CY vessel system with the increased SRT (56 d 20-CY), may best optimize methane production in terms of the system footprint for 10 to 50 horses.

Either for residual waste removal or feedstock delivery, both the onsite batch and regional continuous systems are assumed to require horse waste transport. The fuel consumed during this transport is viewed as a system energy sink, and can be subtracted from the equivalent energy generated from combusting methane to produce electricity. The critical transport distance (Equation 3.13) is the distance at which all the equivalent energy produced in the form of electricity equals the energy consumed for waste transport. Transporting horse waste beyond the critical transport distance would establish a system that consumes more energy than it generates. The critical transport distance was compared for each system type at various horse quantities (Figure 3.15).

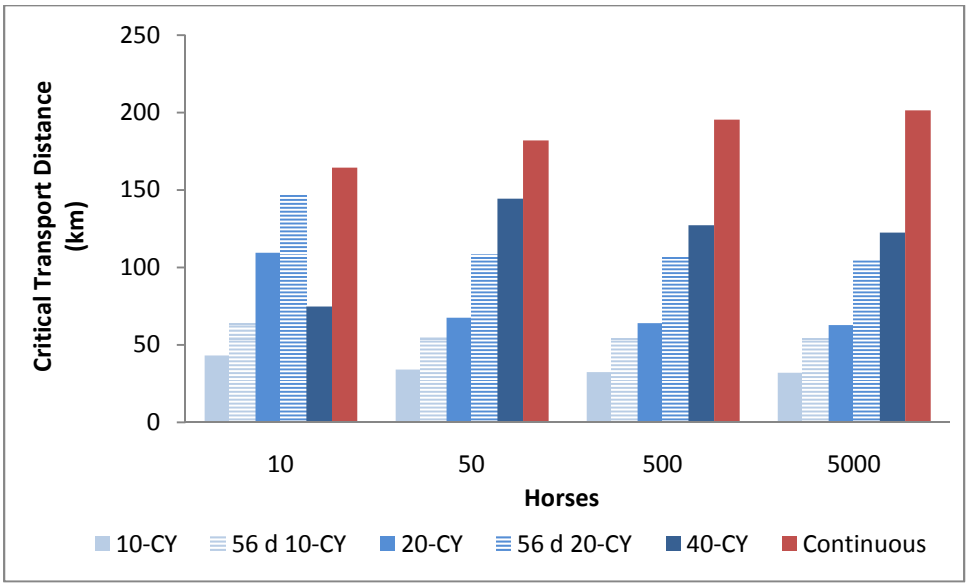

Figure 3.15 - Comparison of critical transport distance for onsite batch and regional continuous systems as a function for horse quantities of 10, 50, 500 and 5,000

The results are dependent on the assumed fuel economy of the transport vehicle (1.79 km/L), but the model can be readily altered to assess different inputs. The difference between the recoverable system energy and the energy consumed by the system as a function of particular parameters, such as transport distance, are important for

developing horse waste handling guidelines, policies and regulations. As expected, the increased energy recovery potential observed for the continuous type system corresponds to a greater critical transport distance as compared to the batch systems.

Throughout this analysis the feedstock energy content has been held constant (277 L CH_4/kg VS) for comparison of different system types, but variability in the waste energy content as a function of animal feed or bedding type and quantity can change modeled outcomes and force different conclusions about system viability. For example stall waste mixtures containing soft wood chip bedding had a G_{pot} of less than half that of horse manure alone, because the softwood chip bedding is scarely degradable under anaerobic conditions [143] (Table 3.1). Therefore model outputs for a range of feedstock energy contents between 100 and 300 L CH_4/kg VS was examined (100% difference). The effect of feedstock energy content on recoverable methane was not found to be directly proportional. For the 10-, 20- and 40-CY batch systems a 177% decrease in feedstock energy content from 277 to 100 L CH_4/kg VS corresponded to an average recoverable methane decrease between 34% and 47%. The 10- and 20-CY batch systems with a SRT of 56 versus 28 days were more sensitive to the decrease in feedstock energy content (177%) and recovered, on average, between 62% and 75% less methane than had been predicted with the greater feedstock energy content.

3.5 Conclusions, Implications, and Future Investigation

The centralized continuous-flow, complete mix anaerobic digester system was consistently more effective at recovering methane and corresponded to a lower normalized capital investment (energy investment) for horse quantities above approximately 80. Further, its space footprint was always smaller than the batch system.

The greatest difference in cost per kWh of electricity produced between the 40-CY batch and continuous system was for the largest horse quantity considered (5,000 horses), indicating that there is a greater advantage for employing continuous processes with larger systems. However, the biofuel generation potential analysis, which normalized the recoverable methane to the system space footprint (footprint biofuel capacity), showed that batch systems may best optimize methane production in terms of the system space footprint for horse quantities between 10 and 50.

Doubling the retention time of the 10- and 20-cubic yard (56 d 10-CY and 56 d 20-CY) batch systems increased the recoverable methane potential on a VS basis, and reduced the required capital investment per kWh of electricity. However, the 10-CY batch systems, even with the retention time doubled, required greater capital investments per kWh of electricity as compared to the continuous system. The 56 d 20-CY batch system (greater retention time) was favorable as compared to the 40-CY batch system for horse quantities up to 25, and both the 56 d 20-CY and 40-CY batch systems were favorable as compared to the continuous system up to 80 horses.

Although the batch system (40-CY) was found to cost less to construct per horse as compared to the continuous system, the cost per kWh of electricity produced was greater among batch systems above approximately 80 horses. The largest capital cost for the batch system was the structure to house the reactors. When the cost of the structure is subtracted, the capital investment per kWh of electricity produced by the batch system is less than that of continuous system for the range of horse quantities assessed, but the outsized footprint requirements for batch systems makes large batch systems unrealistic. Batch systems would be most desirable on small farms (less than 50 horses), where

existing infrastructure is available to house the reactors, and the waste heat generated during electricity production could be utilized as well.

If horse waste management strategies include waste or residual waste removal, the regional continuous digester system appears to be more advantageous compared to onsite batch systems for larger farms (greater than 50 horses), especially those farms with preexisting infrastructure to house the batch digestion system. Regardless of the system type employed, the energy content of the feedstock waste is critical to methane recovery and process viability. This means that digester operators need to include bedding type and quantity as a process parameter. Further, additional incorporation of intermittent mixing into the batch reactors should be investigated to determine if capital and operational costs associated with mixing could be offset by enhanced methanogenesis.

In terms of optimizing biogas recovery, maximizing revenue and minimizing the system footprint, the continuous system is more desirable as compared to the batch system over a broad range of horse quantities. Concerning the farm owner's relative stake in a particular process, the regional system could provide greater advantages than individually operated batch systems if the waste or waste residue is to be removed from the farm and if the regional system is operated as a cooperative. Another advantage of the regional digester is its ability to further process the digested residue by composting.

There are several areas where additional investigation would be required to implement effective regional digesters. In terms of maximizing energy generation and minimizing consumption as a result of material transport, digester geographical location would be critical. Using the predicted critical transport distances, land values and local horse densities, appropriate locations would need to be identified. Further, the prospect of

mixing multiple agricultural and food waste streams should be considered as it would affect both methane generation and digester location.

Regarding batch system optimization, the results indicate that a critical standard vessel size exists that maximizes biogas accumulation and minimizes capital costs. This is evident as the cost of the 10-CY batch system as a function of total energy production is more than the 20-CY system, but the 20-CY system is less than the 40-CY system. Identifying the optimum tradeoffs between reactor size, system cost, and energy production potential would be critical in developing viable onsite batch digestion systems.

The results from this model do not seek to predict, quantifiably, system profitability, but rather to assess overall economic viability as well as to inform policies and decision making regarding horse waste management. The value of grants, incentives and carbon credits can be considered using such results for various system configurations, and the model parameters can be varied depending on geographic location and farm size.

Chapter 4

4. Effect of Ammonia Removal by Simulated Stripping or Aeration to Stimulate Nitrification on Methane Production in Laboratory-Scale Anaerobic Batch Reactors

[Babson, D. and Fennell, D. to be submitted to Applied Microbiology and Biotechnology]

4.1 Abstract

Ammonia accumulates in anaerobic digesters as it is released during degradation of organic nitrogen compounds. Accumulation of ammonia-nitrogen in digesters can limit methane production via toxicity to microorganisms, and the digestate may require energy intensive treatment downstream to avoid adverse environmental effects from nitrogen release. The goal of this study was to examine the effect of nitrogen loading and the resulting total ammonia nitrogen (NH_3/NH_4^+) (TAN) concentration on methane production in anaerobic batch reactors. In some reactors, TAN removal was accomplished by physical removal (simulated stripping) and in others via aeration to stimulate partial nitrification, to be followed by denitrification post-aeration.

Simulated organic waste feedstocks with three different nitrogen loadings were created by varying the ratios of laboratory grade rabbit food, the dairy protein, casein, and cellulose that were loaded into each reactor. Two suites of reactor sets were established; half were maintained at mesophilic conditions (35°C) and half were maintained at thermophilic conditions (55°C). For each level of nitrogen loading there were triplicate reactors for (1) controls that had no ammonia removal, (2) systems that underwent physical removal of TAN via simulated stripping and (3) systems that underwent aeration to stimulate nitrification. Methane production in each reactor was

normalized to a volatile solids (VS) added basis so that production from the various feedstocks and conditions could be compared.

As expected, lower methane production was observed for higher nitrogen loadings. Among control reactors with no treatment to remove nitrogen, high nitrogen loadings corresponded to greater aqueous phase TAN concentrations. The digestion in the low nitrogen loading reactors produced 350-1,000 mg TAN/L, versus the high nitrogen loading reactors which produced 3,700-5,200 mg TAN/L. Cumulative methane production was as much as 96% less in the high nitrogen loading controls (8.9 ± 1.1 mL CH_4/g VS) compared to the low nitrogen loading controls 204.4 ± 26.0 mL CH_4/g VS).

Simulated ammonia stripping was intended to mimic stripping that could be achieved via treatment of digestate with addition of chemical base to increase the pH, gas purging to volatilize ammonia, re-neutralization and recycle to the reactors. This was accomplished through exchange of digestate with fresh TAN-free anaerobic medium which had elevated concentrations of salts to mimic the chemical treatment. The method used to simulate ammonia stripping typically reduced the total ammonia (TAN) concentration by approximately 30% (± 4.4%) per treatment, but it also resulted in removal of soluble substrates (e.g., volatile fatty acids (VFAs)) since liquid was removed from each reactor. Stripping was repeated weekly until the TAN fell below 250 mg/L. Among medium- and high-nitrogen feedstocks, stripping enhanced methane production by 95%—increasing methane production from 57.8 ± 28.0 mL/g VS in controls to 112.6 ± 4.3 mL/g VS in stripped reactors—and 360%—with methane production increasing from 8.9 ± 1.1 mL/g VS in controls to 40.9 ± 1.4 mL/g VS —, respectively, in reactors maintained at thermophilic conditions. Stripping improved methane production among

reactors with a high-nitrogen feedstock maintained at mesophilic conditions by 48%—increasing production from 50.5 ± 0.7 mL/g VS in controls to 74.9 ± 1.0 mL/g VS in stripped reactors. In low nitrogen loading reactors, methane production was less in stripped reactors than in controls, likely as a result of removal of VFAs during the simulated events. Ammonia stripping was shown to be most beneficial in terms of enhancing methane, ammonia and energy recovery for feedstocks with high nitrogen loadings. The results also indicate that separate hydrolysis and fermentation reactors could be beneficial for optimizing simultaneous ammonia recovery and methane generation for medium- and high-nitrogen feedstocks by reducing ammonia toxicity and excessive VFA accumulation in the digester.

4.2 Introduction and Literature Review

4.1.1 Conversion of Organic Compounds in Anaerobic Systems

One established technology for extracting energy from organic waste is anaerobic digestion [29-30]. During anaerobic digestion, complex polymers such as polysaccharides (carbohydrates), lipids (fats/oils) and proteins are converted to methane and carbon dioxide during several metabolic stages, and these degradation processes are mediated by a number of different groups of microorganisms [198-199]. Biomass energy is ultimately liberated as methane gas. Ammonia is liberated when nitrogen containing compounds such as proteins and amino acids are degraded by proteolytic bacteria, and when urea is hydrolyzed by ureolytic microbes. The biochemical steps of methane production during anaerobic digestion are indicated in Figure 4.1 [200].

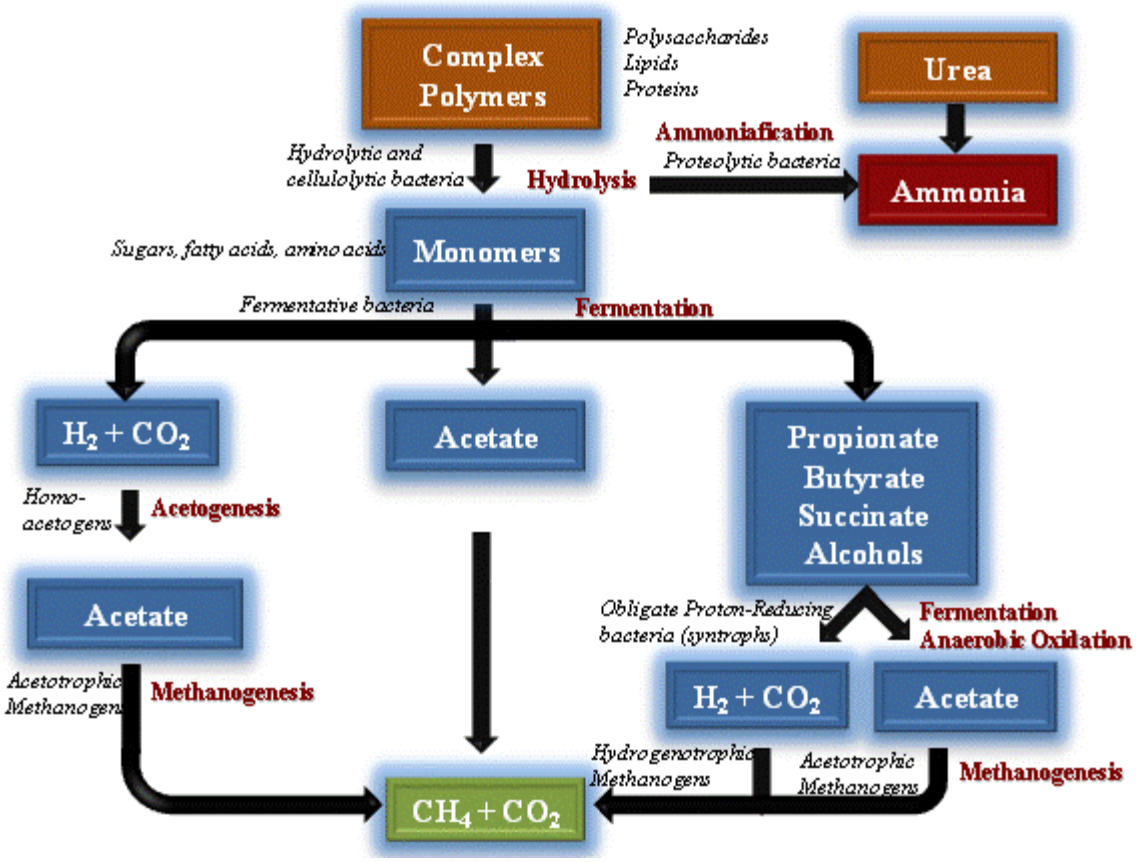

Figure 4.1 - Chemical, biochemical and microbial mediated pathways of anaerobic digestion. Adapted from Rittman and McCarty (2001)

During hydrolysis, the higher order carbon structures comprising the polysaccharides, lipids, and proteins of the biomass are degraded to sugars, fatty acids and amino acids, respectively [198]. For feedstock wastes containing greater amounts of particulate matter such as food waste, animal manure or sewage sludge, hydrolysis is typically the rate limiting step [201-202]. Gujer and Zehnder (1983) found that when hydrolysis is rate limiting, methane generation kinetics are controlled by and proportional to the rate of particle solubilization [199].

The sugars and acids generated during hydrolysis are next fermented to a heterogeneous mixture of organic acids, carbon dioxide, and hydrogen. During

acidogenesis, volatile fatty acids (VFAs) such as propionic and butyric acids are generated [199]. Zinder (1988) showed that acidogenesis is typically favorable thermodynamically as long as the partial pressure of hydrogen is maintained under 10^{-3} atmospheres (atm) [203]. In particular, propionate degradation is limited by elevated hydrogen partial pressures [204]. The partial pressure of hydrogen can be controlled to below 10^{-3} atm by effective removal of hydrogen via hydrogen-consuming microorganisms (hydrogenotrophic methanogens or homoacetogens) [198, 203]. Recent research activities have sought to optimize both fermentative hydrogen production and methane generation from anaerobic systems [205]. The formation of acetate from hydrogen and carbon dioxide (homoacetogen mediated) has not been studied widely [198], but has been shown to account for less than 5% of the total acetate synthesis in digesters [206].

Methanogenesis is a form of microbial anaerobic respiration, during which methanogenic archaea use inorganic carbon (carbon dioxide or bicarbonate) as the terminal electron accepter [207]. Methanogens are strict anaerobes and oxygen inhibits their growth and viability [207]. The most common substrates for methanogenesis in anaerobic digesters are acetate, hydrogen and carbon dioxide. Reaction 4.1 and Reaction 4.2 describe the pathways involved.

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{Reaction 4.1}$$

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2H_2O \qquad \text{Reaction 4.2}$$

Acetotrophic (or aceticlastic) methanogens mediate the production of methane from acetate (Reaction 4.1), and hydrogenotrophic methanogens facilitate methane generated by carbon dioxide and hydrogen (Reaction 4.2) [208]. According to McCarty

(1964), acetate decarboxylation accounts for 72% of the methane production on a chemical oxygen demand (COD) basis, and the remainder is attributed to carbon dioxide reduction [209]. As a result of the relatively small contribution from carbon dioxide reduction during methane generation, acetotrophic methanogenesis is often considered the rate limiting step for methane formation [198].

Because the products of acidogenesis are the reactants for methanogenesis, there is a syntrophic relationship between acetogens and methanogens [207]. The balance in the relationship between these microbial groups can be assessed by measuring the changes in VFA concentration in the effluent [210]. If acidogenesis occurs at a faster rate than methanogenesis, VFAs can accumulate in the digester liquid, causing the pH to fall, and the reactor may subsequently fail [198]. VFA effluent concentrations between 50 and 250 mg/L are desirable for normal anaerobic system operation [210].

4.1.2. Organic Nitrogen Release and Inorganic Nitrogen Toxicity

As proteolytic bacteria degrade proteins and amino acids and ureolytic microbes degrade urea, ammonia is released [44]. Although digester effluents containing ammonia can be a component in fertilizers, release of excess nitrogen to surface waters can cause eutrophication and infiltration into groundwater can pollute aquifers. Land or surface water discharge of digestate is often regulated [42]. Since wastewater streams containing ammonia must typically be treated, it is of critical importance to understand the processes controlling this contaminant accumulation and to find better methods for ammonia management. Thus, all engineered systems utilizing anaerobic processes to produce bioenergy, such as anaerobic digesters and bioreactor landfills, should have a plan for managing ammonia [42, 211]. For anaerobic digesters treating animal manures or other

agricultural wastes, the digestate is often land applied to recycle nitrogen back to the soil. Regulations on applying animal manures to land are increasing, and there must be acceptably situated and sufficient land to attenuate the nitrogen [212-213].

Management of ammonia liberated during the degradation of organic matter containing nitrogen and urea is a particular concern during anaerobic digestion [34, 214-216]. Ammonia nitrogen, in high concentrations, has been shown to limit methanogenesis because it can be toxic to anaerobic microbial communities [216]. In addition, of the four major groups of anaerobic microorganisms involved in the breakdown of organic material, methanogens are the least tolerant of ammonia [217].

Total ammonia nitrogen (TAN) consists of free ammonia (NH_3) and the ionized ammonium ion (NH_4^+), which are in equilibrium in aqueous systems as indicated by Reaction 4.3.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad \text{Reaction 4.3}$$

The ratio of NH_3-N/NH_4^+-N in an aqueous system is governed by the pH and temperature and related by Equation 4.1.

$$[NH_3 - N] = \frac{[TAN]}{(1 + \frac{[H^+]}{K_a})} \qquad \text{Equation 4.1}$$

Where NH_3-N is the free ammonia nitrogen concentration and K_a is the dissociation coefficient that is temperature dependent. Free ammonia (NH_3) increases with pH and temperature and is more inhibitory to methanogenic communities than ammonium ion (NH_4^+) because of its ability to cross the cell membrane and disrupt physiological processes [218-219]. Although TAN is needed by anaerobic microbial

communities as a source of nitrogen for biosynthesis (below 200 mg/L is beneficial) [220], ammonia is toxic to microbial communities.

Ammonia inhibition during anaerobic digestion is well documented [216, 219, 221-225]. However, thermophilic microorganisms have also been shown to be more tolerant of ammonia [226]. In acclimated thermophilic digesters, Sung and Liu (2003) showed 40 to 60% inhibition of methanogenesis at 5 to 6 g/L TAN, and complete inhibition at 8 to 13 g/L TAN [225]. Methanogenic populations can become acclimated to higher TAN concentrations. Calli et al. (2005) observed shifts in populations of methanogenic archaea and acetogenic fatty acid-degrading bacteria using detection of 16S rRNA genes during anaerobic digestion at nitrogen loadings up to 6 g/L TAN with corresponding free ammonia nitrogen concentrations of 0.8 g/L, suggesting emergence of populations less susceptible to ammonia [227]. Borja et al. (1996) reported ammonia toxicity at TAN concentrations greater than 5 g/L, but were able to maintain stable activity up to 7 g/L TAN but a higher TAN concentrations reduced methane production was observed [221]. Controlled continuous anaerobic digestion processing under steady-state conditions could allow methanogenic microbial communities to become acclimated to higher TAN concentrations, and such systems have been shown to generate methane unhindered at TAN concentrations reaching 11,000 mg/L [228]. Thus, control of C:N ratios of digester feedstocks is needed for successful digestion, as is microbial community acclimation.

Landfills also produce high ammonia concentrations in leachate during the methanogenic phases of operation. A literature review of bioreactor landfill operation by Berge et al. (2005) indicated that TAN may reach up to 5,000 mg/L [34] while Kjeldsen

et al. (2002) indicated TAN concentrations of up to 2,500 mg/L were observed in landfills [229].

Common methods for removing ammonia from waste streams include: (1) increasing the pH (typically from ~7 to ~11) of the liquid stream to shift TAN to primarily ammonia in accordance Equation 4.1, and then removing the ammonia via gas stripping [230-231]; (2) use of biological nitrification – denitrification (Reaction 4.4 and Reaction 4.5) or Anammox (Reaction 4.6) to convert ammonia first to nitrite or nitrate, and then to convert nitrite or nitrate to nitrogen gas; and (3) precipitation and recovery of ammonium as the mineral struvite ($(NH_4)MgPO_4 \cdot 6H_2O$) [27].

$$NH_3 + 2\ O_2 \rightarrow HNO_3 + H_2O \qquad \text{Reaction 4.4}$$

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad \text{Reaction 4.5}$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad \text{Reaction 4.6}$$

More attention will be given to these various nitrogen removal strategies, and the relative advantages and disadvantages of each will be compared in Chapter 5. Regardless of the nitrogen removal method, it is important to recognize the potential negative effect of ammonia accumulation on methanogenesis and biogas production in any particular anaerobic waste conversion scenario, and it is of critical importance to have methods of mitigating ammonia build-up. Recycling liquid streams with ammonia-nitrogen removed by stripping (see Chapter 5) could be a means of diluting digester TAN concentrations and optimizing biogas generation. Further, the concentrated ammonia gas stream, obtained from stripping, could become the reforming fuel for catalytic reforming producing inert nitrogen gas as well as the fuel gas hydrogen. Thus, for an anaerobic digester system generating methane and ammonia-nitrogen rich digestate effluents, the

inclusion of an ammonia recovery and reforming system to generate hydrogen could allow more fuels to be produced by a single system. A design scheme for an integrated system that could recover methane and ammonia as biofuels will be discussed in Chapter 5.

4.2.2 Rationale and Objectives

In-vessel anaerobic digestion and traditional and bioreactor landfills are vulnerable to toxicity when ammonia is released from organic matter and urea during anaerobic degradation. The accumulation of ammonia-nitrogen in the digester medium or landfill leachate could limit methane production. Further, nitrogen rich waste streams require either an adequate land area for disposal of nutrients (e.g., as land-applied digestate), or energy intensive treatment such as nitrification-denitrification downstream (e.g., for landfill leachate or municipal digester supernatant).

Removing TAN from anaerobic digesters could improve biogas generation by decreasing the toxic effect of accumulated ammonia, and the recovered ammonia could be used to generate hydrogen, an additional biofuel.

Without a more detailed understanding of the specific process tradeoffs between organic degradation to produce biogas and hydrolysis-fermentation to release TAN, challenges in process control could limit optimization of integrated digester systems that seek to simultaneously maximize both methane and ammonia accumulation.

The overall goal of this study was to compare the relative effectiveness of ammonia mitigation via either ammonia stripping or enhancement of nitrification-denitrification in anaerobic batch reactors with different nitrogen loadings. The specific objectives were to (1) analyze performance of batch digesters to elucidate changes in

TAN and methane generation for three simulated waste feedstock carbon to nitrogen (C:N) ratios reacted under mesophilic and thermophilic conditions, (2) quantify the effect of intermittent aeration on methane production and ammonia removal, (3) quantify the effect of ammonia stripping on methane production and ammonia removal, and (4) quantify energy recovery tradeoffs under those two scenarios for ammonia mitigation.

4.3 Methods and Materials

Preliminary studies to examine the effect of intermittent aeration on the fate of nitrogen species were performed using landfill reactors containing slurries of highly degraded MSW obtained from the Burlington County Resource Recovery Complex (BCRRC) in Bordentown, NJ. The heterogeneous composition of the waste samples resulted in large deviations among replicates and quantifying the make-up of the starting material, as well as assuring that the original composition was consistent among replicates, was not achieved (data not shown). Thus, subsequent studies, reported here, were performed using a "synthetic", defined, waste comprised of differing amounts of protein (casein), cellulose and laboratory grade rabbit food.

