Kinetic Modeling and Experimentation of Anaerobic Digestion

by

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Submitted to the
Department of Mechanical Engineering
in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Science in Mechanical Engineering

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ABSTRACT

Anaerobic digesters convert organic waste (agricultural and food waste, animal or human manure, and other organic waste), into energy (in the form of biogas or electricity). An added benefit to bio-digestion is a leftover high-grade organic fertilizer.

Models of the anaerobic digestion process do exist, but either rely on simple algebraic equations instead of biochemical reactions, or consider so many external parameters that they become overly complicated and require much input information and computation time. This work provides an intermediate kinetic model that predicts biogas output over time with few inputs. This kinetic model is justified by a small-scale laboratory experiment, and parameters are adjusted to match experimental results. This model can be used to optimize design parameters for an anaerobic digester, and provides information such as the relationship between digester sizing and feed rate. The process used here may be expanded to other feedstock materials and repeated for other similar applications, in an effort to expand anaerobic digestion systems as a clean energy source.

Thesis Supervisor: Alex Slocum
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BIOGRAPHICAL NOTE

Jonathan Rea is a mechanical engineering student at MIT graduating with minors in Energy Studies and Economics. The son of Edward and Rebecca Rea, he is originally from Palo Alto, California. He is a captain of the MIT varsity baseball team, and has been selected to the NEWMAC Academic All-Conference Team 3 times. He is a member of the Kappa Sigma fraternity and the Pi Tau Sigma Mechanical Engineering Honor Society. Following graduation from MIT, he will be joining the Materials Science Ph.D. program at the Colorado School of Mines.

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1. Introduction

Anaerobic digesters convert organic waste (agricultural and food waste, animal or human manure, and other organic waste), into energy (in the form of biogas or electricity). The benefits that the anaerobic digestion process provides are waste management, energy production, and fertilizer production.

Waste management is very important in both urban and rural settings. Most industrialized parts of the world already have waste management systems, though they often can be improved with regards to environmental impact. Rural areas often lack sanitation or reliable waste management systems, and this is a highly valuable service for health and environmental reasons.

Anaerobic digestion can provide energy to those who do not already have it, or can produce clean energy as an alternative to carbon-intensive energy production. Energy provided to those who do not already have it enables societies to accomplish more, and allows for a much higher quality of life. Clean energy is gaining more importance as global energy consumption grows and humans have more of an impact on the global climate.

The fertilizer by-product is another benefit that can add value to an anaerobic digestion system. Once a feedstock is consumed by the anaerobic digestion process, the leftover material can be used as a soil additive to enhance crop production. In rural settings, this fertilizer is best used locally or on-site of the anaerobic digester.

Biogas produced from anaerobic digestion often has high amounts of sulfur, which is what causes an uncomfortable smell. This is only very problematic if the intent is to use the biogas in a fuel cell, because the sulfur will poison the fuel cell. There are sulfur scrubbers available to remove the sulfur if the intent is to use the biogas in a fuel cell, but this adds significantly to cost. If the gas is just to be burned as cooking fuel or in a generator, then sulfur production is not necessarily a problem.

1.1 Biochemical Process of Anaerobic Digestion

Anaerobic digestion is a process of degradation of a substance in the absence of oxygen. The process occurs in the stomachs of animals, and the same biological process found in nature can be replicated and controlled by engineers. There are four major steps of anaerobic digestion, shown in figure 1 and described in detail in the following sections.