4.3.1. Reactor Protocols

In the simulated waste digesters tested, the nitrogen content of the feedstock and the operating conditions of the digesters were varied to examine the impact of TAN concentration on methane production, and to evaluate ammonia removal strategies. To create variable nitrogen contents, different amounts of laboratory grade rabbit food (Harland Teklad Global Diets, Indianapolis, IN), casein (pure, Acros Organics, Fair Lawn, NJ), and cellulose (pure, Sigma-Aldrich Inc., St. Louis, MO) were added (Table 4.1).

Table 4.1 - Composition of synthetic wastes to examine ammonia production and removal in anaerobic batch reactors

Bottle Set	Rabbit Food (g)	Casein (g)	Cellulose (g)	Inoculum (mL)	Medium (mL)
Inoculum	0	0	0	20	80
Low-N	1	0	3	20	80
Medium-N	3	0	1	20	80
High-N	2	2	0	20	80

The maximum theoretical methane production was determined based on the type of substrate added. The calculated oxygen demand (COD') per gram was calculated from standard ($C_nH_aO_bN_c$) variables (Equation 4.2) [232].

$$COD'/Mass = \frac{16 \cdot (2n + 0.5a - b - 1.5c)}{12n + a + 16b + 14c} \qquad \text{Equation 4.2}$$

Theoretical methane production was then calculated based on the relationship that 8 g of COD' equals 1 electron equivalent, and that 8 electron equivalents equal one mole of methane. The molecular formula of cellulose ($C_6H_{12}O_5$) and casein ($C_{47}H_{48}N_3O_7S_2Na$) are both known, but the composition of the rabbit food was estimated from the proportions of crude protein (16.9%), crude oil (3%), crude fiber (14.3%), ash (8%), carbohydrate (30.9%), starch (23.3%) and sugar (7%), as provided by the manufacturer. An empirical formula of $C_{0.332}H_{0.458}O_{0.118}N_{0.0117}X_{0.08}$ was derived to represent the rabbit food by estimating the crude oil as Linoleic Acid ($C_{18}H_{32}O_2$) and the protein as a combination of tryptophan and glycine, yielding a nitrogen ratio appropriate for crude protein (approximately 1 g N/6.4 g protein).

One set of low (feedstock C:N = 102.2), medium (feedstock C:N = 33.0) and high (feedstock C:N = 17.1) nitrogen ratio reactors were operated without any perturbation as

anaerobic digester controls; a second set had the ammonia removed from the solution weekly using a simulated stripping process to maintain the TAN concentration at or below 250 mg/L, as described in Section 4.3.1, and a third set was intermittently aerated by adding oxygen weekly (Table 4.2). All variations in feedstock composition and treatments applied were replicated for both mesophilic (35°C) and thermophilic (55°C) conditions.

Table 4.2 - Operational treatments to examine ammonia production and removal in anaerobic batch reactors. *NA = not applicable

Treatment	30 mL of Oxygen Added	Ammonia Stripped
Control	NA	NA
Intermittent Aeration	Weekly	NA
Ammonia stripping	NA	Weekly

All reactor configurations and treatments were set-up and conducted in triplicate.

4.3.2 Reactor Operation

Reactors consisted of 160 mL glass serum bottles sealed with butyl rubber stoppers (Wheaton Science Products, Millville, NJ). Substrates were added to reactors, a purge gas of 100% argon (Ar) was initiated, 20 mL of mesophilic anaerobic digester sludge (Joint Meeting of Essex and Union Counties, NJ) was added as inoculum to the mesophilic reactors and 20 mL of thermophilic digestate (Rutgers EcoComplex pilot scale food digester, Florence, NJ) was added as inoculum to the thermophilic reactors. The reactors were then filled to 100 mL with anaerobic minimal salts medium [233].

Rather than actually removing liquid from the batch reactors, chemically increasing the pH, performing ammonia stripping, chemically neutralizing the liquid and returning the treated liquid back into the bottles, a simulated stripping process was

utilized. The simulated stripping process was used to minimize unnecessary differences between replicates, since the objective of these experiments was not to optimize the stripping process itself. During simulated stripping, 50 mL of medium was removed from the reactors weekly and modified medium reflecting a perfectly executed stripping process was used to replace the removed liquid. The modified medium was prepared according to Fennell et al. (1997) [233] but contained no ammonia (TAN = 0 mg/L), and was additionally altered to reflect chemical additions that would be necessary to achieved ammonia removal and re-neutralization in a real stripping process. The increased ion concentration resulting from the artificial stripping process was determined by measuring the initial ammonium concentration and using reaction stoichiometry involved in the real stripping process (Reaction 4.7 and Reaction 4.9). First, the pH of the liquid would have been increased by addition of lime $Ca(OH)_2$ (Reaction 4.7) and the equilibrium between ammonium and ammonia, would be shifted to ammonia (Reaction 4.8). Finally, excess lime would be converted to calcium carbonate by purging with carbon dioxide (Reaction 4.9).

$$Ca(OH)_2 \rightarrow Ca^{2+}_{(aq)} + 2\ OH^-_{(aq)} \qquad \text{Reaction 4.7}$$

$$NH_4^+{}_{(aq)} + OH^-_{(aq)} \rightarrow NH_{3\ (aq)} + H_2O \qquad \text{Reaction 4.8}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{Reaction 4.9}$$

To simulate this process, the medium [233] had additional calcium chloride ($CaCl_2$) added to account for the stoichiometric amount of calcium needed for ammonium (NH_4^+) removal (Reaction 4.8) during stripping.

Aerated bottles were injected with 30 mL pure oxygen (25° C, 1 atm) once weekly.

Reactors were incubated at 35°C (mesophilic) and 55°C (thermophilic) for a period of 12 weeks (84 days). Sampling and analyses were conducted weekly.

4.3.3 Analytical Techniques

Gas was wasted from the batch reactors once per week and the volume was measured at atmospheric pressure using a gas-tight plastic syringe or a water displacement system constructed from a 100 or 500 mL burette. The methane content of the biogas was determined by removing an 0.25 mL headspace sample from each reactor using a gas-tight syringe (Valco® Precision Sampling, Baton Rouge, LA), and injecting the sample into an Agilent 6890N Gas Chromatograph (GC) equipped with a Flame Ionization Detector (FID) (Agilent Technologies, Santa Clara, CA) and a GS-GasPro column (Agilent Technologies, Santa Clara, CA). Helium was the carrier gas at a constant pressure of 131 kPa (19 psi). The oven temperature was held at 150°C. The resulting chromatographic peak area was compared to a five-point calibration curve prepared by identifying peak areas from known volumes of methane (99% purity; Matheson Tri-Gas, Inc., Montgomeryville, PA) between 0.01 and 0.25 mL (gas-tight syringe, Valco® Precision Sampling, Baton Rouge, LA) and converting to percent volume.

Total aqueous ammonia species were measured weekly. The pH of aqueous samples was adjusted to less than 2 using 20-mN methanosulfonic acid to convert all dissolved ammonia to ammonium ion, and the ammonium ion concentration was obtained by ion chromatography (IC) (Dionex ICS-1000 ion chromatograph; Dionex Corporation, Salt Lake City, UT). The concentration was expressed as total ammonia nitrogen (TAN) in mg/L. Each sample was centrifuged at 10,000 rpm for 3 minutes to

remove solid particles. The sample supernatant was diluted 1,000 times (5 μL sample supernatant to 4.995 μL MilliQ water) before being placed into an individual 5 mL IC analytical vial. The mobile phase in the ion chromatograph was a 20-mN solution of methanosulfonic acid (prepared using MilliQ water) filtered through a 0.45-μ filter. Sample ammonium ion (TAN) concentrations were calculated based on dilution and derived from a standard curve prepared in MilliQ-water and run concurrently (standard range: 0.0625 mM to 1 mM).

Three different substrates were used in this experiment: cellulose, casein and laboratory rabbit food. The cellulose and casein were assumed to be 90% total solids (TS), with 100% of TS being volatile (VS). The total solid and volatile solids content of rabbit food was determined to be 100% and 92.2%, respectively, according to Standard Methods [234].

The samples that were centrifuged and filtered for TAN determination were also used for organic acid (VFAs) analysis. The filtrate was diluted 4.6:1 using milliQ water and then analyzed on a Beckman Coulter® System Gold™ HPLC (Beckman-Coulter, Inc., Fullerton, CA) using a Bio-Rad® Aminex HPX-87H organic acid analysis column (Bio-Rad Laboratories, Hercules, CA). Detection was by UV at a wavelength of 210 nm. The column was held at 60°C, and the mobile phase, 5.0 mM H_2SO_4, was configured at a flow rate of 0.6 mL/min. Chromatographic peak areas for samples were quantified by comparison to standard curves over a concentration range from 62.5 mg/L to 1,000 mg/L for acetic, propionic, and butyric acids (Sigma-Aldrich Co., St. Louis, MO). The total VFA concentration was determined by summing the molar amounts of each individual acid.

4.3.4. Data analyses

Data were collected over a 12-week (84-day) period. Data collected from individual bottles were averaged and results were presented as an average plus or minus one standard deviation for each treatment. The cumulative biogas and methane for each reactor was compiled and average values within replicates were used for comparisons.

The ammonia removed during the simulated stripping process was determined from TAN measurements. The ammonia removed was expressed on a potential energy output (21.3 J/mg-TAN) basis in order to assess the overall energy output of both methane from anaerobic digestion and hydrogen from catalytic reforming.

4.4 Results and Discussion

4.4.1 Methane and Biogas Production

The cumulative methane production from each set of treatments is shown in Figure 4.2.

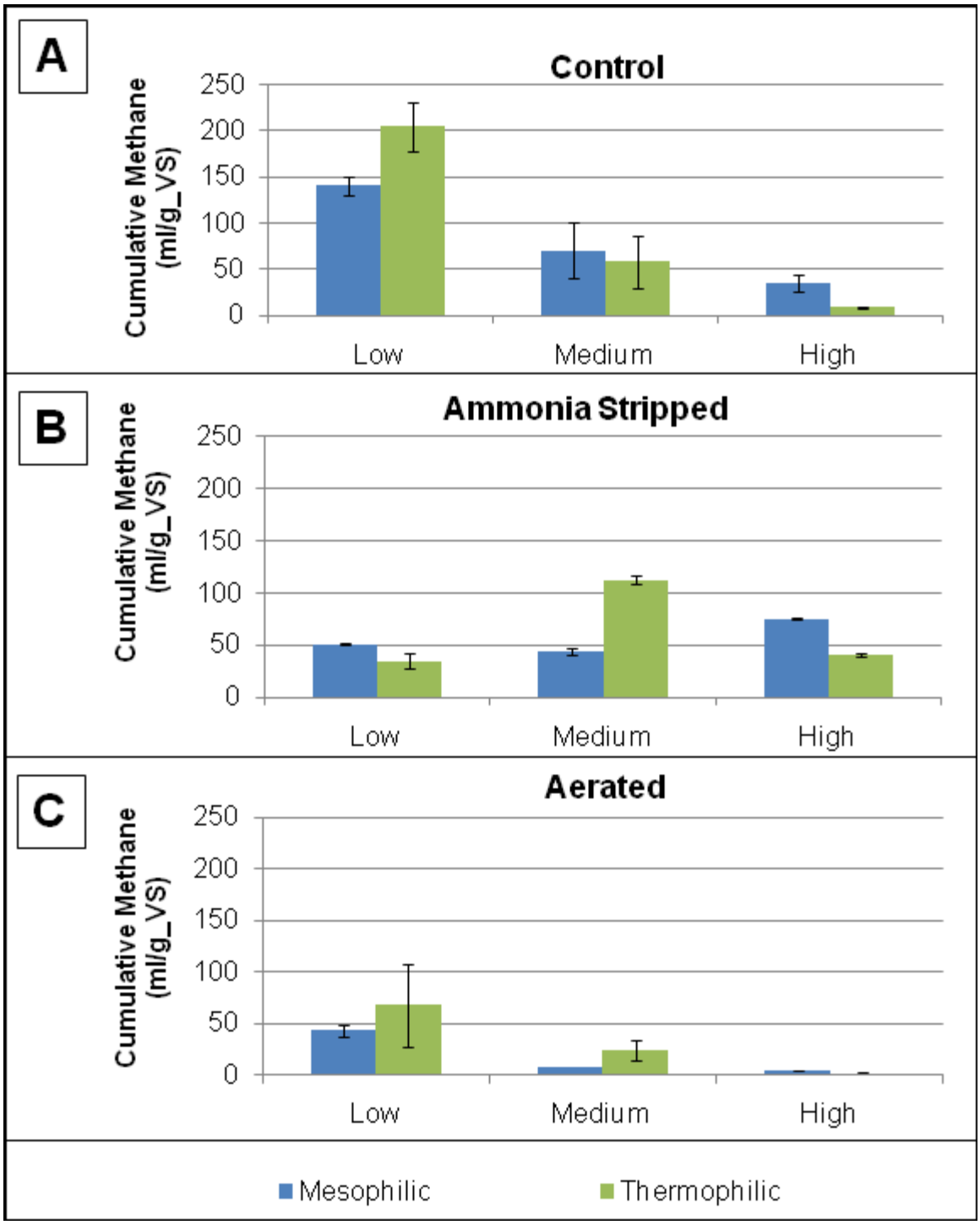

Figure 4.2 - Comparison of cumulative (total over 84-day period) methane production for both mesophilic and thermophilic reactors with low-, medium- and high-nitrogen feedstock loadings: (A) control with no treatment, (B) ammonia stripped, and (C) aerated

Increasing the nitrogen loading of the feedstock material (low- to high-nitrogen) resulted in a corresponding decrease in methane accumulation in both control and aerated reactors under mesophilic and thermophilic conditions. Ammonia stripped reactors, which allowed nitrogen species to be removed from the batch system at weekly intervals, did not show consistent trends based on initial nitrogen loadings. For mesophilic ammonia stripped reactors, the methane generation was roughly equivalent from low- to high-nitrogen loadings with the medium-nitrogen loading generating the least methane (43.47 $\pm$ 3.11 mL CH_4/g VS) and the high-nitrogen loading generating the most methane (74.90 $\pm$ 0.96 mL CH_4/g VS). For thermophilic ammonia stripped reactors, the medium-nitrogen loading generated the most methane (112.59 $\pm$ 4.32 mL CH_4/g VS), while the low- and high-nitrogen content reactors generated substantially less methane (34.82 $\pm$ 7.46 and 40.94 $\pm$ 1.37 mL CH_4/g VS, respectively). Increasing the nitrogen loading was expected to decrease methane generation, and this effect is shown by the corresponding decrease in methane accumulation in control reactors as the nitrogen loading increased. There was a more dramatic decline in cumulative methane production from low to high among thermophilic controls, perhaps indicating that the microbial populations were more sensitive to ammonia levels or that the increased temperature enhanced the toxicity of aqueous ammonia. Gallert and Winter (1997) showed, however, that some thermophilic methanogens are less sensitive to ammonia [222], perhaps suggesting other factors also affected methane generation in this case.

The effect of ammonia stripping and aeration is compared explicitly in Figure 4.3.

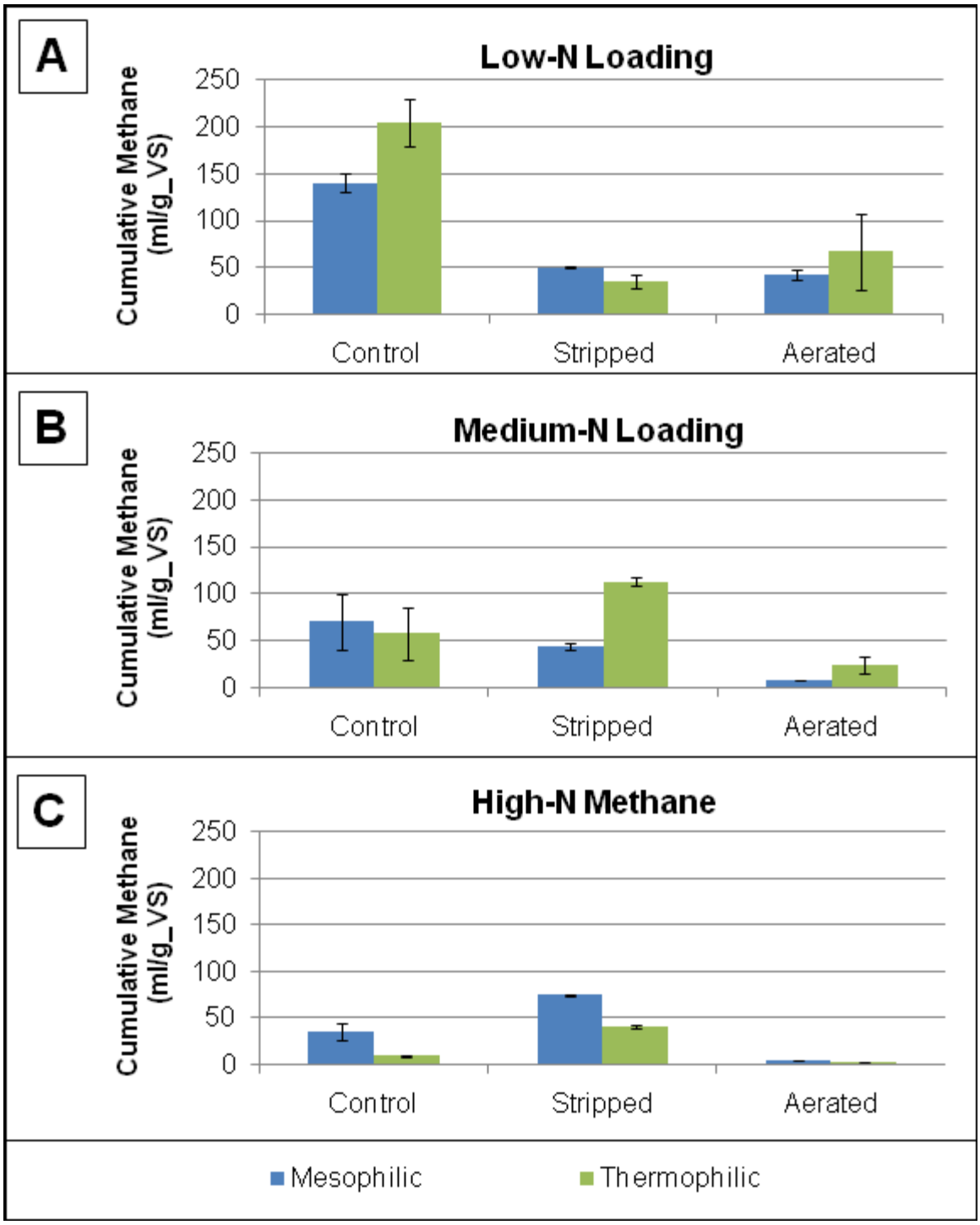

Figure 4.3 - Comparison of cumulative biogas production for both mesophilic and thermophilic reactors with control and two treatments and three nitrogen loading scenarios: (A) low-nitrogen, (B) medium-nitrogen, and (C) high-nitrogen

The greatest methane accumulation for both mesophilic and thermophilic reactors was observed for low-nitrogen loadings with no treatment (140.31 $\pm$ 9.88 and 204 $\pm$ 25.98 mL CH_4/g VS, respectively). By a substantial margin, thermophilic inoculum and incubation generated more methane than mesophilic inoculum and incubation for low nitrogen loadings with no treatment (Control). Ammonia stripping and aeration significantly decreased methane accumulation for reactors receiving the low-nitrogen loading, but differences between mesophilic and thermophilic inoculum and incubation were not statistically significant (based on an examination of error bars). For mesophilic reactors receiving the low-nitrogen loading, a 64.0% decrease in methane production was observed as a result of ammonia stripping and a 69.4% decrease in methane production was observed as a result of aeration. An 83.0% and 67.0% decrease in methane generation was observed as a result of ammonia stripping and aeration, respectively, in thermophilic reactors receiving the low-nitrogen loading. The statistically significant decrease in methane production between mesophilic and thermophilic reactors, as a result of ammonia stripping, could indicate that the thermophilic reactors facilitate substrate solubilization (hydrolysis) more rapidly, resulting in greater substrate loss (VFAs) during the stripping process. Ammonia stripping improved cumulative methane yields for both mesophilic and thermophilic reactors with high-nitrogen loadings, but only thermophilic reactors were improved by a statistically significant amount (beyond calculated standard deviations) as a result of ammonia stripping with medium-nitrogen loadings. Aeration decreased the cumulative methane yields for both mesophilic and thermophilic reactors with medium and high-nitrogen loadings.

The greatest amount of methane was generated with low-nitrogen loadings and no treatment, but some reductions in methane generation, resulting from higher-nitrogen loadings, were mitigated by removing nitrogen species via ammonia stripping. This is evident in cases where reactors that received stripping treatments produced more methane as compared to untreated controls (medium and high-nitrogen thermophilic and high-nitrogen mesophilic reactors).

Methane produced was <30% of the total biogas generated, with the majority balance being carbon dioxide. The effect of nitrogen loading and treatments on the methane content of the accumulated biogas for mesophilic and thermophilic reactors is compared in Table 4.3.

Table 4.3 - Comparison of total biogas generated and percent methane for mesophilic and thermophilic reactors with low, medium and high nitrogen loading and two treatments

		Mesophilic Reactors		Thermophilic Reactors	
	Nitrogen Loading	Total Biogas (mL/g VS)	Methane (%)	Total Biogas (mL/g VS)	Methane (%)
Control	Low	574.62 ± 2.64	24.4 ± 1.7	734.83 ± 9.74	27.8 ± 3.5
	Medium	298.99 ± 71.09	23.4 ± 9.9	282.00 ± 74.99	20.5 ± 9.9
	High	229.97 ± 22.34	15.4 ± 3.9	162.68 ± 1.76	5.5 ± 0.7
Ammonia Stripped	Low	261.35 ± 10.28	19.3 ± 0.3	220.55 ± 33.51	15.8 ± 3.4
	Medium	255.31 ± 2.35	17.0 ± 1.2	389.80 ± 4.32	28.9 ± 1.1
	High	298.04 + 1.40	25.1 ± 0.3	229.28 ± 6.99	17.9 ± 0.6
Aerated	Low	183.58 ± 39.84	23.4 ± 3.2	327.30 ± 167.43	20.6 ± 12.4
	Medium	282.76 ± 146.08	3.0 ± 0.0	224.47 ± 46.95	10.3 ± 4.0
	High	150.88 ± 3.33	3.0 ± 0.2	141.35 ± 3.18	1.3 ± 0.4

The greatest amount of biogas among both mesophilic and thermophilic reactors was observed for low-nitrogen loadings with no treatment (574.62 ± 2.64 and 734.83 ±

9.74 mL/g VS respectively). These reactors also produced somewhat larger fractions of methane compared to most other observed results (24.4 ± 1.7% and 27.8 ± 3.5%, respectively), but all reactors produced less methane as a fraction of the total biogas than was expected [235]. In fact, enhanced nitrogen loadings tend to increase the methane content of the biogas [235]. This indicates that normal anaerobic digestion was disrupted either by the excessive TAN (approximately 5,000 mg/L in high-nitrogen loaded cases) or VFA concentrations (greater than 3,000 mg/L in all controls).

The greatest biogas methane content among the mesophilic treatments was 25.1 ± 0.3% methane, which was the observed average for the ammonia stripped reactors with high-nitrogen loadings. Among the thermophilic reactors, the highest observed methane fraction was 28.9 ± 1.1% for ammonia stripped medium-nitrogen loaded reactors. In both mesophilic and thermophilic reactors, the second highest methane fraction observed was among the low-nitrogen loaded controls.

For both mesophilic and thermophilic sets, the lowest cumulative biogas yield and smallest methane fractions were observed among the high-nitrogen loaded aerated reactors. This result indicates that while aeration reduced methane production relative to biogas production, aeration also reduced overall biogas production as well. An inert chemical indicator, resazurin, that would turn the reactor medium pink in the presence of oxygen, was used during these studies. Following aeration the media would turn pink, but the pink color would rapidly diminish (within 6 hours) indicating rapid and complete consumption of the oxygen added. More oxygen was only added after another 7 days had passed. If the entire amount of oxygen added was coupled to aerobic degradation of organic matter (COD') it is expected that 30 mg COD' would be consumed each week.

In turn, this would mean that that COD' was not available for methanogenesis and thus 16 mL of methane that could have been produced would not be produced. Thus over 12 weeks of operation it is estimated that the aerated controls would have produced 192 mL less methane than controls. The actual deficit was 97 $\pm$ 10 mL and 137 $\pm$ 40 mL among low-nitrogen loaded mesophilic and thermophilic reactors, respectively. Among both mesophilic and thermophilic reactors, the deficit was less than expected (192 mL) indicating that methane was not optimized in either reactor type, but that methane generation in thermophilic reactors more closely matched expected methane production than mesophilic reactors.

It appears that oxygen addition severely limited methanogenic processes from occurring, by removing substrate or damaging methanogenic communities or both, which in-turn limited the total methane accumulation. Ultimately, the amount and frequency of oxygen addition served to limit anaerobic processes from occurring and caused aerated reactors to produce less biogas and methane than reactors with no treatment.

4.4.2 Aqueous Nitrogen (TAN)

A comparison of the TAN in the bulk liquid of the reactors is shown in Figure 4.4.

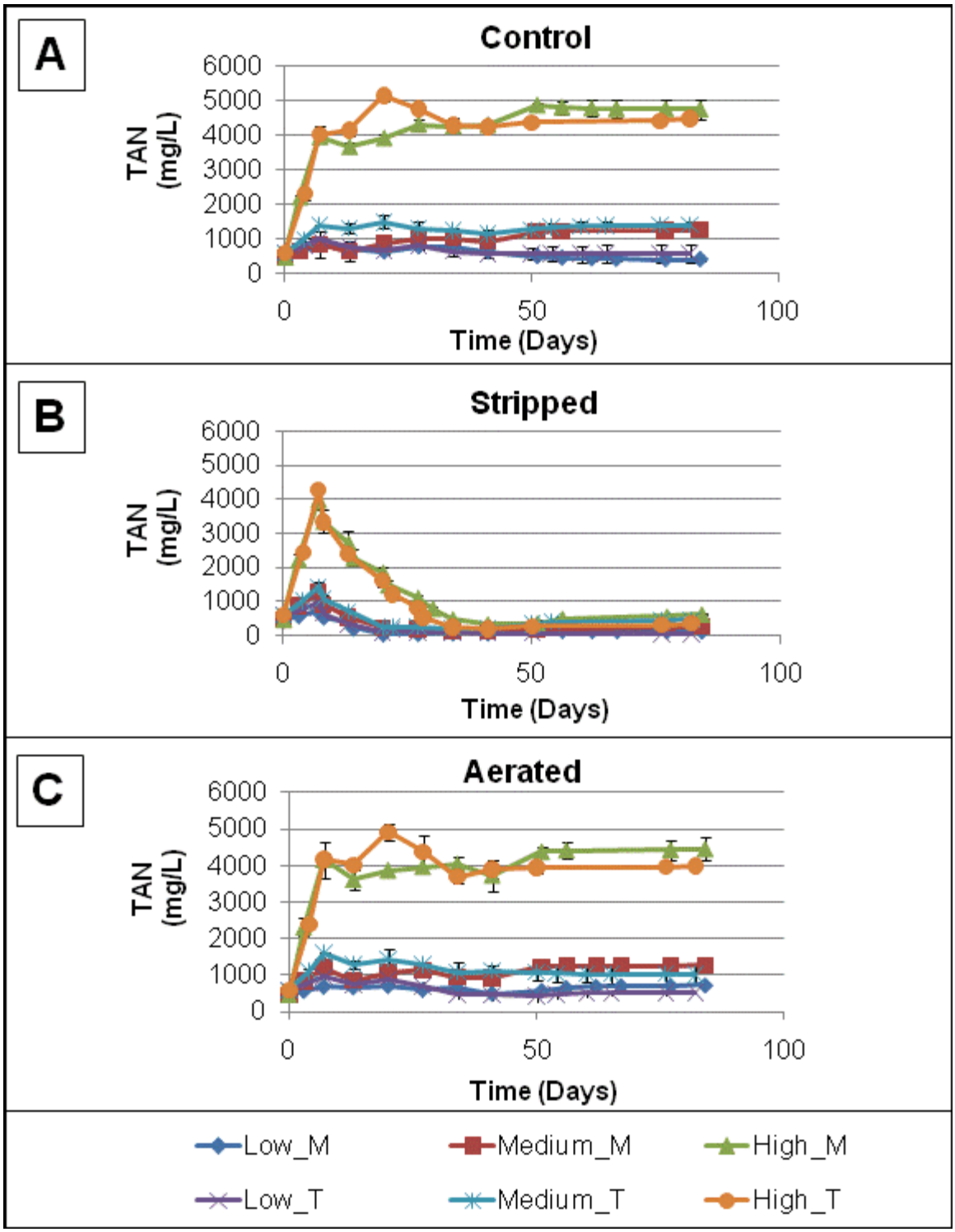

Figure 4.4 - Comparison of aqueous ammonium concentration for both mesophilic (M) and thermophilic (T) reactors with low, medium and high nitrogen feedstock loadings and three treatments: (A) control (no treatment), (B) ammonia stripped, and (C) aerated

Ammonia release from the feedstock material occurred rapidly with the highest observed aqueous TAN concentrations typically being observed after just 7 days. The two exceptions occurred for the thermophilic reactors with high-nitrogen loadings in both the controls and aerated cases, which yielded the highest aqueous TAN concentrations after 20 days.

The control and aerated reactors (Figure 4.4A and 4.4C) were nearly identical with respect to TAN, showing rapid nitrogen species solubilization, followed by relatively stable and consistent TAN concentrations throughout the experiment with defined and differentiated concentrations depending on initial nitrogen loading of the feedstock. As expected, lowest to highest-nitrogen loadings corresponded to lowest and highest TAN concentrations. Negligible differences between aerated reactors and controls indicated that the aeration treatments had no quantifiable effect on nitrogen species evolution. This also indicates that little or no nitrification likely occurred in aerated reactors.

Ammonia stripped reactors (Figure 4.4B) also showed rapid nitrogen species solubilization with the highest TAN concentrations being observed after 7 days. The ammonia stripping treatments were started on day 8, and repeated weekly. The data show that TAN was effectively removed (typically ~30% of aqueous TAN) as a result of each treatment.

Ammonia stripping also had the unintended effect of removing soluble substrate and likely contributed to the lower overall methane yields seen among low-nitrogen

loaded reactors that received the stripping treatment. Thermophilic reactors with low-nitrogen loading and no treatment produced the greatest amount of methane, but higher nitrogen loadings and treatments more dramatically decreased cumulative thermophilic methane accumulation.

Analysis of VFA concentrations in the reactor media showed that the high-nitrogen feedstock was more rapidly solubilized than the low- and medium-nitrogen feedstocks, reaching total VFA concentrations above 12,000 mg/L in mesophilic reactors and 20,000 mg/L in thermophilic reactors within 7 days. Among low- and medium-nitrogen loaded reactors VFA concentrations reached maximums between 3,700-6,000 mg/L and 7,000-7,500 mg/L, respectively, after 7 days with no substantial differences between mesophilic and thermophilic reactors. VFA concentrations typically reached maximums within 7 days, and diminished slightly over time. The simulated stripping process reduced VFA concentrations by the same percentage as TAN concentrations (approximately 30%). In general, the rate at which VFAs accumulated in the reactor media increased as nitrogen loading (low to high) of the feedstock increased. Thus, it appears that possible side effects of increasing the feedstock nitrogen content (by increasing protein concentration) are that it increased the rate and extent to which the feedstock was hydrolyzed, or it decreased the rate at with VFAs were converted to methane. It is also possible (likely) that the high-nitrogen substrate used was more rapidly biodegraded than cellulose.

4.4.3 Equivalent Energy Comparison

Testing the effect of ammonia stripping on anaerobic digestion processes is important because ammonia stripping could possibly remove harmful nitrogen species

from the digestion system, improving overall methane generation while recovering ammonia gas, a chemical energy storage vehicle for hydrogen, simultaneously.

The sum of the potential energy associated with methane generation as well as hydrogen from recovered ammonia-nitrogen was quantified for each reactor type (Figure 4.5).

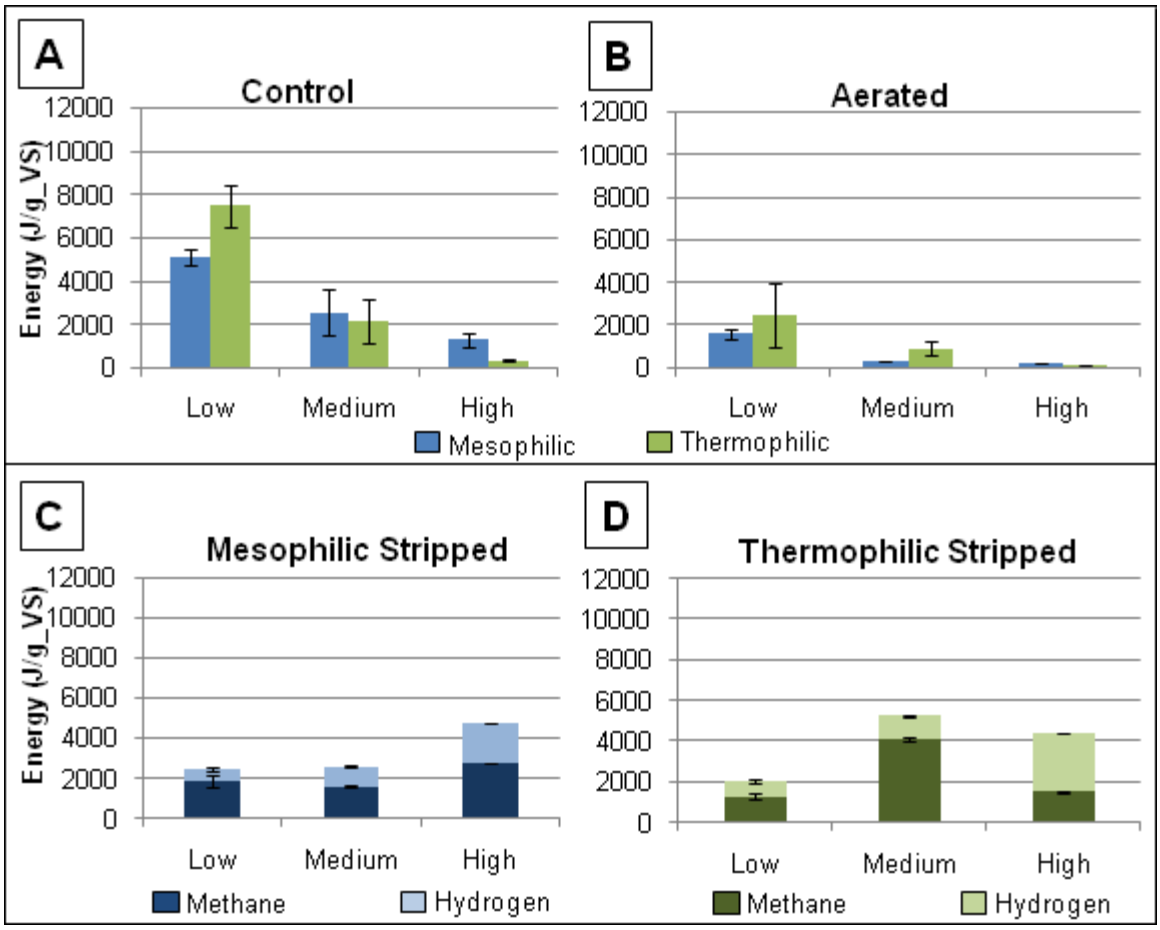

Figure 4.5 - Comparison of potential energy from methane and hydrogen for both mesophilic and thermophilic reactors with low, medium and high nitrogen feedstock loadings and three treatments: (A) control (no treatment), (B) aerated, (C) ammonia stripped mesophilic, and (D) ammonia stripped thermophilic

Note that mesophilic (Figure 4.5C) and thermophilic stripped (Figure 4.5D) reactor data are shown separately because the associated hydrogen energy from ammonia recovery is

considered. As compared to the control reactors, stripping reduced overall energy recovery potential for both mesophilic and thermophilic reactors with low-nitrogen loadings, but improved the energy recovery potential for medium- and high-nitrogen thermophilic reactors and high-nitrogen mesophilic reactors. The potential methane energy alone was observed to nearly double among medium- (2115.7 to 4118.7 J CH_4/g VS) and more than quadruple among high-nitrogen (327.4 to 1497.7 J CH_4/g VS) thermophilic reactors indicating that stripping was beneficial in terms of energy production independent of ammonia recovery. With the exception of high-nitrogen loaded thermophilic reactors (65.8% from H_2 versus 34.2% from CH_4), potential hydrogen energy from ammonia recovery did not exceed potential methane energy generated. Ammonia stripping reduced the methane yield for low nitrogen loadings, but improved methane production for higher nitrogen loadings indicating that there exists some critical initial C:N ratio for which ammonia stripping becomes most beneficial.

For feedstocks that hydrolyze rapidly, releasing ammonia and VFAs that may exceed inhibitory concentrations, it may be beneficial to utilize a separate hydrolysis and fermentation reactor prior to moving on to methanogenesis in a second digester . This would allow toxic levels of TAN to be removed via stripping prior to methanogenesis and the VFA loading to the second digester to be controlled, optimizing the relationship between acidogenesis and methanogenesis. As discussed in Chapter 3 (*Section 3.2.1*), phase-separated anaerobic digestion has been employed to avoid acidification problems and enhance methane production, but it has not been used as a means of avoiding ammonia toxicity and enhancing ammonia recovery.

4.5 Conclusions

Increasing the nitrogen loading of the feedstock enhanced the rate of substrate solubilization and corresponded to a higher TAN concentration in model anaerobic batch reactors. As expected, lower methane production was observed for higher nitrogen loadings. The smallest methane accumulation (1.8 $\pm$ 0.6 mL/g VS) was observed among aerated thermophilic reactors with high nitrogen loadings. Aeration was shown to have very little or no effect on TAN concentrations, and reduced both biogas and methane generation substantially as compared to controls. The method used to simulate ammonia stripping also removed dissolved substrate (VFAs), likely causing less methane to be generated among low-nitrogen feedstocks. Among medium- and high-nitrogen feedstocks, stripping enhanced methane production in reactors maintained at thermophilic conditions. Stripping also improved methane production among reactors with a high-nitrogen feedstock maintained at mesophilic conditions. Ammonia stripping was shown to be most beneficial in terms of enhancing methane, ammonia and energy recovery for feedstocks with high nitrogen loadings, and undesirable for low nitrogen loadings because the simulated stripping process employed in this study also removed soluble substrate for methane generation as well as TAN. The results indicate that separate hydrolysis and fermentation reactors could be beneficial for optimizing ammonia recovery and methane generation for higher-nitrogen feedstocks by reducing ammonia toxicity and excessive VFA accumulation in the digester. Ultimately, energy recovery can not be maximized without optimizing methane generation and ammonia recovery simultaneously, indicating the need for system designs that could enhance both processes.

Chapter 5

5. Anaerobic Digestion for Methane Generation and Ammonia Reforming Hydrogen Production: Theoretical Analysis of a Model System

[Babson, D., Prakash, S. and Fennell, D. to be submitted to Biomass and Bioenergy]

5.1 Abstract

In traditional anaerobic digestion, organic matter is converted to methane gas (a biofuel), and unwanted byproducts, such as ammonia, are liberated as the organic material degrades. If recovered, ammonia can be catalytically converted to generate hydrogen (an additional biofuel). A theoretical design scheme for an integrated system to carry out anaerobic digestion, ammonia separation, and hydrogen recovery has been established to determine system energy requirements and potential biofuel (methane and hydrogen) outputs. Energy demands such as heating, fluid pumping, reactor mixing and ammonia reforming were characterized, and compared to the potential biofuel outputs over a range of possible feedstock carbon to nitrogen (C:N) ratios. The total recoverable energy decreased as the feedstock C:N ratio decreased because less carbon was available for methane production. However, the overall system energy balance was positive and indicated that the integrated system generates more potential energy in the form of methane and hydrogen than it consumed over a broad range of C:N ratios. For feedstock C:N ratios below 21 (g C/g N), ammonia stripping became the greatest system energy demand, and consistently increased as a fraction of the total system energy demand as the nitrogen loading increased (C:N ratio decreased). Several process energy integration cases were assessed. With no process energy integration, the system required between 23% and 34% of the total energy generated (parasitic losses), but under optimized

conditions this could be reduced to between 8% and 17%. Although the recoverable energy decreased as the feedstock C:N ratio decreased, normalizing total integrated energy potential (hydrogen plus methane) to the stoichiometric methane potential for a given C:N ratio indicated that the integrated process generated more energy than anaerobic digestion alone. Decreasing the C:N ratio of the feedstock also improved the biogas quality by increasing the methane fraction by as much as 29% (above 80% CH_4). Finally, the model identified important process tradeoffs to be optimized such as the recycle flux and minimum liquid set point. The model also provided a basis and justification for further research of such processes.

5.2 Introduction and Literature Review

5.2.1 Anaerobic Digestion Processes and Applications

In recent years, major attitudinal shifts have occurred in the environmental engineering and science professions promoting wastes as resources rather than just material requiring disposal [27]. Waste as a resource can be envisioned both as a means of reducing energy demands by eliminating the need for producing raw materials, and producing usable energy from the feedstock itself [28]. One established technology for extracting energy from waste is anaerobic digestion [29-30]. One of the most prevalent large-scale applications of anaerobic digestion in the U.S. is in landfills where anaerobic conditions dominate the operational timeline. In landfilling, municipal solid waste (MSW) and other wastes are interred in contained in-ground systems for final disposal [37]. However, as of 2006 approximately only 23% (400 of 1,754) of landfills in the

United States utilized recovered biogas for energy production while 77% simply flared it without recovering energy [236-237].

Continuous, large-scale and integrated organic waste handling systems that employ highly engineered anaerobic digesters as stand-alone systems along with other processes to maximize energy outputs while mitigating harmful environmental and health effects from wastes are desirable [51] and this approach is commonly practiced outside the US [238]. Specifically, anaerobic digestion of crop biomass, agricultural wastes and residuals, and source-separated mixed organic wastes have been tested and employed at full scale for decades in European countries (nearly 200 digesters, 2010 [238]), China (10,000 digesters, 1986 [239]) and India (2,000,000 digesters, 2000 [240]), among other places [46-47].

In the US, application of anaerobic digestion is primarily for municipal solid waste (MSW) landfills [107], wastewater treatment plant (WWTP) sludges [208] and animal manures [241]. There are more than 500 large (influent flow greater than 5 million gallons per day) municipal wastewater treatment facilities using anaerobic digestion for energy recovery in the United States [242]. Approximately 400 landfills around the country capture and produce energy from landfill gas [243]. Further the USEPA reports a total of 150 animal manure digesters in the US [241]. Anaerobic digestion has been underutilized in the US for a variety of economic and technical reasons including low energy prices, lack of governmental incentives, the need for suitable land for siting facilities and disposal of residuals, the need to heat the process to achieve acceptable conversion efficiencies, and the reputation of the process as odor-generating and difficult to operate [213, 244-246].

5.2.2 Inorganic Nitrogen Mitigation and Removal

The environmental advantages of anaerobic digesters include stabilization of biochemical oxygen demand, generation of biogas to offset fossil fuel, production of digestate to use as a soil amendment, and reduction of the environmental footprint associated with landfilling [46, 48]. However, several environmental concerns dictate post-treatment steps needed for the residual digestate produced during anaerobic digestion of organic feedstocks [247-248]. Of particular concern are system discharge streams containing nitrogen species that can be toxic in aqueous ecological systems, facilitate eutrophication, diminish oxygen availability, and reduce the efficiency of chlorine disinfection in drinking water [211].

Recall from Chapter 4 that the two primary forms of inorganic nitrogen species present in anaerobic digesters (and digestate) are ammonium ion (NH_4^+) and free ammonia (NH_3), which are in equilibrium in aqueous systems (Reaction 5.1), and that the total ammonia nitrogen (TAN) is the sum of the two.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad \text{Reaction 5.1}$$

The ratio of NH_3-N to NH_4^+-N in an aqueous system is governed by the pH and temperature (Equation 5.1).

$$[NH_3 - N] = \frac{[TAN]}{(1 + \frac{[H^+]}{K_a})} \qquad \text{Equation 5.1}$$

Where NH_3-N is the free ammonia nitrogen concentration and K_a is the temperature dependent dissociation coefficient.

Application of anaerobic digestate to land as a soil amendment must be carefully managed to avoid release of excess nitrogen to surface waters and the atmosphere and infiltration to groundwater. Particularly affected by these problems are swine, poultry, and dairy operations, where land application of digestate is an important disposal route [224, 249-254]. Ma et al. (2005) estimated that for Tompkins County, New York with a total dairy herd of 9,500, approximately 20,000 acres of suitable land would be needed to house digesters and solids/liquids handling systems and to provide a land sink for the resulting digestate [213]. In addition, large domestic WWTP digesters located in metropolitan environments at a distance from suitable land disposal must treat ammonia onsite via nitrification/denitrification or haul nitrogen-rich streams or products to distant land sinks [213]. Anaerobic digester supernatant currently recycled to the influent of some WWTPs may account for as much as 30% of the incoming nitrogen loading to the facility [255] and constitutes a substantial regulatory concern and energy sink. Ammonia contained in leachate is also an important factor controlling the long-term monitoring and post-closure concerns of MSW landfills [34].

Conventional biological nutrient removal combines nitrification (Reaction 5.2) [256] and denitrification (Reaction 5.3) [257] in optimized reactors.

$$NH_3 + 2\ O_2 \rightarrow H^+ + NO_3^- + H_2O \qquad \text{Reaction 5.2}$$

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad \text{Reaction 5.3}$$

These processes require long solids retention times and energy intensive aeration to accommodate nitrifying bacteria [258]. Further, denitrification mediated by heterotrophic bacteria either diverts carbonaceous substrates from methane generation in digesters or requires external electron donor addition in wastewater applications [259].

To reduce energy and oxygen demands and eliminate the need for external electron donor addition, new biological nitrogen removal processes have been studied. One method is partial nitrification of ammonium to nitrite followed by anaerobic ammonium oxidation (Anammox) mediated by specialized bacteria that use a coupled redox process convert ammonium plus nitrite to nitrogen gas (Reaction 5.4) [260]. Combined processes of partial nitrification of ammonium to nitrite followed by denitrification over nitrite (Canon/Sharon processes [259, 261] have been characterized or developed [258].

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad \text{Reaction 5.4}$$

Although these newer biological nitrogen treatments reduce process energy demands as compared to conventional nitrification and denitrification, they do not eliminate the treatment energy demands completely nor do they allow ammonia fuel products to be recovered.

In addition to environmental concerns of released nitrogen, nitrogen removal from integrated digester systems, especially from systems with liquid recirculation, is important for maintaining optimal methane generation because ammonia at high concentrations has been shown to inhibit methanogenesis [216]. Ammonia builds up in digesters when proteins, urea, nucleic acids and other nitrogenous compounds degrade, and must be controlled by removal or by altering feedstock carbon to nitrogen (C:N) ratios to prevent methane inhibition [44] (Chapter 4).

5.2.3 Ammonia Recovery and Utilization

Ammonia is a valuable industrial and agricultural chemical. The price of ammonia produced synthetically via the Haber–Bosch process is between $330 and $375

dollars per metric ton (tonne) (2010) [262]. Synthetically generated ammonia is used to produce agricultural fertilizer and chemical products, such as solvents, cleaning agents and refrigerants [263]. Ammonia has also been proposed as a source of hydrogen [264] and bioammonia as a sustainable fuel source is receiving increased interest for a variety of applications [265]. Ammonia has a high-density of hydrogen per unit volume on a weight basis of source material (0.1765 g H_2/g NH_3), and compares favorably to other materials used for hydrogen storage. However, a high temperature (~ 800-900°C) is required for efficient thermal reforming to generate hydrogen from ammonia, and as mentioned previously, ammonia is expensive to produce chemically. Ammonia that is liberated biologically in anaerobic digesters or landfills could be harvested and utilized as a source of hydrogen. By considering an alternative use for the ammonia, a potential environmental pollutant could be converted directly to energy. To accomplish this, the ammonia must be efficiently recovered from the digestate or leachate.

One method for removing aqueous ammonia-nitrogen and recovering ammonia is via ammonia gas stripping [230-231]. Ammonia stripping is facilitated by introducing the dissolved aqueous ammonia stream to the top of a packed stripping column as a stripping gas is pumped into the bottom of the column. The gas pumped into the bottom flows counter-current to the ammonia rich liquid, and the contact between the gas and liquid exploits the relative volatilities of the liquid and the dissolved ammonia to remove ammonia to the gas phase [266]. The liquid, with the ammonia-nitrogen removed, exits the bottom as the stripping gas and ammonia exit the top of the column.

Air is commonly used as the ammonia stripping gas [230-231, 267], but carbon dioxide in the air can react with lime in the highly alkaline liquid to form calcium

carbonate and cause scaling. More energy intensive ammonia stripping processes using steam as the stripping gas have been tested and employed [268]. While reducing scaling caused by carbon dioxide in air, employing steam as the stripping gas increases the operating temperature and pressure of the column, and reduces the volume of stripping medium (steam) required [268]. Utilizing air as the stripping gas produces a top column product consisting of a mixture of ammonia gas, water vapor and air, but utilizing steam produces a top product that is greater than 97% ammonia gas [268]. Regardless of the stripping gas employed, an appropriately designed ammonia stripper can reduce the ammonia-nitrogen concentration in the bottoms effluent stream to less than 10 ppm [268].

The ammonia gas stream either directly or after concentration can become the reforming fuel for catalytic reforming producing inert nitrogen gas as well as the fuel gas hydrogen (Reaction 5.12). Thus, for an anaerobic digester system generating biogas containing methane and ammonia-nitrogen rich digestate effluents, the inclusion of an ammonia recovery and reforming system to generate hydrogen could allow additional fuel to be produced. Because ammonia can be toxic to anaerobic microbial communities, as discussed earlier, some municipal and agricultural wastes are less amenable to anaerobic digestion. The amount of ammonia released during degradation is a function of the feedstock carbon to nitrogen (C:N g/g) ratio that varies greatly depending on the source (Figure 5.1; values from literature [269]).

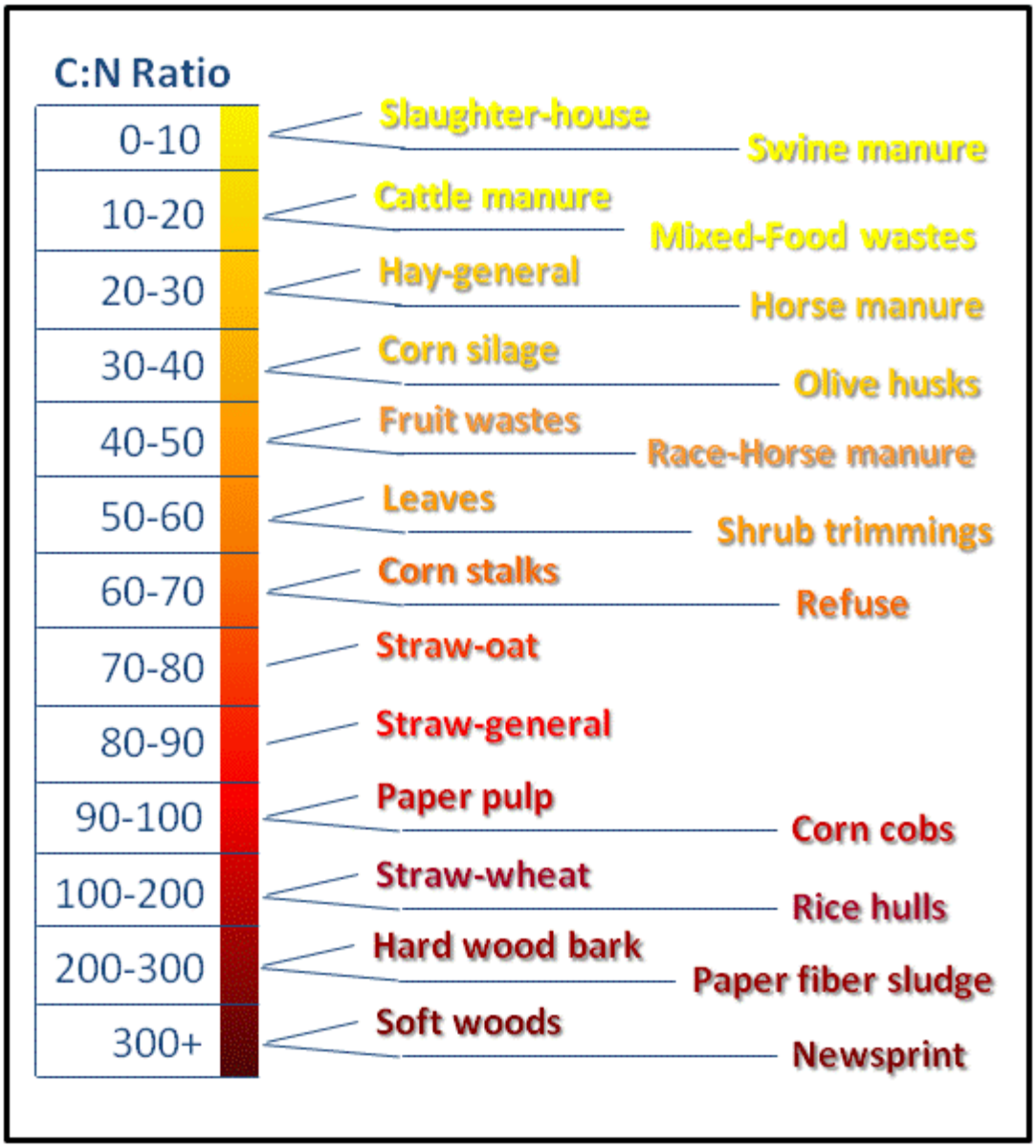

Figure 5.1 - List of common biomass wastes sorted by the material carbon to nitrogen (C:N) ratio [269]

Incorporating numerous organic waste streams into a comprehensive biomass waste management infrastructure could maximize available biomass feedstocks for energy recovery while minimizing expenditures attributable to waste hauling and other repetitive management practices. Co-digestion of multiple waste streams has been

extensively studied. Numerous laboratory-scale single, multiphase, and continuous co-digestion studies have been considered [270-275], and many co-digestion mixtures have been shown to enhance overall methane production [276-278]. If a system does not have multiple streams serving to dilute ammonia accumulation from low C:N ratio feedstocks, an integrated system that can rapidly remove ammonia and recycle ammonia-free liquid to the digester could improve digester viability. Moreover, the ammonia could be utilized downstream.

Development of a model for a theoretical integrated Anaerobic Digestion – Bioammonia to Hydrogen (ADBH) system, tested using a range of potential organic waste inputs under steady-state operating conditions where methane and ammonia are recovered for energy, is needed. This allows for a first assessment of the system-wide energy balance, and could identify factors needing further research or investigation in order to achieve a workable, energy yielding system. This analysis could improve energy integration in waste management systems by identifying the potential energy that could be recovered from nitrogen treatment processes such as recovery of ammonia.

5.2.4 Rationale and Objectives

Anaerobic digestion is an established technology used to stabilize wastes and produce methane for energy applications [29]. The effluents from anaerobic digestion processes contain ammonium, phosphate and suspended solids, which can make subsequent land application or biological treatment technically, environmentally or economically unfavorable [211]. To reduce energy requirements for N-removal processes, anaerobic ammonia oxidation (Anammox), where specialized bacteria couple ammonium and nitrite in a redox process producing nitrogen gas, has been studied.

However, Anammox requires partial aerobic oxidation of ammonia to nitrite, and thus, does not entirely eliminate energy requirements, nor does it allow ammonia to be recovered as a value-added product. Physical methods that remove ammonia prior to biological treatment have been considered for nitrogen management for digestate. For example, ammonia-stripping processes have been used for treating or pretreating animal waste slurries [267, 279-280], landfill leachate [281] and urea fertilizer plant wastes [282]; however, they have not been extensively studied as a means of ammonia removal from digester effluents [283]. Additionally, while ammonia has been considered for use as a chemical storage compound for molecular hydrogen [284-286], the ammonia stripping process used to remove nitrogen from wastes has not as yet been coupled to energy production via recovery of hydrogen in an integrated process.

One of the main drivers for developing and employing anaerobic digestion processes for wastewater, sludge and organic wastes is to maximize energy recovery via methane production [287]. However, residual material that remains after anaerobic digestion, including dissolved ammonia, may require energy intensive operations and processing downstream to prevent environmental contamination [258]. Thus, employing technologies to recover ammonia from digestate and recovering its available energy could improve the overall system energy balance.

The main hypothesis of this work is that an integrated ADBH system could operate under a net positive energy balance. Although some methane produced by the digester must be utilized to catalytically generate hydrogen from bioammonia, additional energy will be recovered as hydrogen. To test this hypothesis, a conceptual model of an ADBH system was developed and used to evaluate the energy balance when feedstocks

of varying carbon to nitrogen (C:N) ratios were utilized. Note that this study, the energy balance estimates theoretical energy inputs and outputs based on a first law of thermodynamics analysis and does not account for process entropy losses. Thus, this study seeks to (1) establish a theoretical design scheme for an integrated system to carry out anaerobic digestion and ammonia recovery to maximize overall energy generation, (2) characterize the energy demands and potential production in the forms of methane and hydrogen from the considered integrated system, (3) identify important process tradeoffs, and (4) identify areas for further scientific and engineering research needed to produce a net-positive energy ADBH system.

5.3 Description of the Model Anaerobic Digestion - Bioammonia to Hydrogen (ADBH) System

A theoretical integrated organic waste handling system was established to allow system performance and an overall energy balance to be analyzed. The goal of operation of the system designated as the "Anaerobic Digestion-Bioammonia to Hydrogen" (ADBH) system was to maximize biofuel production – methane from anaerobic digestion and hydrogen from ammonia reforming. The ADBH system components shown in Figure 5.2 and described in Table 5.1 include an anaerobic digester (or biological ammonia generator) that stabilizes waste, produces biogas containing methane and carbon dioxide and produces digestate that contains the liberated TAN. Further, the system contains a solid - liquid separator that concentrates the solids in the digestate for further disposal, and that produces a liquid leachate that contains the soluble TAN. In addition, two pH shift reactors are included to first raise the pH of the leachate to convert most of the TAN to ammonia, then later to neutralize the pH for eventual recycle to the digester. After the

liquid leachate pH has been increased, ammonia is recovered in a stripper, and finally, a microcombustor that uses methane from the digester as an energy source is used for ammonia reforming to produce hydrogen. Descriptions of the ADBH system flows indicated by arrows in Figure 5.2 are shown in Table 5.1.

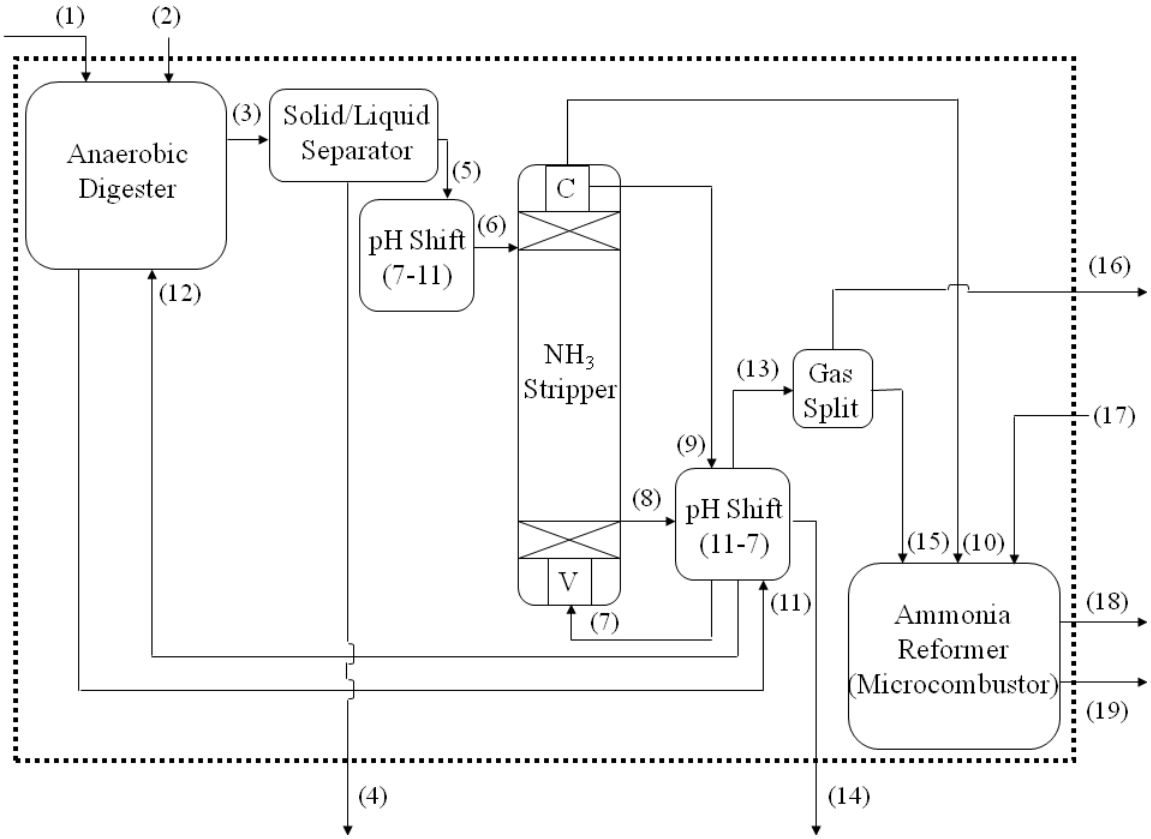

Figure 5.2 – Theoretical Anaerobic Digester - Bioammonia to Hydrogen (ADBH) system schematic with proposed stream flow configuration

Table 5.1 – Theoretical Anaerobic Digester - Bioammonia to Hydrogen (ADBH) system flow descriptions

Number	Type	Phase	Components
1	Influent	Solid	Organic waste feedstock
2	Influent	Liquid <1% TS	Aqueous stream (TAN = 200 mg/L)
3	Internal	Slurry 10% TS	Digestate
4	Effluent	Semi-Solid 99% TS	Digestate solids with $CaCO_3$ precipitate
5	Internal	Liquid <1% TS	Digestate leachate (TAN = $NH_4^+{}_{(aq)}$ + $NH_{3\,(aq)}$)
6	Internal	Liquid <1% TS	Digestate leachate (TAN = $NH_{3\,(aq)}$)
7	Recycle	Liquid	Digestate leachate with N removed
8	Internal	Liquid <1% TS	Digestate leachate with N removed (Alkaline)
9	Recycle	Liquid	Digestate leachate with N removed
10	Internal	Gas	$NH_{3\,(g)}$
11	Internal	Gas	Digester Biogas (CH_4, CO_2)
12	Recycle	Liquid <1% TS	Digestate leachate with N removed (Neutral)
13	Internal	Gas	Enhanced Biogas (CH_4, CO_2)
14	Effluent	Liquid <1% TS	Digestate leachate with N removed (Neutral)
15	Internal	Gas	Enhanced Biogas (CH_4, CO_2)
16	Effluent	Gas	Effluent Enhanced Biogas (CH_4, CO_2)
17	Influent	Gas	Air
18	Effluent	Gas	H_2/N_2
19	Effluent	Gas	Exhaust (CO_2, H_2O)

5.4 Model System Development and Analytical Methods

The theoretical ADBH system (Figure 5.2) consists of an anaerobic digester, an ammonia gas recovery system, and an ammonia reformer (microcombustor) system. All individual component/reactors sizes, the internal mass flows, and the effluent mass flows

are varied as a function of the specified influent flow values for Stream 1, the solid organic waste flow, and Stream 2, the influent additional liquid flow. Stream 2 is controlled by the specified operating moisture content in the digester, and the internal liquid recycle flow (Stream 12). The inclusion of Stream 2 would also allow for additional aqueous phase ammonia-nitrogen to be treated by the system, if the added liquid is ammonia-bearing. The volumetric or mass flow and composition of the influent streams may be varied to allow numerous system scenarios to be evaluated. In the following sections, each system component is described and the incoming and outgoing mass or volumetric flows and incoming or outgoing energy flows are indicated.

5.4.1 Anaerobic Digester (AD) Component

The anaerobic digester (Figure 5.3) consists of the anaerobic reactor; incoming flows Stream 1, organic waste; Stream 2, additional liquid; and Stream 12, liquid recycle; and outgoing flows Stream 11, biogas; and Stream 3, the digestate slurry. In addition, required heat and power inputs to maintain the digester at the desired temperature and to facilitate mixing are included.

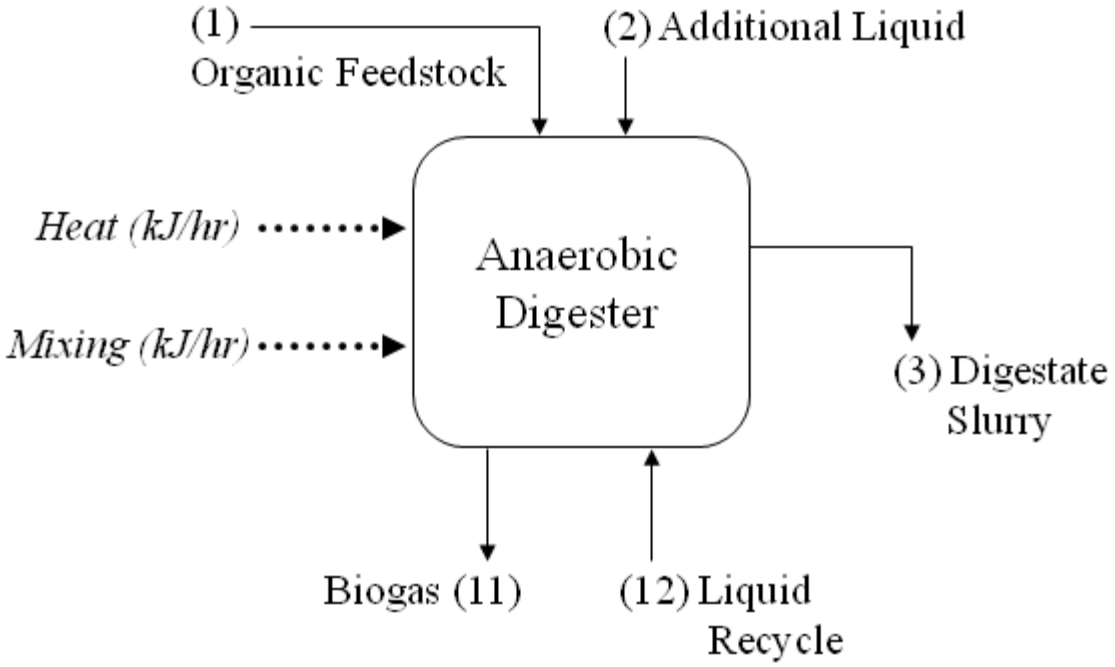

Figure 5.3 - Anaerobic digester component schematic showing mass or volumetric flows (solid arrows) and energy flow (dotted arrows)

Influent Stream 1 for the digester is characterized by the organic waste input quantified as a dry solids feedstock mass flow rate, and is assigned both a specific carbon to nitrogen (C:N) ratio and a degradable organic fraction. It was assumed that the degradable organic fraction of the inlet solids was 80% [208]. Additionally, the reactor moisture content, the nitrogen content ([TAN]) of the additional liquid stream and the internal leachate recycle flow following nitrogen stripping (Stream 12) are shown.

The feedstock molecular makeup was designated to facilitate computation of the methane, carbon dioxide and TAN produced during anaerobic digestion. The TAN of the digestate at pH 7.0, will contain 3.8% and 96.2% ammonia and ammonium ion,

respectively, based on the temperature (55° C) and equilibrium coefficient (Equation 5.1). Two separate molecular formulae were considered. First, the conversion of the degradable fraction of the organic matter to methane (CH_4) and carbon dioxide (CO_2) was via Reaction 5.5 [107].

$$C_6H_{10}O_4 + 1.5\ H_2O \rightarrow 3.25\ CH_4 + 2.75\ CO_2 \qquad \text{Reaction 5.5}$$

Organic compounds containing nitrogen were modeled as $C_{2n}H_{5n}O_{2n}N_n$ to allow the molar amounts of nitrogen to vary in response to the designated C:N ratio of the feedstock. It was assumed that the organic nitrogen fraction proceeded via Reaction 5.6 [288].

$$C_{2n}H_{5n}O_{2n}N_n + 0.5n\ H_2O + H^+ \rightarrow 0.75n\ CH_4 + 1.25n\ CO_2 + n\ NH_4^+ \qquad \text{Reaction 5.6}$$

TAN ($NH_4^+{}_{(aq)}$ plus $NH_{3\,(aq)}$) is dissolved in the digestate and exits in the slurry, Stream 3. The overall stoichiometry of the methanogenic breakdown of the feed stock was thus the sum of Reactions 1 and 2 (Reaction 5.7).

$$C_{(6+2n)}H_{(10+5n)}O_{(4+2n)}N_n + (1.5 + 0.5n)\ H_2O + n\ H^+ \rightarrow$$
$$(3.25 + 0.75n)\ CH_4 + (2.75 + 1.25n)\ CO_2 + n\ NH_4^+ \qquad \text{Reaction 5.7}$$

Where n, the stoichiometric amount of nitrogen contained in the feed stock formula, can be computed from the C:N ratio of the influent feedstock as shown in Equation 5.2.

$$n = \frac{6 \cdot (AW_{Carbon})}{(C:N)_{ratio} \cdot (AW_{Nitrogen}) - 2 \cdot (AW_{Carbon})} \qquad \text{Equation 5.2}$$

Where, n is the stoichiometric amount of nitrogen contained in the feedstock molecular formula (mol N/mol feedstock), there are 6 moles C per mol of the organic portion of the feedstock and 2 additional moles of C per mol of feedstock for each mol N added, AW_{carbon} is the atomic weight of C (12 g C/mol C), $AW_{nitrogen}$ is the atomic weight

of nitrogen (14 g N/mol N) and $C:N_{ratio}$ is the carbon to nitrogen ratio (g C/g N) contained in the feedstock.

To account for the portion of the feedstock's ($C_{(6+2n)}H_{(10+5n)}O_{(4+2n)}N_n$) electron equivalents that are synthesized into biomass, as well as the amount of ammonium utilized as cellular nitrogen, the fraction of the feedstock diverted to biomass (f_s) is calculated (Equation 5.3) [208, 232, 289].

$$f_s = f_s^0 \cdot \left[\frac{1+(1-f_d)\cdot b\cdot T}{1+b\cdot T}\right] \qquad \text{Equation 5.3}$$

Where, f_s^0 is specified to be 0.05 (typical for methanogens) [289], f_d is the fraction of the biomass that is biodegradable (0.80), b is the decay rate (0.03 d^{-1}) [208], and T is the retention time (20 d). The fraction of feedstock used to power microbial growth is f_e ($f_s + f_e = 1$) [208, 232, 289].

Including the fractions of the feedstock diverted to cellular material and powering cell growth, modifies the overall digester reaction stoichiometry (Reaction 5.8) [208].

$$C_aH_bO_cN_d + (2a + d - c - 0.45\cdot e\cdot f_s - 0.25\cdot e\cdot f_e)\ H_2O \rightarrow$$
$$(0.125\cdot e\cdot f_e)\ CH_4 + (a - c - 0.2\cdot e\cdot f_s - 0.125\cdot e\cdot f_e)\ CO_2 + (0.05\cdot e\cdot f_s)\ C_5H_7O_2N$$
$$+ (d - 0.05\cdot e\cdot f_s)\ NH_4^+ + (d - 0.05\cdot e\cdot f_s)\ HCO_3^- \qquad \text{Reaction 5.8}$$

Where a (6 + 2n), b (10 + 5n), c (4 + 2n) and d (n) correspond to the feedstock material ($C_{(6+2n)}H_{(10+5n)}O_{(4+2n)}N_n$), and e is $e = 4a + b - 2c - 3d$ [208]. Ekama (2009) used similar bioprocess stoichiometry development methods to model system wide mass balances of a wastewater treatment plant [290].

Anaerobic digesters are typically operated at either 35° C or 55° C, and while the associated conversions are exothermic, the heat generated is not sufficient to sustain autothermal operation. Thus, external heating is required to raise the temperature of the

influent material to the desired digestion temperature, and to maintain the digester at the operating temperature accounting for heat losses across the boundaries of the digester. Heat losses in piping between the digester and heat source can be neglected with appropriate construction and insulation [180, 291], and was not considered. The heat (kJ/hr) needed to raise the temperature of the influent flows ($Q_{influent}$) to the operating temperature is given by Equation 5.4.

$$Q_{\text{influent}} = \overline{m} \cdot Cp_{water} \cdot \Delta T \qquad \text{Equation 5.4}$$

Where m, is the combined mass flow rate of Streams 1 and 2, Cp_{water} is the specific heat capacity of water (4.1813 $kJ \cdot kg^{-1} \cdot K^{-1}$), and ΔT is the temperature difference (40 K or °C for thermophilic operation) from ambient conditions to the digester operating temperature. It was assumed that the specific heat capacity of the influent flows were identical to that of water [180].

Heat loss across the boundary of the digester was the sum of losses from the sides, top, and bottom of the reactor, and were computed using Equation 5.5.

$$Q_{loss} = \sum U_i \cdot A_i \cdot \Delta T_i \qquad \text{Equation 5.5}$$

Where, U, is the overall heat transfer coefficient [$J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$], A, is the surface area (m^2) across which heat loss is occurring, and ΔT, is the temperature drop (°C) across the boundary. The digester wall is assumed to be constructed of plain concrete 300 mm thick, insulated (U_{wall} = 0.8 $J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$ [180] with a ΔT_{wall} = 40° C), the floor is plain concrete, 300 mm thick, in contact with dry earth (U_{floor} = 1.7 $J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$) [180]; ΔT_{floor} = 35° C), and the cover is fixed concrete 100 mm thick, and insulated with 25 mm of insulating board (U_{cover} = 1.6 $J \cdot m^{-2} \cdot s^{-1} \cdot {}^{\circ}C^{-1}$ [180]; ΔT_{cover} = 40° C). The heat transfer area (A) (m^2) is a function of the digester volume and aspect ratio.

The digester was assumed to be a continuously stirred tank reactor (CSTR; mechanically mixed). The power required to continuously mix the slurry contained was assumed to be a function of the digester volume and was obtained by Equation 5.6 [180].

$$P_{digester} = UP_{digester} \cdot V_{digester} \qquad \text{Equation 5.6}$$

Where, $P_{digester}$, is the required mixing power [kJ/hr], $UP_{digester}$, is the unit power for a typical CSTR digester (0.0065 kW/m^3 [180]), and $V_{digester}$, is the digester volume (variable depending upon specified operating flows and retention time).

The solids-liquid separation unit handling digestate flow from the digester, was assumed to be a gravity separation unit operating at 95% efficiency [292]. The unit size was a function of the influent digestate total solids content (%TS), the volumetric flow rate, the average assumed particle size (0.5 mm) [292], and the specified solids removal efficiency (95%) [292]. Flow through the unit was assumed to be driven by the hydrostatic pressure drop between the digester and the first pH-shift reactor.

5.4.2 Ammonia Gas Recovery Component

The ammonia gas recovery system consisted of two pH-shift reactors and an aqueous ammonia stripper, as well as Streams 5-14 (Figure 5.4) that account for the digestate leachate pre- and post- treatment to increase pH and convert ammonium to ammonia, along with gaseous flows to the stripper to transfer ammonia from the liquid to gaseous phase.

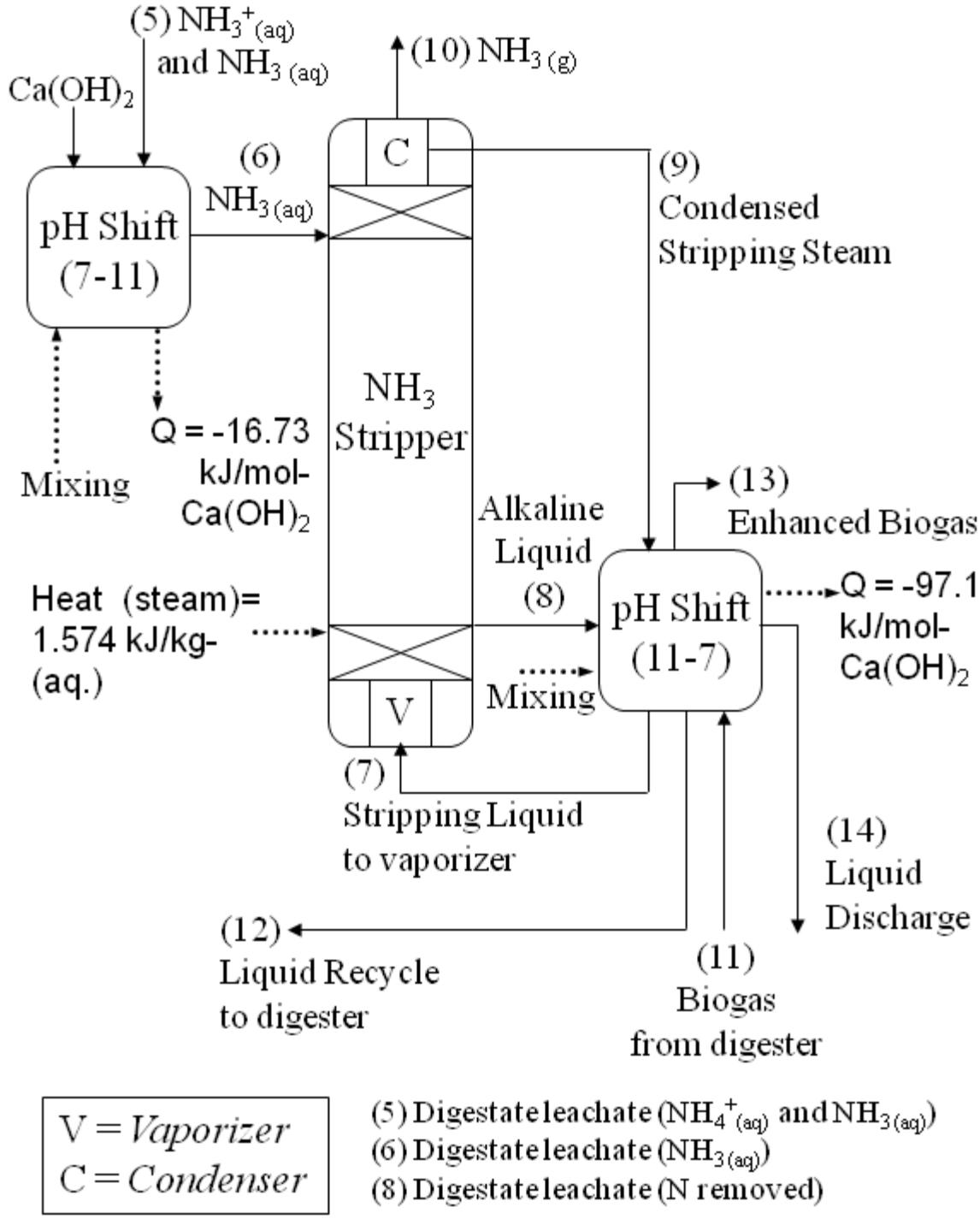

Figure 5.4 - Ammonia recovery system schematic showing relevant streams and energy flow

Ammonium ion in the digestate (Stream 5) is converted to aqueous ammonia in the first pH shift reactor where calcium hydroxide (lime) is added to increase the pH from 7 to 11 (Reactions 5.9 and 5.10).

$$Ca(OH)_2 \rightarrow Ca^{2+}_{(aq)} + 2\ OH^-_{(aq)} \qquad \text{Reaction 5.9}$$

$$NH_4^+{}_{(aq)} + OH^-_{(aq)} \rightarrow NH_{3\ (aq)} + H_2O \qquad \text{Reaction 5.10}$$

Aqueous phase ammonia contained in Stream 6 is then stripped to the gas phase in the ammonia stripper using steam produced from Stream 7. The alkaline, ammonia free digestate (Stream 8) flows to the second pH shift reactor and the pH is neutralized using biogas from the digester, Stream 11 (Reaction 5.11).

$$Ca^{2+} + 2\ OH^- + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{Reaction 5.11}$$

This neutralization process removes carbon dioxide from the biogas stream and thus produces a biogas stream with higher methane content (Stream 13). The biogas stream exiting the second pH-shift reactor is said to be “enhanced” because the methane content has been increased by removing some carbon dioxide.

Energy is required to power the ammonia stripper and to homogenize the reactants in the pH-shift reactors; however, process heat can be recovered from Reactions 5.9 and 5.11, and is included in the model. Elston et al. (2003) considered aqueous ammonia stripping technologies for selective catalytic reduction applications (SCR) [268]. Comparing air and steam as stripping mediums they identified power requirements for aqueous ammonia stripping (19 wt.% $NH_{3\ (aq)}$) for a range of aqueous mass flows [268]. A linear relationship between power demand and the aqueous mass flow rate was observed. Based on these results, the power requirements for stripping ammonia from the

digestate leachate using air and steam was determined to be 0.265 kJ/kg-aq., and 1.574 kJ/kg-aq. respectively [268].

The potential heat produced during Reactions 5.9 and 5.11 is obtained from the standard enthalpy of formation for the reactants and products (Equation 5.7) [293].

$$\Delta H_{reaction} = \sum_{i}^{products} v_i \cdot \Delta H_{f,products} - \sum_{i}^{reactants} v_i \cdot \Delta H_{f,reactants} \qquad \text{Equation 5.7}$$

Where $\Delta H_{reaction}$ is the enthalpy of the reaction (kJ/mol), v_i is the stoichiometric coefficient for each reactant or product, $\Delta H_{f,products}$ is the heat of formation for the products (kJ/mol), and $\Delta H_{f,reactants}$ is the heat of formation for the reactants (kJ/mol). The enthalpy of formation ($\Delta H_{reaction}$) is -16.73 kJ/mol for Reaction 5.9 and -97.101 kJ/mol for Reaction 5.11 respectively [294]. Heat from these exothermic reactions can be captured and the model compares the amount of heat consumed and generated. The model assumed a conservative internal heat transfer efficiency of 35% [295], but it did not estimate the additional energy required to optimize internal heat utilization, for example through the use of additional pumping to and from a heat exchange unit. The sensitivity of the latter assumption, however, was assessed as part of the energy integration cases considered.

Mixing in each of the pH-shift reactors was assumed to occur via velocity gradient mixing with retention times of 30 seconds (s). Rapid mixing operations with effective chemical dispersion and contact require an average velocity gradient of 500 s^{-1} [296]. The power to maintain velocity gradient mixing was calculated using Equation 5.8.

$$P_{Mixing} = \sum G^2 \cdot \mu \cdot V_i \qquad \text{Equation 5.8}$$

Where, P_{mixing} is the total required power (kW) to mix both pH-shift reactors, G is the average velocity gradient (1/s), μ, is the liquid viscosity (μ = 9.82E-04 kg·s^{-1}·m^{-1}), and V_i is the volume (m^3) of the pH-shift reactor (variable depending on specified operating flows, and retention time).

5.4.3 Ammonia Reforming (Microcombustor) Component

The microcombustor component of the system (Figure 5.5) consists of two separate processes. The first is combustion to heat the catalyst, and the second occurs in the catalyst chamber where ammonia reforming converts the incoming $NH_{3\ (g)}$ (Stream 10) to nitrogen and hydrogen (Stream 18). To drive the reforming reaction, high temperatures are produced by a heating unit. A fraction of the enhanced biogas (Stream 13) is diverted from the splitter to the microcombustor (Stream 15), combined with air (Stream 17), and burned, producing combustion exhaust (Stream 19).

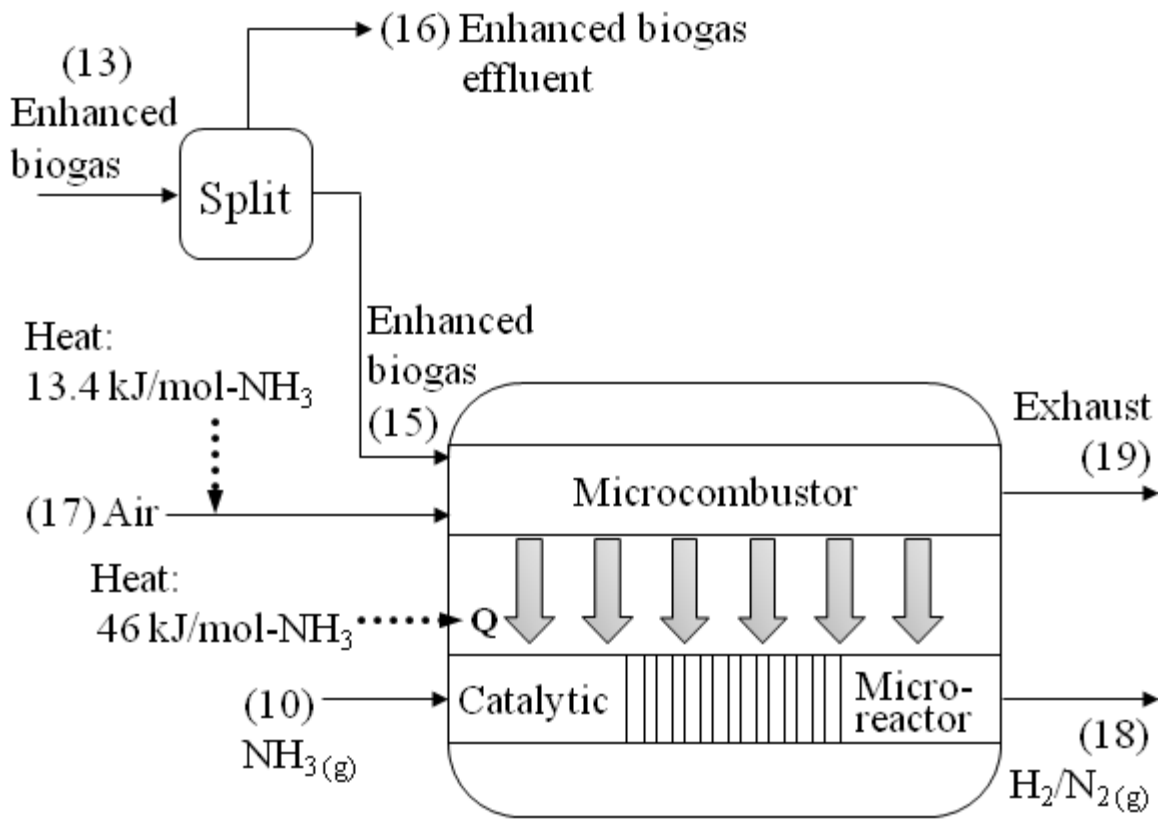

Figure 5.5 - Ammonia reforming system schematic showing relevant streams and energy flows

The ammonia reforming reaction is shown in Reaction 5.12.

$$2\ NH_{3\,(g)} \rightarrow N_{2\,(g)} + 3\ H_{2\,(g)} \qquad \text{Reaction 5.12}$$

The reforming process is endothermic requiring 46 kJ/mol-NH_3 of heat to proceed. The reaction proceeds at 850° C with nearly 90% efficiency [297], and the air stream is assumed to be at 15° C, thus requiring 13.4 kJ/mol-NH_3 of heating. The amount of biogas diverted to the microcombustor is dependent on the methane content of the biogas, the energy demand, that is a function of the $NH_{3\,(g)}$ flow rate (Stream 10), and the heating value of methane that was assumed to be 50 MJ/kg (lower heating value of methane for combustion) [193].

5.4.4 - Stream transfer pressure-drop and pumping energy requirements

Power demands resulting from movement of internal gas and aqueous flows were estimated using mass and energy balances for individual streams. The associated power, P_i ([kJ/hr]), as a function of the required pressure drop and stream flow volume was obtained by applying Equation 5.9.

$$P_i = \Delta p_i \cdot \overline{V}_i \qquad \text{Equation 5.9}$$

The volumetric flow rate, $\overline{V}_i$ ([m^3/hr]) was a calculated output that depends on input flow values (Streams 1 and 2 specified) as well as the individual reaction mass balances of each process component. The required pumping pressure drop, Δp ([Pa]), was obtained by simplifying the energy balance for a given scenario (Figure 5.6).

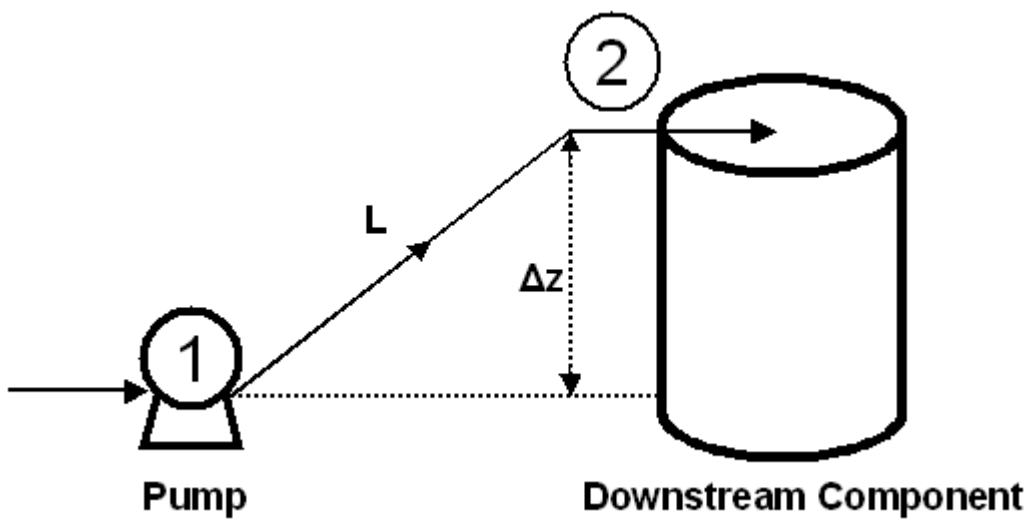

Figure 5.6 - Schematic showing a generic configuration for process stream pressure-drop requirements

Equation 5.10 gives the overall energy balance for the stream between points 1 and 2.

$$\Delta\left(\frac{u^2}{2}\right) + g \cdot \Delta z + \frac{\Delta p}{\rho} + F = 0 \qquad \text{Equation 5.10}$$

Where u ([m/hr]) is the stream velocity, g ([m/hr^2]) is the gravitational constant, ρ is the fluid density ([kg/m^3]) and F ([m^2/hr^2]) is the frictional energy loss. The velocity and density of incompressible aqueous streams will remain constant between points 1 and 2, but compressible gas stream velocity and density can vary proportionally along the length of the pipe. However, steady-state continuity implies that both compressible gas and incompressible aqueous steams have identical mass fluxes ($u_1 \cdot \rho_1 = u_2 \cdot \rho_2$ [kg/m^2·hr]) at points 1 and 2 (Figure 5.6). For incompressible fluid streams (considered aqueous streams), the overall stream energy balance (Equation 5.10) can be simplified and rewritten (Equation 5.11).

$$\Delta p_{Liquid} = -\rho\left(g \cdot \Delta z + F\right) \qquad \text{Equation 5.11}$$

Where, Δp_{Liquid} is the required pressure drop (kg/s·m) for liquid streams. Equation 5.10 for compressible gas streams can also be simplified assuming that the velocity of the gas stream is less than one third the speed of sound in the fluid [298], and the effects of changes in elevation are negligible compared to frictional energy losses (Equation 5.12).

$$\Delta p_{Gas} = \rho \cdot F \qquad \text{Equation 5.12}$$

Where, Δp_{Gas}, is the required pressure drop (units) for gas streams. Energy losses due to friction result from the shear force, F ([kg·m/s^2]), exerted by the pipe wall on the fluid over the length of the pipe (Equation 5.13) [299].

$$F = 4 \cdot \tau_w \cdot \frac{L}{D} \qquad \text{Equation 5.13}$$

Where τ_w ([kg·m^{-2}·hr^{-1}]) is the shear stress, L ([m]) is the length of the pipe and D ([m]) is the inside pipe diameter. By introducing a dimensionless term, the friction factor (f), the

shear stress acting upon the fluid flow can be expressed as the ratio of the wall shear stress to the inertial force per unit area resulting from the encroachment of the stream considered (stream density, ρ, and velocity, u) normally against the pipe wall [299] (Equation 5.14).

$$f = \frac{\tau_w}{\frac{1}{m}\rho \cdot u^2} \qquad \text{Equation 5.14}$$

Where m is a constant corresponding to a specific version of the friction factor (Fanning friction factor m=2, Moody friction factor n=8 [299]). The Fanning (f_F) version of the friction factor (m=2) was utilized because it can be calculated explicitly (Equation 5.16).

Rearranging Equation 5.14 in terms of the shear stress (τ_w) and inserting into Equation 5.13 allows the energy loss due to friction to be expressed (Equation 5.15).

$$F = 2 \cdot f_F \cdot \rho \cdot u^2 \cdot \frac{L}{D} \qquad \text{Equation 5.15}$$

The Fanning friction factor (f_F) can be obtained explicitly from an equation derived using experimental data (Equation 5.16) [299].

$$f_F = \left\{ -1.737 \cdot \ln\left[0.269 \cdot \frac{\varepsilon}{D} - \frac{2.185}{\mathrm{Re}} \cdot \ln\left(0.269 \cdot \frac{\varepsilon}{D} + \frac{14.5}{\mathrm{Re}} \right) \right] \right\}^{-2} \qquad \text{Equation 5.16}$$

Where ε is the effective surface roughness (0.046 mm for commercial steel), and Re is the Reynolds number (Equation 5.16 valid for Re > 4,000). Equation 5.17 defines the dimensionless Reynolds number.

$$\mathrm{Re} = \frac{\rho \cdot u \cdot D}{\mu} \qquad \text{Equation 5.17}$$

Where, μ [$(kg \cdot m^{-1} \cdot hr^{-1})$] is the fluid viscosity.

All process equipment handling liquid phase fluids (digester, pH-shift reactors, and stripper) were assumed to be cylindrical. The volume of each reactor was a function of the retention time and total volumetric flow to the reactor (Equation 5.18).

$$V_{reactor} = \overline{V}_{Inlet} \cdot T \qquad \text{Equation 5.18}$$

Where, $V_{reactor}$, is the reaction vessel volume (m^3), $\overline{V}_{Inlet}$, is the total volumetric flow rate to the vessel (m^3/hr) and, T is the retention time (hr). The height of the reactor was determined by assuming a variable input value based on a typical aspect ratio (ASP) for the type of reaction vessel being considered and by applying the equation for a cylinder in terms of the selected aspect ratio (Equation 5.19).

$$H_{Reactor} = \frac{(2 \cdot ASP)^{2/3} \cdot V_{Reactor}^{1/3}}{\pi^{1/3}} \qquad \text{Equation 5.19}$$

Where, $H_{Reactor}$ ([m]), is the height of the reactor, and ASP, is the aspect ratio for the reactor. For a system configuration where each process component (e.g., digester, stripper) is set up on the same horizontal plane, the vertical shift (Δz) for a specific liquid stream is the difference between the fluid heights in the two adjacent process components. Since all liquid fluid streams are assumed to have the same density, the required pressure drop for each liquid stream relative to any other aqueous stream depends only on its specific vertical shift (Δz) (Table 5.2).

Table 5.2 - Equations used to calculate vertical shift (Δz) for liquid streams, and corresponding pressure drop (Δp). (H = vessel height [m], ρ = fluid density [kg/m^3], Δz = vertical shift [m])

Stream	Δz	Δp (vertical shift)
2	$H_{Digester}$	$\rho \cdot g \cdot \Delta z_2$
5	$H_{pHshift_1} - H_{Digester}$	$\rho \cdot g \cdot \Delta z_5$
6	$H_{Stripper} - H_{pHshift_1}$	$\rho \cdot g \cdot \Delta z_6$
8	$H_{pHshift_2} - H_{Stripper}$	$\rho \cdot g \cdot \Delta z_8$
12	$H_{Digester} - H_{pHshift_2}$	$\rho \cdot g \cdot \Delta z_{12}$

Inserting Equation 5.15 in for F in Equations 5.11 and 5.12 gives the final version of the pressure-drop for the aqueous (incompressible) and gas (compressible) streams respectively (Equations 5.20 and 5.21).

$$\Delta p_{Aqueous} = -\rho\left(g \cdot \Delta z + 2 \cdot f_F \cdot u^2 \cdot \frac{L}{D} \right) \qquad \text{Equation 5.20}$$

$$\Delta p_{Gas} = 2 \cdot f_F \cdot \rho \cdot u^2 \cdot \frac{L}{D} \qquad \text{Equation 5.21}$$

The associated power as a function of the required pressure drop and stream flow volume for each internal stream is assessed based on the assumed process configuration. Assumed values for a specific process configuration or stream are input variables in the model allowing different configurations and operating conditions to be tested and the effects observed.

Although not a fluid stream, the energy of transporting the feedstock (Stream 1) into the digester is calculated by determining the work required to raise its mass to the

height of the digester assuming the energy utilization in the transport process is 35% efficient (internal efficiency).

5.4.5 – The Mass and Energy Balance Model

Material and energy flows for the hypothetical system are a function of the input flows, which can be varied to estimate a system-wide energy balance for a range of possible input values and material compositions. The model was constructed in a Microsoft Office Excel spreadsheet (Microsoft Corporation, Redmond, WA) and input variables and flow stream dependence were propagated throughout the model system. The model consists of a separate worksheet for each of the three parts of the integrated system, but dependent flows on any one worksheet correspond to and are linked to appropriate flows or energy values in another (Appendix III).

The modeled outputs were a function of the assumed inputs, which were held constant while the feedstock C:N ratio was varied (Table 5.3).

Table 5.3 - Variable input values for analysis of C:N ratio impact on system energy accumulation

Variable Description	Input Value
C:N Ratio	Variable (3 to 136, (g C/g N))
Dry-Solids Mass Flow	1,000 kg TS/hr
Fraction of Feed Stock Degraded	0.80
Moisture Content (wt.% water)	90.0%
Aqueous TAN Loading (in Stream 2)	100 mg NH_4^+-N/L
Percent Recycle of Stream 8	65.0%
Ambient-Digester Temperature Difference	40.0 °C
Internal Efficiency	0.35

Three separate operating cases were examined for comparison (Table 5.4). For all cases, identical inputs as tabulated in Table 5.3 were used, but the modeled outputs were calculated differently, based on different assumptions.

For Case 1, designated the base case, outputs result from calculations using the previously described assumptions made about each process component, and a recoverable fraction (0.35) of the internal process energy is assumed to be conserved. Specifically, for Case 1, the heat generated from chemical reactions and the hydrostatic pressure available from each reactor is assumed to be available to offset heating and pumping requirements elsewhere in the process. In Case 2, the same assumptions are made as for Case 1 with an additional assumption that the system is more highly integrated and utilizes the hydrogen rich stream (Stream 18) as the stripping gas, reducing the stripping power requirements from 1.574 to 0.265 kJ/kg-aq. In Case 3, it is assumed that no energy integration is included.

Table 5.4 - Energy integration case descriptions for ADBH system

Case	Case Description	Model Inputs	Energy Integration
Case 1	Conservative energy integration	Table 5.3	• System recovers small fraction (0.35) of available heat and fluid momentum potential (pressure drop)
Case 2	Optimized system	Table 5.3	• System recovers small fraction (0.35) of available heat and fluid momentum potential (pressure drop). • System uses fraction of available N_2/H_2 stream
Case 3	Not integrated	Table 5.3	• System doesn't recover available heat or utilize available momentum potentials to drive flow.

5.5 – Model Application

The energy balance model was used to identify the effect of the feedstock C:N ratio on the viability of operating the integrated system with respect to obtaining an overall positive energy balance in Cases 1, 2, and 3 delineated in Table 5.4. Viability was assessed only on thermodynamic energy inputs and outputs without considering process economics, chemical process kinetics, entropy changes, or effluent fuel prices. A first law of thermodynamics analysis was conducted to estimate the theoretical maxima for the energy output of the envisioned ADBH system to identify conditions where net energy output exceeds energy input. Further research will be needed to assess other aspects of process viability, such as economics and feasibility of the design to account for irreversible (entropy) losses.

5.6 – Results and Discussion

The system equivalent energy balance from methane, hydrogen, heat and power were analyzed for a range of feedstock C:N ratios that produced a range of total ammonia-nitrogen (TAN) concentrations in the digester from 20 mg/L to 10,000 mg/L. The range was obtained by varying the influent dry-solids C:N ratio (g C/g N) between 3.0 and 136 (3.0:1 and 136:1). Higher C:N ratios were not considered because above 136, the feedstock nitrogen, even combined with the additional liquid nitrogen loading, was too low to support microbial cell growth as predicted by Reaction 5.8. Case 1 outputs are described in detail in Section 5.6.1. Case 2 and Case 3 outputs are presented, contrasted and discussed separately in Section 5.6.2.

The effect of system energy integration tested by calculating Cases 1, 2 and 3 did not change system mass fluxes of carbon and nitrogen. Figure 5.7 and Figure 5.8 show the percent mass fluxes for carbon and nitrogen, respectively, for a specified feedstock C:N ratio of 3.0.

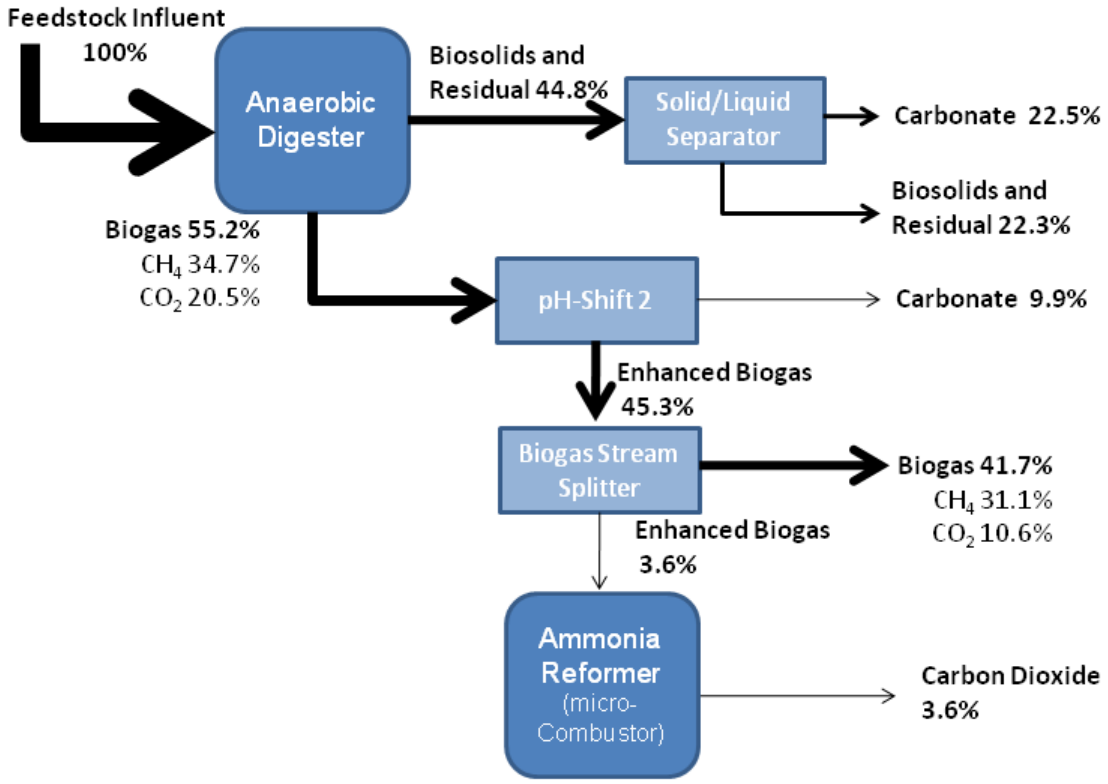

Figure 5.7 - ADBH mass percent flux of carbon with feedstock C:N ratio of 3.0

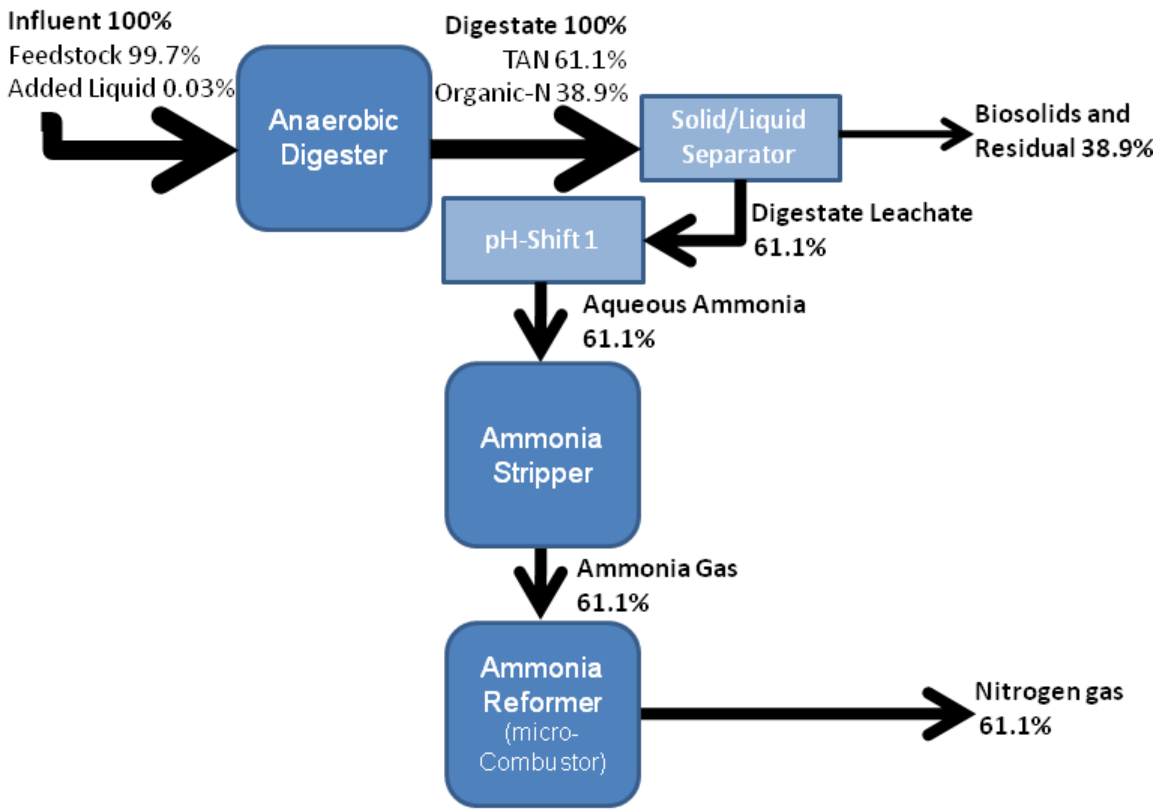

Figure 5.8 - ADBH mass percent flux of nitrogen with feedstock C:N ratio of 3.0

The greatest mass percent carbon in the effluent from the ADBH system operating with a feedstock C:N ratio of 3.0 will be associated with carbonate (32.4%), and methane (31.1%). The remainder will be associated with residual (residual feedstock and biosolids) solids (22.3%), and carbon dioxide gas (14.2%). The greatest mass percent nitrogen in the effluent will be associated with nitrogen gas (61.1%), and the remainder will be associated with residual solids (38.9%).

5.6.1 Base Case (Case 1) Analysis

5.6.1.a – Fuel, Heat and Energy Analysis

As the C:N ratio decreases (organic nitrogen content increases), the operating TAN concentration in the digester increases. The model indicates, as expected, that as the operating TAN concentration in the digester increases, more hydrogen is recovered from the microcombustor and more heat is recovered from the pH-shifts as depicted in Figure 5.9.

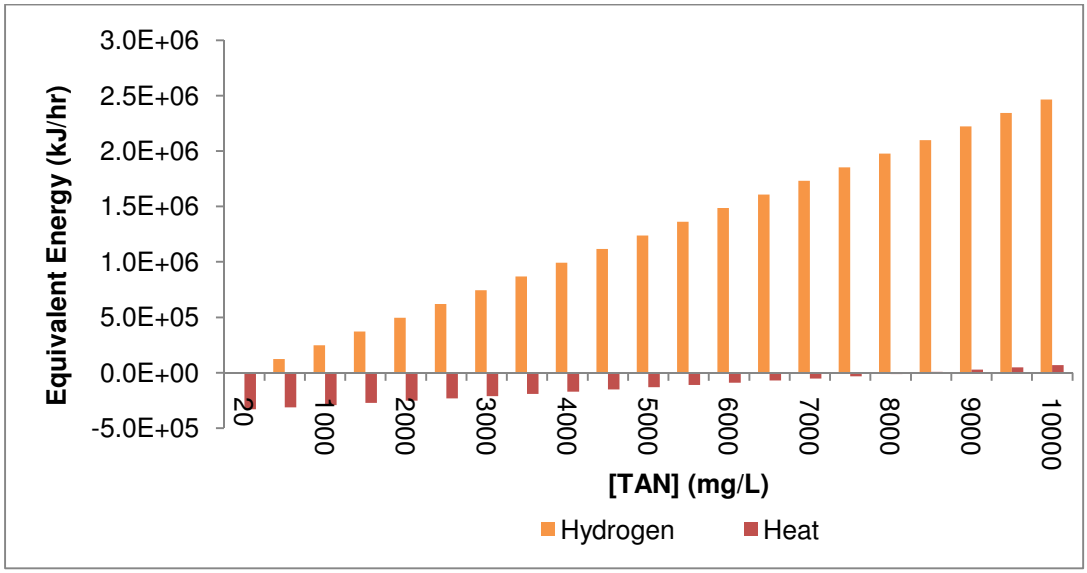

Figure 5.9 - Equivalent energy for hydrogen and heat generated as the TAN concentration in the digester increases (TAN is a function of feedstock C:N ratio)

The heat energy required to operate the digester (to elevate feed flows and to maintain the digester at 55 °C) was not offset by the heat generated during the pH-shifts for TAN concentrations below 7,500 mg/L, and thus, the system requires additional heat for operation up to that TAN concentration. The additional heat required, however, decreases as the operating TAN concentration in the digester increases, because the heat produced in the pH-shift reactors are a function of the TAN concentration. The equivalent energy

from hydrogen increases linearly as the operating TAN concentration in the digester increases between 20 and 10,000 mg/L (between C:N ratios of 136 and 3.0).

The mass of ammonia (kg/hr) recovered increases as the TAN concentration increases, which increases the power required to strip the dissolved ammonia from the aqueous phase. However, since the stripping power is a function of the total aqueous mass flow, the marginal increase in the ammonia recovered has a minimal impact on the stripping power demand.

The mass fraction of the enhanced biogas stream diverted to facilitate heating and reforming in the microcombustor also increases as the amount of ammonia gas increases. In return for the methane energy diverted to the microcombustor, an increasing amount of hydrogen energy is recovered (Figure 5.10). Note that the sum of the equivalent energy associated with the biogas and hydrogen streams is the net system biofuel energy generation (Figure 5.10).

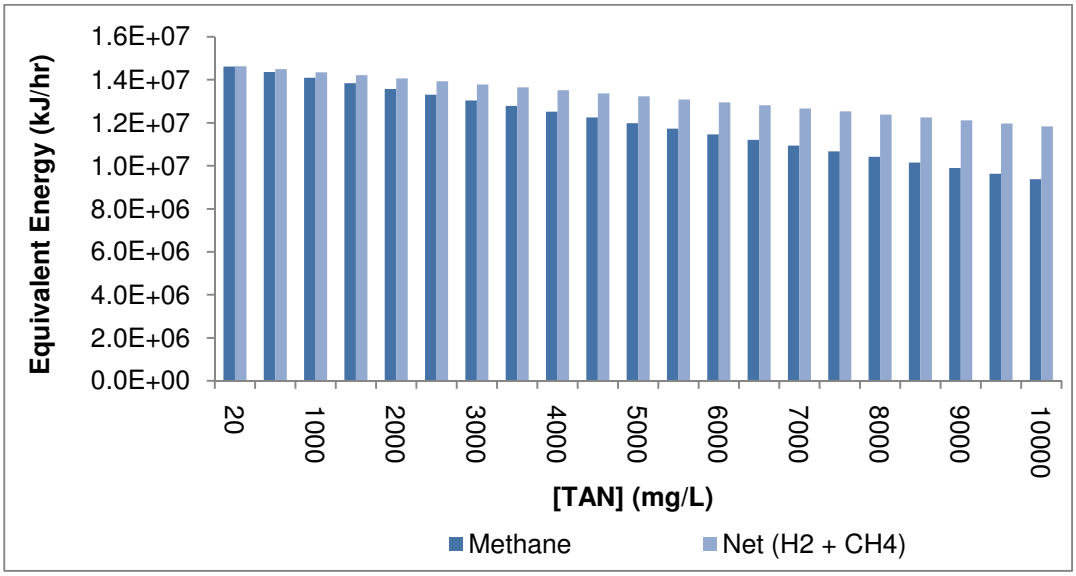

Figure 5.10 - Comparison of methane generation and net system energy generation as a function of the steady-state digester TAN concentration (TAN is a function of feedstock C:N ratio)

The net system biofuel energy generation decreases linearly as a function of the operating TAN concentration. The relative contribution to the net energy of methane and hydrogen, shows that methane is decreasing and hydrogen is increasing as the C:N ratio decreases and TAN increases (Figure 5.11).

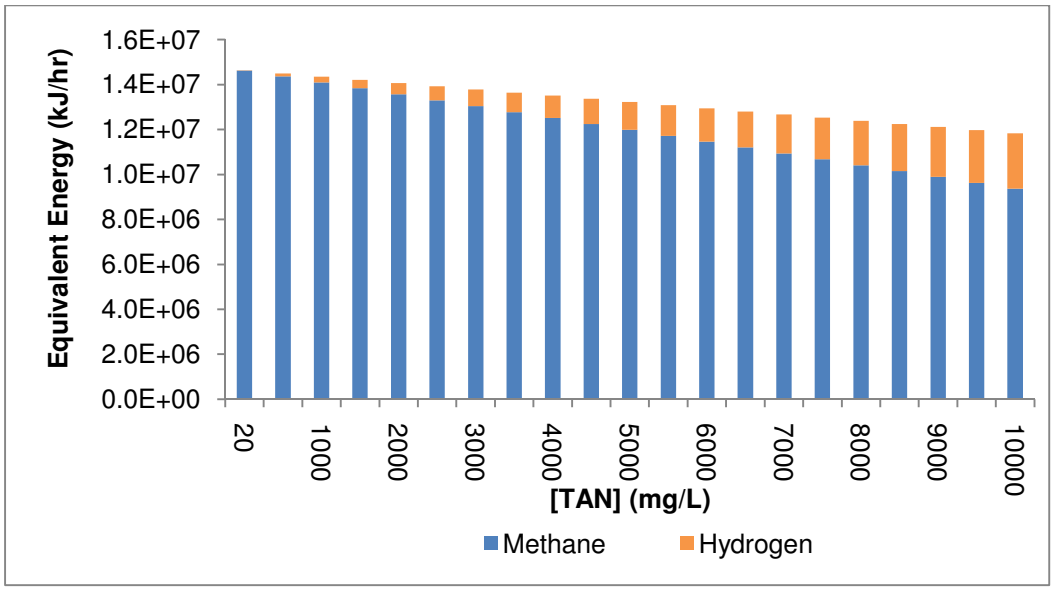

Figure 5.11 - Net system energy generation attributable to methane and hydrogen respectively as a function of steady-state digester TAN concentration (TAN is a function of feedstock C:N ratio)

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It does not appear that when the digester is coupled with the ammonia stripping and reforming system that the loss in methane to power the microcombustor is compensated by the recovered hydrogen energy because the sum of equivalent methane and hydrogen energy at 10,000 mg/L TAN is less than the equivalent methane energy at 20 mg/L TAN. This finding initially suggests that the ammonia stripping and hydrogen recovery process requires more energy than it produces, but this is not always the case.

The operating TAN concentration in the digester is controlled by the feedstock C:N ratio, which was varied between 136 (20 mg/L) and 3.0 (10,000 mg/L). Based on Reaction 5.8, the total amount of methane that can be produced from a fixed mass of organic substrate decreases as the C:N ratio decreases (Figure 5.12).

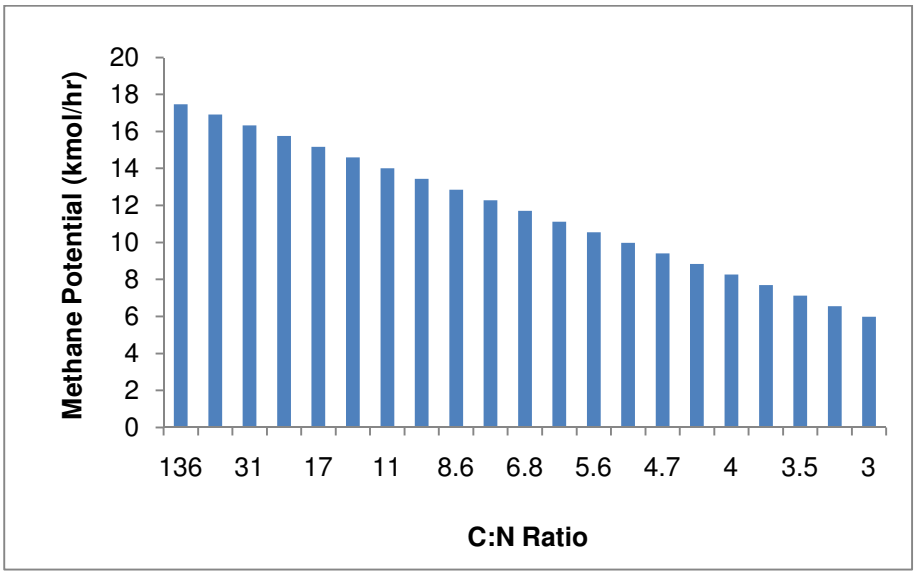

Figure 5.12 - Potential methane production rate as a function of feedstock stoichiometry (controlled by feedstock C:N ratio)

Therefore, the available methane energy from the initial substrate as a function of the mass flow rate decreases as the C:N ratio decreases. This occurs because as the C:N ratio decreases, more of the model substrate described in Reaction 5.7 is incorporated and as a result of the reaction stoichiometry (Reaction 5.8), the moles of C available for producing methane decreases. The amount of C capable of becoming methane is a function of the substrate, not the ADBH system being considered. Therefore, to further evaluate the system, the energy generated and consumed by the process was normalized to methane production potential for the feedstock at each C:N ratio (Figure 5.13).

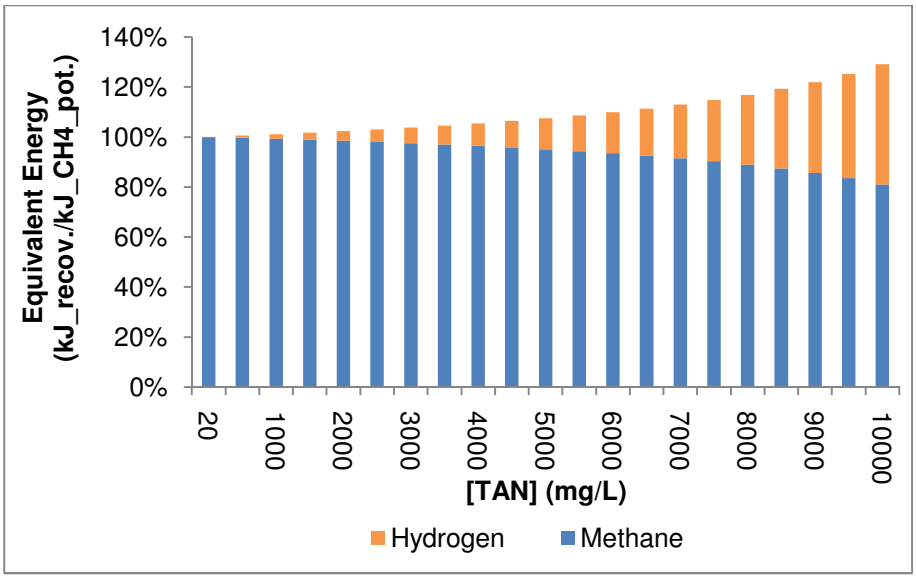

Figure 5.13 - Energy from methane and hydrogen as a percentage of the potential methane production versus operating digester TAN concentration (TAN is a function of feedstock C:N ratio)

The normalized output considers the total potential recoverable energy outputs calculated for methane and hydrogen for a range of C:N ratios. As the C:N ratio approaches infinity (no N in feedstock), the methane produced approaches the total methane potential of the substrate (100% in Figure 5.13) that is based on the stoichiometry from Reaction 5.8 and the defined fraction of the degradable portion defined in Table 5.3. As the C:N ratio decreases (TAN concentration in the digester increases), and ammonia stripping with hydrogen recovery is utilized, some methane is diverted to the microcombustor to power the ammonia reforming process, and thus, the methane recovered decreases as compared to the potential methane. However, the normalized result shows that the reduction in methane via diversion to heat the microcombustor is compensated by the hydrogen energy produced (Figure 5.13). Results above 100% indicate that the total recoverable energy from the ADBH process

recovering both hydrogen and methane exceeds the potential recoverable energy from methane recovery alone.

When the system energy consumption is calculated, however, it appears that the recovered hydrogen energy equivalent is not sufficient to offset the system energy requirements (Figure 5.14).

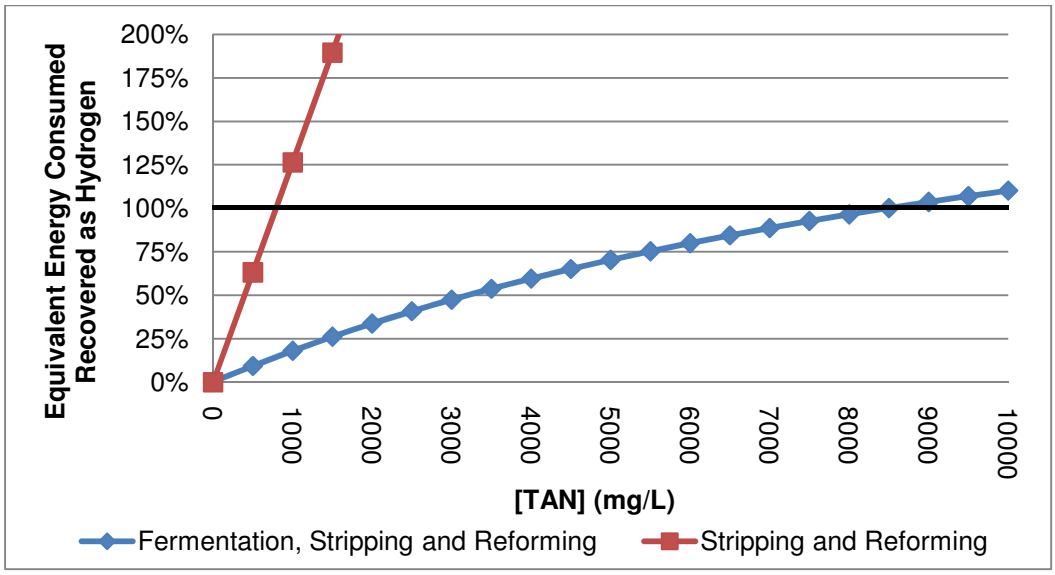

Figure 5.14 – Comparison of the percent of equivalent energy consumed that is recovered as hydrogen as a function of the operating TAN in the digester: (Blue) relative hydrogen recovery considering fermentation, ammonia striping, and reforming, and (Red) stripping and reforming only

The amount of energy consumed by the system to generate (via fermentation), recover and reform ammonia is greater than the equivalent hydrogen energy generated, for TAN concentrations below approximately 8,500 mg/L (C:N < 3.7). However, the amount of energy consumed by the system to simply recover and reform ammonia without fermentation, is only greater than the equivalent hydrogen energy generated for TAN concentrations below approximately 1,000 mg/L (C:N < 31). Operation of the ADBH system may not be favorable for feedstock C:N ratios greater than 31 (C:N above 31

corresponds to digester TAN less than 1,000 mg/L), but a separate ammonia fermentor could be considered when operating the ADBH system with feedstock C:N ratios below 3.7 (C:N below 3.7 corresponds to digester TAN greater than 8,500 mg/L). In general, operating the ADBH system at TAN concentrations above 1,000 mg/L (C:N less than 31) improves the overall energy balance as compared to anaerobic digestion with methane recovery alone.

5.6.1b – Influent Feedstock Effects on Digester TAN and Biogas Quality

The effect of the influent feedstock C:N ratio on digester TAN and effluent biogas quality was analyzed by assuming and holding constant one set of specific operating conditions (Table 5.3). Although the operating TAN concentration in the digester is used as a reference for the observed energy outputs in this analysis, the C:N ratio of the dry solids flow controls this reference point as other inputs are held constant. The operating TAN concentration is used as a reference because high TAN concentrations (above 5,000 – 6,000 mg/L) can substantially decrease methanogenesis [300]. A dry solids C:N ratio between 6.8 and 5.6 would correspond to digester TAN concentrations above 5,000 to 6,000 mg/L based on the assumed inputs. The relationship between the feedstock C:N ratio and the operating TAN concentration in the digester depends on the solids flow rate, recycle flow rate, set moisture content in the digester, retention time, and digester aspect ratio. For a specified C:N ratio (even for low ratios), the design characteristics of the system could be adjusted to maintain a viable operating TAN concentration in the digester. There would, however, be tradeoffs in system energy outputs because increasing the moisture content, recycle rates, and digester volumes would increase the system size and energy demands.

The ability for the ammonia recovery and reforming components of the ADBH system to pay dividends to the overall energy balance is greater for lower C:N ratios, but C:N ratios below 5.6 could limit methanogenesis and compromise overall system energy recovery. Changes to the digester design parameters could allow lower C:N ratios to be handled, but would also increase system energy consumption. In general, greater energy recovery is observed for higher feedstock C:N ratios, but maximizing energy recovery from the integrated system with lower C:N ratios requires operating the system at the highest possible TAN concentration in the digester.

The C:N ratio of the feedstock also affects the system biogas composition by controlling the amount of carbon dioxide removed from Stream 11 in the second pH-shift reactor (Figure 5.15).

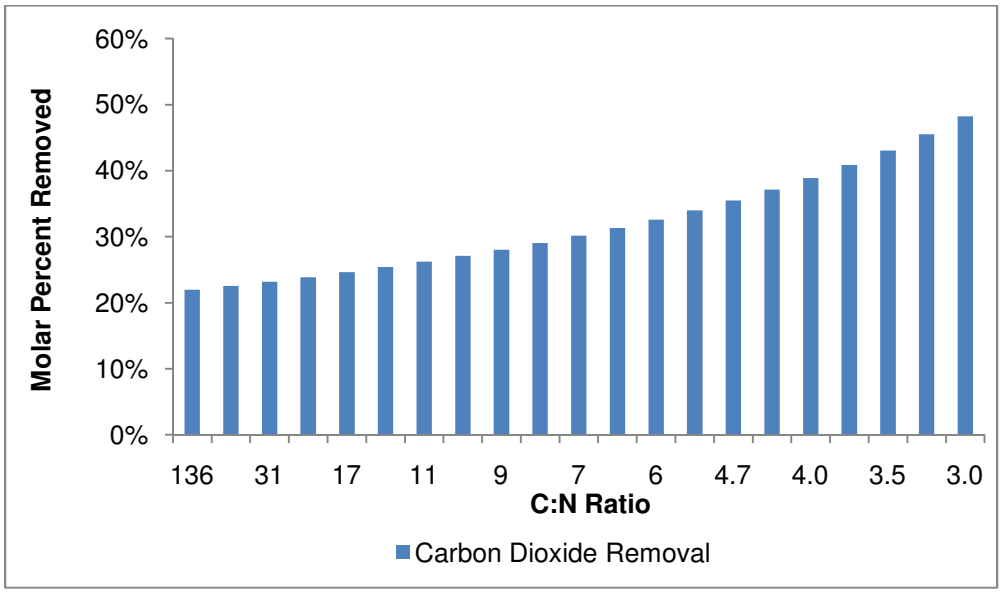

Figure 5.15 - Molar percentage of carbon dioxide removed from ADBH Stream 11 in the second pH-shift reactor as a function of the influent feedstock C:N ratio

Over the considered C:N ratio range, the molar percent of carbon dioxide removed increased from 22.0% to 48.2%. The biogas composition in Stream 11 varied from 54.3%

to 62.8% methane as the C:N ratio moved from 136 to 3.0. The balance of the biogas was carbon dioxide. For feedstock C:N ratios of 136 and 3.0, the methane content leaving the second pH-shift (Stream 13) was predicted to be 64.3% and 80.7% methane, respectively (Figure 5.16). This result presents another tradeoff to be considered. If purified methane is the desired downstream product, decreasing the C:N ratio of the influent solids material stream, can be seen as a means of improving downstream biogas purification. This effect would impact the energy balance for a system seeking to produce a highly concentrated methane product (Figure 5.16).

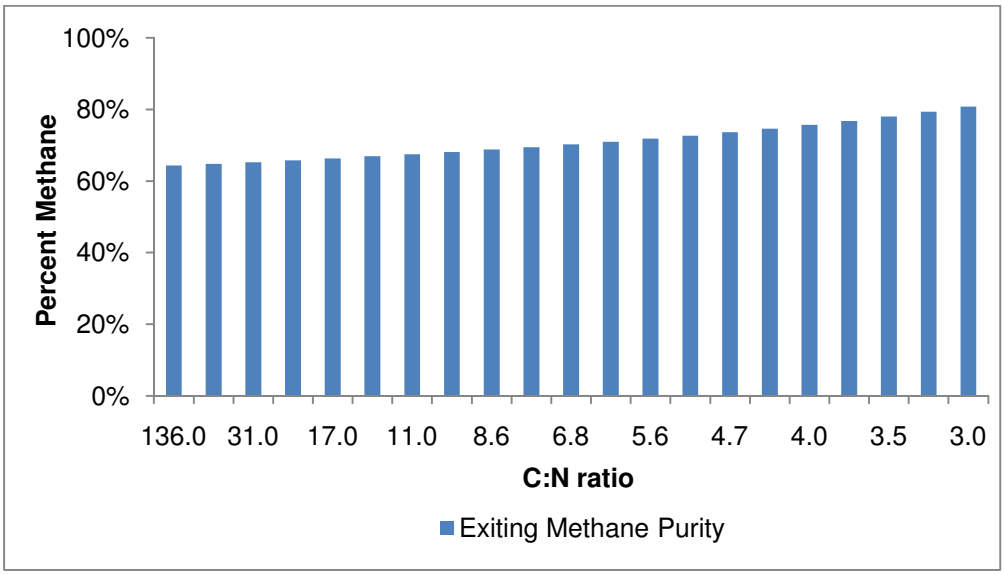

Figure 5.16 - Methane content of biogas exiting the system (Stream 16) as a function of the feedstock C:N ratio

The carbon dioxide removal in the second pH-shift reactor can also be improved by increasing the calcium hydroxide addition to the first pH-shift reactor.

5.6.1c – Power and Pressure Drop Requirements

The total power required for maintaining pressure drops to facilitate stream-fluid transfer accounted for both hydrostatic and frictional requirements. Based on the process

configuration where all process equipment was on the same horizontal plane, the sign for the required pressure drop for a given aqueous stream could be determined (Table 5.5).

Table 5.5 - Equations used to calculate vertical shift (Δz) for liquid streams, and corresponding pressure drop (Δp) as well as the sign of the resulting value based on ADBH process configuration

Stream	Δz	Δp (vertical shift)	Sign
2	$H_{Digester}$	$\rho \cdot g \cdot \Delta z_2$	(+)
5	$H_{pHshift_1} - H_{Digester}$	$\rho \cdot g \cdot \Delta z_5$	(–)
6	$H_{Stripper} - H_{pHshift_1}$	$\rho \cdot g \cdot \Delta z_6$	(+)
8	$H_{pHshift_2} - H_{Stripper}$	$\rho \cdot g \cdot \Delta z_8$	(–)
12	$H_{Digester} - H_{pHshift_2}$	$\rho \cdot g \cdot \Delta z_{12}$	(+)

Positive values for the pressure drop corresponded to a power requirement whose magnitude depended on the volumetric flow rate of the associated stream. Negative signs indicated that the hydrostatic pressure at the beginning of the pipe facilitated the associated stream flow.

Required pressure drops to power fluid flow, compensating for frictional energy losses along the length of the pipe, was considered. The magnitude of the frictional losses and corresponding power required to maintain the calculated pressure drop was almost exclusively a function of the specified influent feedstock mass flow rate, which was held constant throughout the analysis. Thus, it was not unexpected that the total power requirements for pumping (sum of the hydrostatic and frictional power requirements), mixing and ammonia stripping increased by less than 2% (from 3.11E+05

to 3.15E+05 kJ/hr) as the C:N ratio decreases from 136 to 3.0. A comparison of the relative power demands for pumping, mixing and ammonia stripping showed that the mixing in the digester and pH-shift reactors required the most power (Figure 5.17).

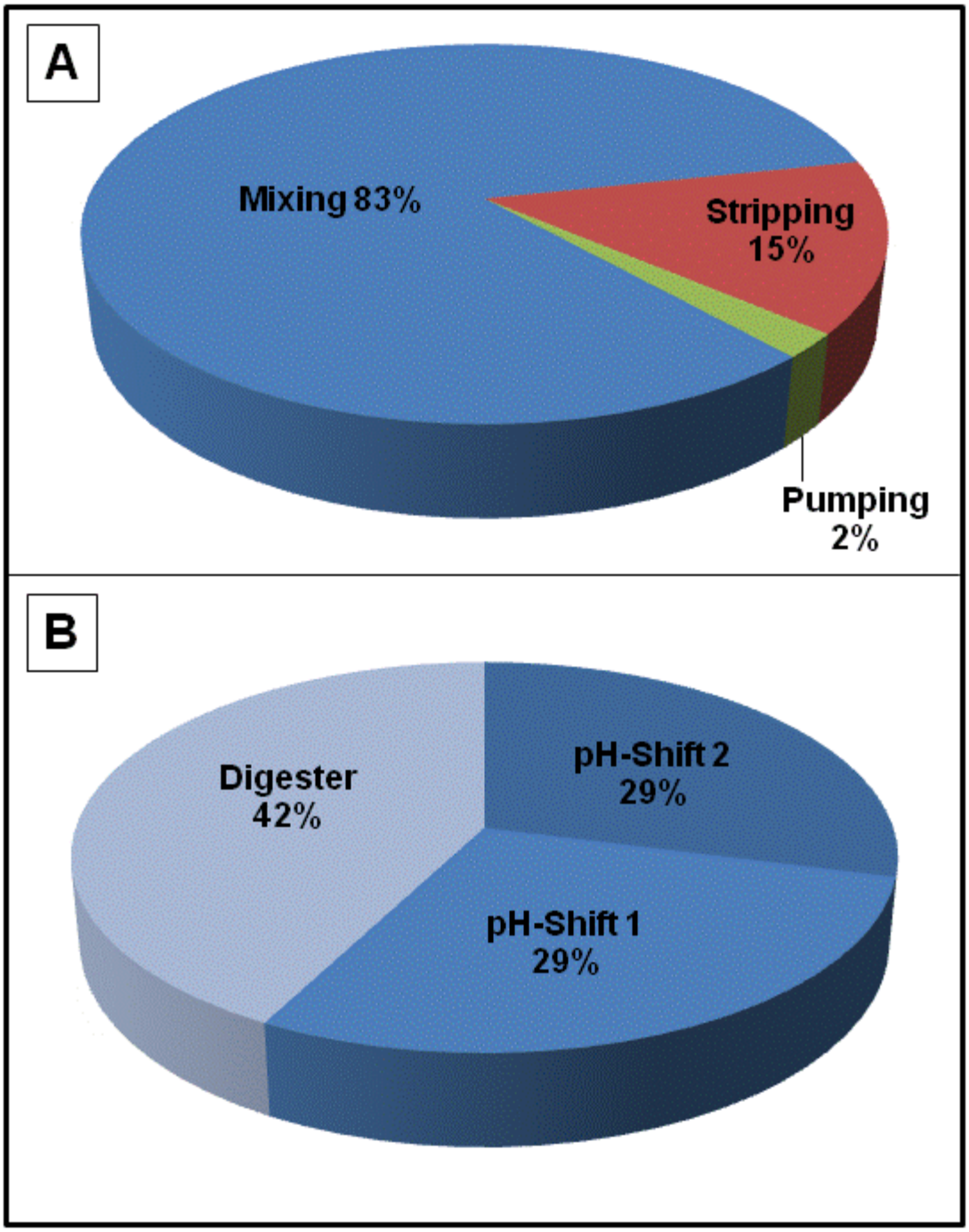

Figure 5.17 – ADBH fractional power requirements: (A) demands for pumping, mixing and ammonia stripping, and (B) relative requirements of mixing in the digester and pH-shift reactors

The sum of the power to sustain mixing in the digester and pH-shift reactors, maintain the pressure drop and facilitate ammonia stripping from the aqueous stream, was two orders of magnitude smaller than the equivalent energy generated as fuel (biogas and hydrogen), and heat (Figure 5.10 and Figure 5.17). Subtracting the total power required from the net energy equivalent generated had a minor impact on the ADBH system energy generation potential. The overall process fuel and heat energy generation as a function of the influent solids C:N ratio is shown in Figure 5.18.

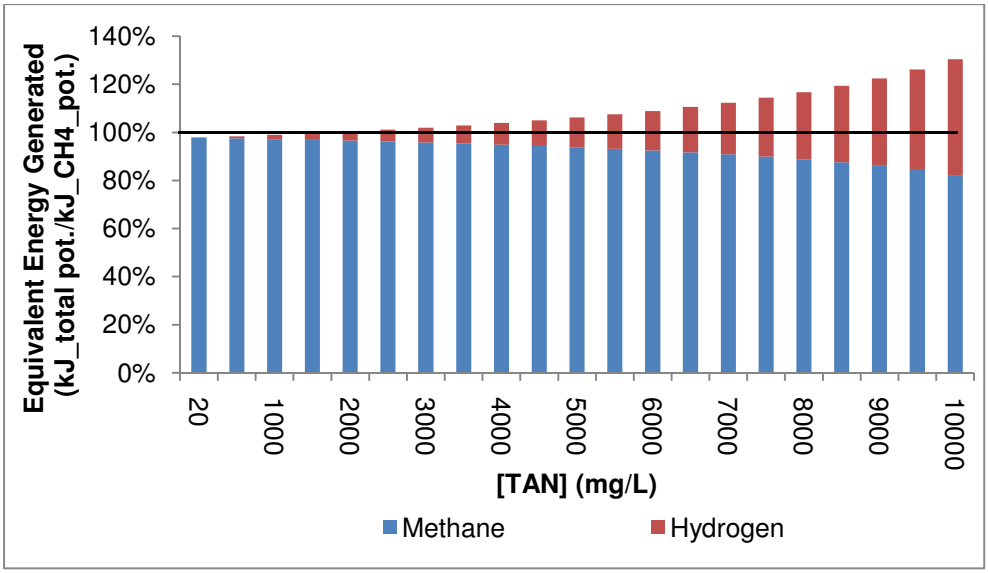

Figure 5.18 - Normalized total equivalent energy generated by ADBH system as a function of the operating TAN concentration in the digester (TAN is a function of feedstock C:N ratio)

The normalized output indicates that above an operating digester TAN concentration of approximately 2,000 mg/L, the total biofuel energy (CH_4 and H_2) output is greater than could be expected to be produced from anaerobic digestion (CH_4) alone.

5.6.2 – Effects of System Integration: Comparison of Cases 1, 2 and 3

The effect of various energy integration scenarios were assessed by comparing the fraction of the energy generated diverted to power the integrated process as a function of the operating digester TAN concentration (Figure 5.19).

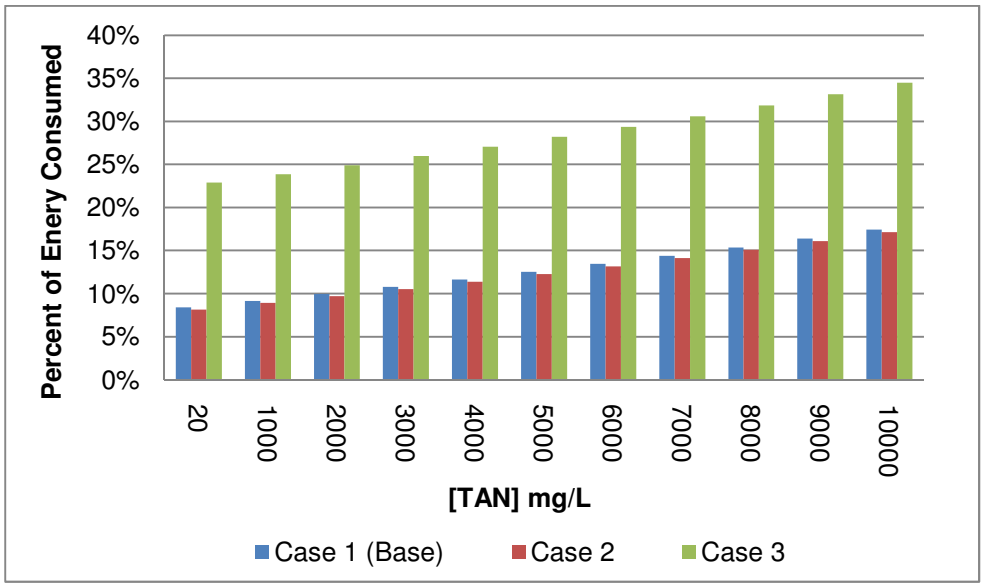

Figure 5.19 – Comparison energy integration (Cases 1-3) on ADBH overall energy consumption measured as a percent of generated energy (Case 1 with conservative integration, Case 2 with conservative integration and gas stripping instead of vapor stripping, and Case 3 with no energy integration)

The percent of the energy required increased as the influent feedstock C:N ratio decreased (corresponding TAN concentrations in the digester increased) for all cases because pumping and mixing requirements downstream from the digester were a function of the mass flow of ammonia. Additionally, the energy content of the feedstock decreased as the C:N ratio decreased, allowing less energy to be generated in the first place (Figure 5.12). The total percentage of energy diverted remained under 35% for all cases and feedstock C:N ratios. The base case (Case 1) and Case 2 did not generate any more biofuel than Case 3, but as expected, they diverted less of it to power the ADBH system.

Case 3 had the highest fraction of its biofuel being diverted to power various system demands for all feedstock C:N ratios because no energy integration was considered in this case. Thus, heat generated and available hydrostatic pressures to facilitate stream flow were not utilized.

Heat and available hydrostatic pressure were considered for integration in Case 1 and Case 2. Case 2 differs from Case 1 in that it considered utilizing a fraction of the available hydrogen and nitrogen stream (Stream 18) as the stripping gas as opposed to steam. For Case 1, liquid vaporization and stripping required 1.574 kJ/kg-aq.; whereas for Case 2, using the available gas stream eliminated the need for vaporization, and ammonia stripping required only 0.265 kJ/kg-aq. The energy required for ammonia stripping in Case 2 assumed that the hydrogen and nitrogen stream (Stream 18) could effectively strip ammonia from the liquid stream as well as air. The advantages of Case 2 would be that the hydrogen and nitrogen stream would be readily available, pre-heated and would not introduce additional carbon dioxide that could cause scaling, but the disadvantage would be that the stripping gas (H_2/N_2) would dilute the effluent ammonia gas stream. Using steam as the stripping gas allows ammonia to be concentrated. It is likely that the minimal reduction in energy use observed by utilizing a fraction of the nitrogen and hydrogen stream for stripping would not be worth diluting the reforming gas stream.

5.7 – Conclusions

The total equivalent energy generated by the ADBH system is greater than the energy consumed to operate the system. When the ammonia recovery and microcombustor system are coupled to the digester system (becoming the ADBH system), the equivalent energy from hydrogen alone is not sufficient to offset system

energy requirements when digester operation was included, and the feedstock C:N ratio was above 3.7 (<8,500 mg/L TAN). Operating the ADBH system increased the total energy recovery potential compared to the methane potential for feedstock C:N ratios less than 31.

The operating TAN concentration in the digester was controlled by varying the C:N ratio of the feedstock material. The ADBH system energy balance remained positive (generating more energy than it consumed) while digesting biomass, removing aqueous ammonia, and reforming ammonia gas to produce hydrogen for all feedstock C:N ratios considered, but the energy balance favored lower C:N ratios. Thus, biomass substrates with lower C:N ratios lend themselves to processing in this integrated process more so than substrates with higher C:N ratios (Figure 5.1). Further, feedstocks with sufficiently low C:N ratios might be better managed by employing a separate hydrolysis-fermentor reactor upstream from the digester. Ammonia release during hydrolysis occurs more rapidly than other anaerobic processes in the digester, and operating a separate hydrolysis reactor could potentially reduce nitrogen loading in the downstream digester. This could be advantageous by preventing ammonia toxicity, and improving methane generation as shown in Chapter 4 in batch studies.

Although the results suggest that the ADBH system recovered more energy from biomass than anaerobic digestion alone, there are substantial process tradeoffs that would need to be considered to optimize this system. For example, this model did not account for microbial sensitivity to aqueous TAN concentrations, and was not sensitive to process kinetics.

More research needs to be conducted before full-scale ADBH systems could be pursued. The tradeoff between recovering more hydrogen by processing biomass with lower C:N ratios, and limiting methane production by inducing ammonia toxicity in the digester has not been quantified. Additionally, the cost for constructing and operating ADBH systems versus the relative benefits of energy generation and nitrogen removal need to be assessed.

Finally, it is useful to consider the alternative to the ADBH process. Since, aqueous nitrogen species are typically a concern for digester effluents, and require subsequent treatment, the energy savings of using ADBH systems versus conventional digestion and downstream nitrogen mitigation processes are important. Biological mediation of aqueous nitrogen species are typically aerobic processes that require organic substrate, and do not offer the prospect of energy recovery. In fact, aeration typically is the greatest energy sink at wastewater treatment plants, and the organic substrate required could be viewed as substrate that is diverted from anaerobic processes that generate methane. Thus, when compared to the alternative, it is plausible that ADBH technology is always energetically favorable.

The results establish that more biomass energy can be recovered by utilizing the ADBH system than by employing digestion alone, and that the ADBH approach may be energetically favorable over a wide range of C:N ratios compared to conventional nitrogen mitigation processes.

Chapter 6

6. Summary, Engineering Significance, Conclusions and Future Considerations

The studies presented sought to establish necessary fundamental knowledge to design waste management systems that handle greater varieties of biomass waste, improve energy recovery via anaerobic processes, and simultaneously avoid pollution from aqueous nitrogen species by developing strategies to recover ammonia as a biofuel. The results presented were obtained from modeling and laboratory-scale experimentation, and broadly sought to improve understanding about each system considered. However, from laboratory-scale reactor, to large-scale waste management systems the focus was to identify factors that improved or diminished the system's overall energy balance. The engineering significance of the models developed and results obtained will be considered by discussing a few specific questions about each system presented.

6.1 Reducing Leachate and Cover Transport Requirements in Burlington County

6.1.1 Scenario development

Using an energy balance and carbon emissions model for the Burlington County waste management system, the relative sensitivity of various system components on overall energy consumption and fossil carbon emissions were determined (Chapter 2). The greatest system energy requirements were to collect MSW from house-to-house and haul it to the bioreactor landfill. However, these system parameters are largely beyond the control of operators. If MSW collection and hauling are not considered, onsite operations (28%) and leachate transport (27%) comprise more than half of the energy

requirements among system components that can be affected by operators at the Burlington County Resource Recovery Complex (BCRRC). Of particular interest are the energy demands of leachate pumping and hauling and additional cover transportation (18%). Collectively 45% of the energy demand, among controllable system parameters, is attributed to leachate pumping and hauling and additional cover transportation at the BCRRC. The effect of the transportation distance on the system energy balance and carbon emissions can be assessed using the model developed.

6.1.2 Effect of leachate pumping and hauling and cover transportation distance on energy balance and carbon emissions

Currently, leachate from the BCRRC is collected and hauled 109 kilometers (68 mi.) to the Passaic Valley wastewater treatment facility in northern New Jersey. The leachate transport truck capacity is 22,000 liters (5,800 gal.), and the number of round-trips (218 km/trip) required is a function of the leachate generation rate. The fuel consumed is calculated using a transport truck fuel efficiency of 2.13 kilometers per liter (5 mi/gal). Soil and glass cullet are used as additional cover materials. Soil is obtained from sources an average distance of 48 kilometers (30 mi.) from the BCRRC, and glass cullet is transported 72 kilometers (45 mi.). Glass cullet and soil arrive in equal volumes (0.10 m^3/tonne MSW) and in equivalent transport vehicles (15.3 m^3/truck). Thus, an average transport distance for additional cover, including glass cullet and soil, is 60 kilometers (37.5 mi). The total controllable energy consumption with continued operation under these conditions was calculated to be 1,277 $\pm$ 222 TJ over 30 years (Chapter 2). The effect on controllable consumption as a function of reductions in leachate and additional cover transport distances was calculated (Figure 6.1).

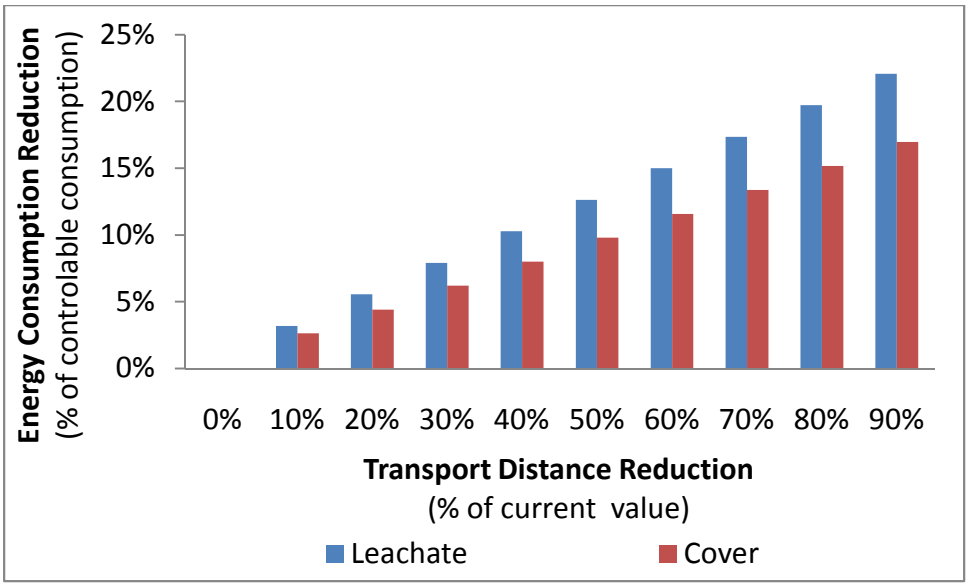

Figure 6.1 - Fractional reduction of controllable energy consumption as a function of fractional reductions in leachate and additional cover transport distance (BCRRC system)

Greater decreases in energy consumption, as a fraction of the transport distance, were observed for leachate transport because its current transport distance is larger and leachate transport will continue longer than cover transport (cover transport will stop in 2018 when waste deliveries end). Thus, reductions in the leachate transport distance will have a greater effect on system energy consumption.

Currently, stormwater is transported 29 kilometers (18 miles) to be treated. Stormwater differs from leachate in that it has not come into direct contact with refuse as leachate has. There is a possibility of sending leachate, or a fraction of it, to a closer stormwater treatment facility. Sending all of the leachate to the closer facility would reduce the leachate transport distance by 73.5% and reduce total controllable consumption by 18.3% (1,277 $\pm$ 222 to 1,043 $\pm$ 181 TJ) over 30 years. Similarly, obtaining glass cullet from a nearer location or not accepting it and receiving twice as much soil as additional cover could be possible. Reducing the current average additional

cover transport distance to 48 kilometers (current transport distance of soil), would decrease the average additional cover distance by 20% and the total controllable energy consumption by 4.4% (1,277 $\pm$ 222 to 1,221 $\pm$ 212 TJ) over 30 years. If both improvements could be made simultaneously, total controllable consumption would be reduced 21.9% (1,277 $\pm$ 222 to 998 $\pm$ 174 TJ) over 30 years saving approximately 250,000 liters of diesel fuel per year (66,000 gal/yr).

6.2 Selecting Biogas Recovery Technology for Oxbow Stables

6.2.1 Scenario development

The decision by a horse farm owner to develop onsite anaerobic digestion technology to recover biogas from horse waste presents numerous tradeoffs, costs and potential benefits to consider. However, little economic or technical information is available regarding anaerobic digestion of horse waste. Thus, methane generation potential, predicted by kinetic modeling, as well as system capital costs, were quantified for onsite-batch and regional continuous anaerobic digestion systems handling horse waste. The model can be used to assess how best to manage horse waste based on farm size and other factors. The farm considered in this analysis is the Oxbow Stables and Riding Club in Hamburg, NJ. Oxbow is a 70 acre horse farm with 56 stalls. Fifty horses typically reside at the facility throughout the year. Spreading on-site has been, and is currently, the waste management practice at this farm, but there is increasing pressure from the state and neighboring residents to find an alternative means of waste handling.

6.2.2 Relative capital costs and methane recovery comparison

Based on the data obtained from *Study II* (Chapter 3), Oxbow could benefit most from developing a high-solids onsite batch reactor system to recover biogas, generate heat and produce electricity. Specifically, a 20-CY standard reactor size and retention time of 56 days should be employed. Under this scenario, a capital investment of $2,900 per horse ($145,000 total system) would be required, but would include an associated structure to house the reaction vessels. The system would cost $800 per horse ($40,000 total) without a structure. Oxbow's geographic location in northern New Jersey would not make it a candidate for infrastructure development without a structure, or other means, to protect the reactors from the elements and maintain the operating temperature of the digesters (35° C). The system footprint is expected to be 202 square meters (m^2), and generate 5 kilowatt-hours per square meter per day (kWh/m^2-day) of electricity and 14 kWh/m^2-day of heat. A normalized energy output of 860 kWh-electricity/horse-year and 2,380 kWh-heat/horse-year could be expected. Over ten years, the energy investment would be $0.14 per kWh-electricity and $0.05 per kWh when using heat and power. The electrical output over 10 years would be 46.8% less than wholesale electrical prices and 70.0% less than retail prices, meaning that the value of the energy generated is sufficient to offset the cost of electricity. The economic projections for this system could be improved by finding a less expensive means of preventing reactor heat losses than constructing a housing structure, and taking advantage of several economic incentives offered by the State of New Jersey (see Table 3.3).

6.3 Heat and Energy Tradeoffs of Thermophilic Versus Mesophilic Anaerobic Digestion

6.3.1 Scenario analysis and parameters

The effect of ammonia stripping and aeration on nitrogen species accumulation and potential energy recovery from laboratory-scale batch digesters was assessed (Chapter 4). Mesophilic (35° C) and thermophilic (55° C) reactor conditions were considered. A simulated organic waste feedstock with three nitrogen loadings was created by varying the ratios of laboratory grade rabbit food, casein and cellulose. Methane accumulation was normalized on a volatile solids (VS) basis so that the various feedstocks could be compared. Among low-nitrogen feedstock controls thermophilic reactors outperformed mesophilic reactors in terms of biogas and methane generation. The Anaerobic Digestion-Bioammonia to Hydrogen (ADBH) system model (Chapter 5) can be used to assess whether the greater quantities of methane recovered from the thermophilic reactors is sufficient to offset the heat requirements necessary to maintain the greater digester temperature and justify thermophilic operation.

6.3.1 Comparison of heat requirements and bioenergy production from thermophilic and mesophilic anaerobic digesters

The greatest biogas-producing mesophilic and thermophilic reactors generated 574.62 $\pm$ 2.64 and 734.83 $\pm$ 9.74 mL/g VS added, respectively. These "best" results were observed among low-nitrogen feedstock controls in both cases. As well as producing more biogas than mesophilic reactors, thermophilic reactors with low-nitrogen feedstocks and no treatment (controls) produced more methane (24.4% CH_4-mesophilic and 27.8% CH_4-thermophilic). Mesophilic reactors with low-nitrogen feedstocks and no treatment

produced only 78% of the biogas, and 68% of the methane that their corresponding thermophilic reactors produced.

The model developed to analyze the ADBH system was used to identify the impact that decreasing the digester operating temperature from 55° C to 35° C, as well as reducing the overall biogas generation by 22% (32% CH_4 reduction, 18% CO_2 reduction) would have on heat requirements and bioenergy generation. The impacts of these changes were limited to biogas conversion and not ammonia release because differences in ammonia nitrogen among both mesophilic and thermophilic reactors were negligible (Chapter 4).

The heat balance was considered for both mesophilic and thermophilic conditions (Figure 6.2).

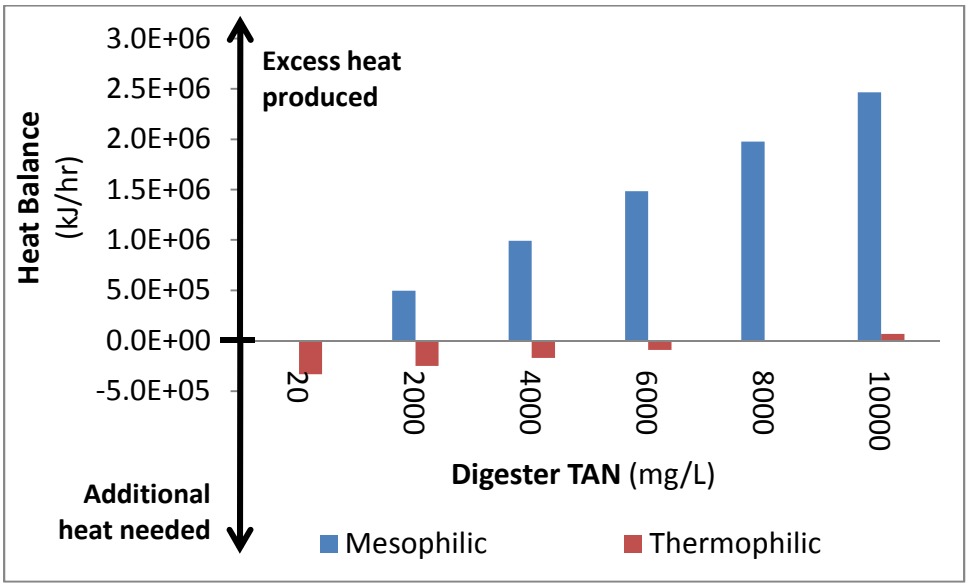

Figure 6.2 - Heat balance obtained using ADBH model and comparing mesophilic (35° C) and thermophilic (55° C) digester operation over a range of digester TAN concentrations

The operating digester temperature had a noticeable effect on the overall system heat balance. While the thermophilic system required additional heat over a large range of

total ammonia nitrogen (TAN) concentrations (up to 8,500 mg/L), the mesophilic system did not require additional heat at any of the TAN concentrations tested.

The system-wide energy balance was considered for both mesophilic and thermophilic conditions (Figure 6.3).

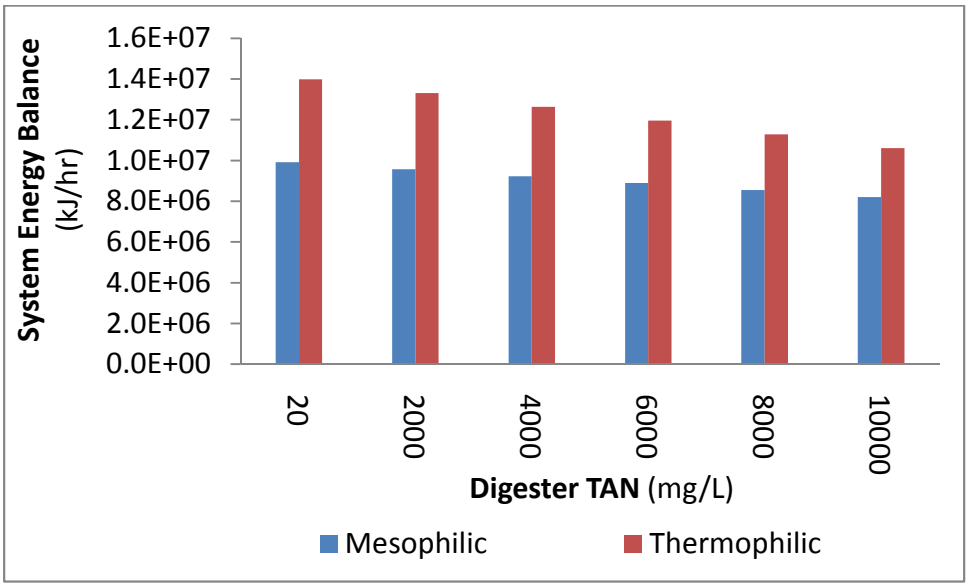

Figure 6.3 - System-wide energy balance obtained using ADBH model and comparing mesophilic (35° C) and thermophilic (55° C) digester operation over a range of digester TAN concentrations

The thermophilic system-wide energy balance was greater than the mesophilic energy balance. This indicates that although the thermophilic system requires more heat to sustain its higher operating temperature, the additional methane generated as a result of thermophilic operation offsets its additional heat demands and generates more fuel energy. Thus, thermophilic operation was shown to be favorable as compared to mesophilic operation independent of the digester TAN concentration.

6.4 Conclusions and Future Considerations

In the short-term, energy recovery from existing U.S. waste management infrastructures, which rely heavily on traditional landfilling and bioreactor landfills, should be improved and enhanced. Steps can be taken to reduce system energy consumption and increase recoverable biogas. However, viewing waste as a fuel and focusing on improving energy-from-waste (EfW) technologies will certainly direct future waste management system design away from landfills and bioreactor landfills.

While improving waste management system technology, however, maximizing energy recovery should not be optimized to the exclusion of all other parameters. For example, waste incineration generates greater amounts of energy per tonne of waste than anaerobic digestion, but it does not have a means to selectively consume the biogenic fraction of MSW and generate valuable end products (fertilizer) from its residuals. In some cases, the energy to generate fertilizer from raw materials would be greater than the difference between energy recovery from incineration and anaerobic digestion. Thus, there is a need for more research to be done to improve life-cycle-assessment (LCA) of waste management systems as well as assessments for conceptual systems. In many cases useful LCA data and results are available, and more work should be done to develop new handling practices and waste management infrastructure based on assessment recommendations.

Anaerobic digestion processes have been studied extensively as a means to recover energy from biomass wastes, and more research should be directed at understanding, improving and optimizing these processes. More needs to be done to characterize these processes as a function of highly diverse waste compositions. This is especially true as more biomass wastes should be incorporated into the energy-from-

waste system. Ideally, source separated MSW could concentrate the organic fraction of the MSW (OFMSW), and the OFMSW stream could be blended with agricultural and commercial food waste streams. Mixed biomass waste management systems could increase anaerobic digester feedstocks, reduce the demand for smaller less efficient digester systems, improve biogas production and become a reliable and more significant source of renewable energy or fuel.

This work illuminated a specific area for future consideration. It concerns characterizing the tradeoffs between hydrolysis-fermentation-acidogenesis and methanogenesis. The impact of volatile fatty acid (VFA) and ammonia accumulation during hydrolysis-fermentation on acidogenesis-methanogenesis need to be explored further. There are two factors that should be studied: first, the relative rates of hydrolysis-fermentation-acidogenesis and methanogenesis as a function of the feedstock; and second, the extent of inhibition of methanogenesis as a result of varying levels of VFAs and ammonia need to be quantified. It is likely, that the best way to optimize methane recovery from digesters is to separate hydrolysis-fermentation-acidogenesis and methanogenesis, and control VFA loadings based on the rate limiting methanogenesis step. However, designing control systems cannot be accomplished without a better understanding of the process kinetics and impacts of over loading.

Finally, the Anaerobic Digestion-Bioammonia to Hydrogen (ADBH) system model developed to assess the potential of recovering ammonia from anaerobic digester systems should be improved to consider irreversible energy losses (entropy) as part of its energy balance. As more data become available it could also be updated to include sensitivity to process kinetics and biological toxicity. Lastly, an economic assessment of

the system should be considered to determine if hydrogen produced in this way is valuable beyond producing an additional fuel stream from anaerobic digester systems.

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Appendix I

A.1. Burlington County Waste Management System Energy Balance Model

A.1.1. Constants and Conversion Factors

Constants		
Variable	Value	Unit
NRG Density Diesel=	48.0369	kWh/gallon
L per gallon	3.7854118	L/gal
CO2_density diesel	2.668	kg-CO2/L-diesel
Cubic feet to meters	35.314667	ft^3/m^3
Diesel NRG Density	37.3	MJ/L
CO2_density LFG	1.797	kg CO2/m^3
Carbon Density for NJ-Electric	0.731	kg-CO2/MJ_Elec-NJ
kWh per J	0.278	kWh/MJ
BTU per kWh	3410	BTU/kWh

A.1.2. Burlington County System Inputs

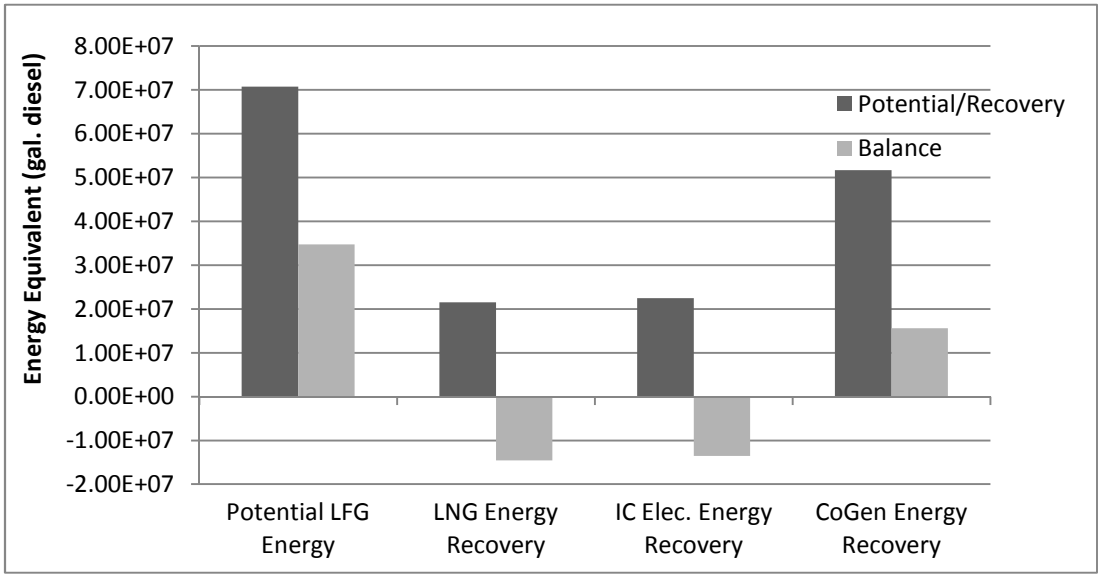
Parameters		
MSW Collection and Transport		
Variable	Value	Unit
Trans. Econ.	5	mi/gal
Coll. Econ.	2	mi/gal
Avg. Dist	16.4501375	mi
MSW/delivery	5.729714	ton/delivery
Additional Cover		
Variable	Value	Unit
CY Cover per ton MSW	0.42	CY/TonMSW
Truck Capacity	20.00	CY
Truck Econ.	5.00	mi/gal
Dist. Glass	90.00	mi

Dist. Soil	60.00	mi
Frac. Glass	0.33	
Transport Out		
Variable	Value	Unit
Leachate Dist. & RT	68	mi
Storm Dist.	18	mi
MPG	5	mi/gal
Truck Capacity	5800	gal
Waste Water Treatment		
Variable	Value	Unit
Temp=	15	C
Altitude=	76	m
Alpha=	0.85	
Beta=	0.9	
Cwalt=	10	mg/L
CL=	3	mg/L
Standard Aerator Eff.	1.2	
LFG Predictions		
Variable	Value	Unit
Methane Generation Potential (Lo) w/o recirc	4411	Cft/ton refuse
Methane Generation Potential (Lo) w/ recirc	5955	Cft/ton refuse
CH4 generation rate constant (k) w/o recirc	0.04	1/yr
CH4 generation rate constant (k) w/ recirc	0.26	1/yr
NRG Density LFG	490	BTU/CF LFG
Recovery Efficiency		
LNG Efficiency	0.30	
IC Elec Effic Calc	0.32	
Cogen Effic.	0.73	

A.1.3. Burlington County System Outputs

OUTPUTS

Energy Generation and Recovery Considerations					
	Total Consumption	Potential LFG Energy	LNG Energy Recovery	IC Elec. Energy Recovery	CoGen Energy Recovery
Total	3.60E+07	7.07E+07	2.15E+07	2.25E+07	5.16E+07
Balance		3.47E+07	-1.45E+07	-1.36E+07	1.56E+07



Fuel Generation per Ton of MSW					
	Tons MSW	Potential LFG Energy (Balance)	LNG Energy Recovery	IC Elec. Energy Recovery	CoGen Energy Recovery
Total (Balance)	6.56E+06	7.07E+07	2.15E+07	2.25E+07	5.16E+07
Fuel/Ton		10.8	3.3	3.4	7.9

Carbon Dioxide Emmisions					
	Potential Offset	LNG Emission	IC Elec. Emission	CoGen Emission	Max Pot. Emission
Total lbs CO2	7.31E+08	-3.06E+08	-2.85E+08	3.29E+08	7.58E+08
lbs CO2/ton MSW	111.5	-46.6	-43.5	50.2	115.6

Appendix II

A.2. Anaerobic Digestion of Equine Waste Model

A.2.1. Onsite Batch System Capital Cost Inputs

Batch System Capital Costs		
System Component	Number	Unit Price
Insulated Structure	1	$100/sq._ft.
Reactor Containers	Variable	$4,200
Pumps	1 pr	$250
Galvanized Pipes	8 pr	$30
Spray Nozzles	6 pr	$6
Gas Valves	6 pr	$15
Teflon Tubing	100 ft. pr	$2
Leachate Storage	1	$1,000
Generator	1	$289/kW
Spray Nozzle	1	$1,000
Safety Equipment	1	$500
Iron Sponge Cylinders	1 pr	$1,000

- Itemized capital costs for needed system components to assemble and operate the proposed onsite batch digester system (Zebib, T. 2009. *Design of a Bio-Energy Recovery System for On-Site Installation at an Equine Facility*. Bioenvironmental Engineering Senior Design Project**.** May 08, 2009. Rutgers University, New Brunswick, NJ)

A.2.2. Constants and Conversion Factors

Constants		
Variable	**Value**	**Unit**
Lbs to kg	0.45359237	kg/lbs
cubic ft to meters	35.3146667	cf/m^3
cubic yards to meters	1.307950547	cy/m^3
square ft to meters	10.7639104	sq.ft./m^2
L_CH4 to kg_CH4	0.000717	kg/L
Energy CH4	55.6	MJ/kg
Energy CH4	15.44	kWh/kg
Electricity	3.6	MJ/kWh
Lower Heating Value CH4	50	MJ/kg
Energy Diesel Fuel	38.6	MJ/L

A.2.3. Assumption Inputs

Assumptions				
Waste Characteristics				
Manure Production per Horse	50			
Bedding per Horse	0			
Waste Volume	25.2	lbs/cf	403.7	kg/m^3
Waste Production	50	lbs/day	22.7	kg/day
TS	0.4133			
VS	0.8204			
Kinetic Parameters				
	Batch	Continuous		
Gpot (L_CH4/kg_VS)	277	277		
Max Rate (L_CH4/kg_VS)	5.5			
Lag (L_CH4/kg_VS per day)	2			
Km		14		
System Parameters				
	Small	Continuous		
Sides & Batch top HTC (kW/(m^2*K))	0.001111	0.0008		
Continuous Top HTC (kW/(m^2*K))		0.00012		
Floor HTC (kW/(m^2*K))	0.00085	0.00017		
Temperature Difference (K)	20	40		
Heat Transfer Efficiency	0.9	0.9		
Insulated Structure Cost ($/sq_ft)	$85			
Generator Efficiency	0.200197	0.31		
Mixing Energy (kW/m^3)		0.0065		
Transport Fuel Economy (mi/gal)	4	mi/gal	1.79	km/L

A.2.4. Equine Waste System Inputs

Inputs		
	Batch	Continous
Horses	5005	5120
Vessel/Delivery Size	40	40
	30.6	31
Miniumum Vessels	258.5	
Number of Vessels	258	
Retention Time	28.0	28.0
Wt% Water		0.85

A.2.5. Equine Waste System Intermediates

Intermediates		
	Batch	Continuous
Waste Characteristics		
Mw (kg/day)	113511.5	1.16E+05
Q (cubic meters per day)	281.2	2.88E+02
SLR (kg/day)	46914.3	4.80E+04
VSLR (kg/day)	38488.5	3.94E+04
VS Input Per Reactor (kg)	4185.8	1.10E+06
Container Characteristics		
Min#Vessels	258.5	
Fill time (days)	0.1	37
Retention (days)	28.0	28.0
Radius (meters)		11
Length (meters)	6.13	
Height (meters)	2.04	27
Width (meters)	2.44	
Side plus Top Area (sq_m)	7993.6	2283
Floor Area (sq_m)	5127.4	394

A.2.6. Equine Waste System Outputs

Outputs		
	Batch	Continuous
Methane Generation		
Cumulative Methane (L_CH4)	1.53E+08	2.04E+08
Cumulative Methane (kg)	1.10E+05	1.46E+05
System Energy Sinks		
Methane Loss (L_CH4)	0.0E+00	0
Heat Requirements (L_CH4)	2.0E+07	4.88E+06
System Energy Generation		
Recoverable Methane (L_CH4)	1.33E+08	1.85E+08
Recoverable Methane (kg)	9.56E+04	1.33E+05
Methane Recovery Rate (kg/day)	3.42E+03	4.74E+03
Methane Recovery per Reactor (kg/reactor)	3.70E+02	1.46E+05
Normalized Output ((L_CH4)/(kg_VS added))	123.4	168.0
Electrical Power Recovery (kWh/month)	3.21E+05	6.91E+05
Electrcial Recovery per Horse (kWh/horse per mo.)	64	135
System Characterisics		
Required Transfers (per mo.)	280	286
Critical Transport Distance (km)	86	201
Insulated Structure Size (sq_m)	5127	

Required Generator Size (kW)	418	
Capital Costs		
Total Cost	$6,125,149	$2,892,682
Cost per Horse	$1,224	$565
Total w/o Structure	$1,433,952	
Per Horse w/o Structure	$287	

Appendix III

A.3. Anaerobic Digestion-Bioammonia to Hydrogen (ADBH) Model

A.3.1. ADBH System Inputs

Inputs		
Dry Weight Flow (kg/hr)	1000	
Fraction of Feed Stock Converted	0.8	
C:N Ratio (g C/g N)	3.0474	
N_n Value		3.85785276
MW_Organic Substrate (g/mol)		435
Molar Flow DOF (mol/hr)		1837.64854
Dissolved CO2 @55C (g_CO2/kg_H2O)	0.6	
Moisture (wt% water)	90.00%	
Water In_NH4+ (mg TAN/L)	200	
Percent Recycle	65.00%	
Digester dT (K)	40	
Internal Efficiency of heat capture and re-use	0.35	
Stream	**Diameter (m)**	**Req. Diam.**
2	0.30	0.30
3	0.45	0.45
5	0.89	0.89
6	0.93	0.93
9	0.92	0.92
11	0.60	0.60
7	0.15	0.04
8	0.15	0.06
10	0.30	0.30
12	0.21	0.21
14	1.00	1.00
16	0.15	0.03

A.3.2. ADBH System Outputs

Outputs

Energy

	Generated (kJ/hr)	Consumed (kJ/hr)	Net (kJ/hr)
Methane	9.37E+06	9.75E+05	8.40E+06
Hydrogen	2.47E+06	0.00E+00	2.47E+06
Heat (Integrated)	1.02E+06	9.49E+05	6.75E+04
Power_Mixing	0.00E+00	2.62E+05	-2.62E+05
Power_Strip. (Steam)	0.00E+00	4.68E+04	-4.68E+04
Power_Pumping (Integrated)	0.00E+00	6.56E+03	-6.56E+03
Power_Strip. (N2/H2)	0.00E+00	7.89E+03	-7.89E+03
Total (Integrated w/steam strip.)	**1.29E+07**	**2.24E+06**	**1.06E+07**
Total (Integrated w/N2/H2 Strip.)	1.29E+07	2.20E+06	1.07E+07
Power_Pumping (Unintegrated)	0.00E+00	1.25E+06	-1.25E+06
Heat (Unintegrated)	0.00E+00	9.49E+05	-9.49E+05
Total (Unintegrated)	1.29E+07	4.43E+06	8.42E+06

Mass Flows

[NH4+] mg/L	10000	
C:N (C)	3	75%
C:N (N)	1	25%

	%CH4	%CO2
Before	62.8%	37.2%
After	80.7%	19.3%

	Stream	**In kg/hr**	**Out kg/hr**
Total Solids	1	1000	
CH4	16	0	156.63
CO2	16	0	197.46
CO2 (aq)	3	0	5.86
CaCO3 (s)	4	0	13.32

H2	18	0	17.24
Water	2, 14	3302.23	3482.35
Ca(OH)2	new1	9.86	0.00
Ca(OH)2	new2	443.75	0
Ca2+ (aq)	14	0	114.94
CaCO3 (aq)	14	0	312.31

Curriculum Vitae

David Babson
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I. EDUCATION

- Ph. D., Rutgers University, New Brunswick, NJ. October 2010
  - Dissertation: *Improving Energy Recovery from Biomass Waste Streams – from Mega-landfills and Biorefineries to Microbial Communities*
- M.S., Rutgers University, New Brunswick, NJ. January 2007
  - *Low Cost Scaleable Synthesis of Disperse, Single and Multicomponent Metal Oxides*
- B.S., University of Massachusetts Amherst, May 2004
  - Thesis: *Development of a Transformation Protocol for* Taxus *Plant Cell Cultures*
  - Honors: Commonwealth (Honors) College, Cum Laude

II. RESEARCH EXPERIENCE

Graduate/Teaching Assistant, 2006-current
Department of Environmental Sciences, Rutgers University, New Jersey

Graduate Research Assistant, 2004-2006
Department of Chemical & Biochemical Engineering, Rutgers University, New Jersey

III. TEACHING EXPERIENCE

General Chemistry Instructor, Summer 2008, 2009 & 2010
Engineers of the Future Summer Program, Rutgers University, New Jersey

Teaching Assistant, Fall 2008
Department of Environmental Sciences, Rutgers University, New Jersey

Pre-Calculus Instructor, Summer 2007
Engineers of the Future Summer Program, Rutgers University, New Jersey

College Algebra Instructor, Summer 2006
Engineers of the Future Summer Program, Rutgers University, New Jersey

Teaching Assistant & Lab Instructor
Department of Material Sciences and Engineering, Rutgers University, New Jersey

IV. PUBLICATIONS

Babson, D., S. Prakash, and D. Fennell. (2010). Anaerobic Digestion for Methane Generation and Ammonia Reforming Hydrogen Production: Theoretical Energy Balance of a Model System. To be submitted to *Biomass and Bioenergy*

Babson, D., K. Sullivan, T. Zebib, M. Brennan, A.J. Both, and D. Fennell. (2010). Comparative Energetic and Economic Analysis of Digestion of Equine Waste on Farms and at Regional Digesters. To be submitted to *Bioresource Technology*

Babson, D., D. Fennell, E. Ravit, and U. Krogmann. (2010). An Energy Balance of a Municipal Solid Waste Management System and its Applications to Burlington County New Jersey. To be submitted to *Waste Management*

Babson, D., and D. Fennell (2010). Effect of Ammonia Removal by Simulated Stripping or Aeration to Stimulate Nitrification on Methane Production in Laboratory-Scale Anaerobic Batch Reactors. To be submitted to *Applied Microbiology and Biotechnology*

Babson, D., U. Krogmann, et al. (2007). Development of a Dynamic Energy Balance to Assess Operating Efficiency of the Burlington County Bioreactor Landfill in New Jersey (USA). Sardinia 2007: Eleventh International Waste Management and Landfill Symposium, Sardinia, Italy, CISA, Environmental Sanitary Engineering Centre.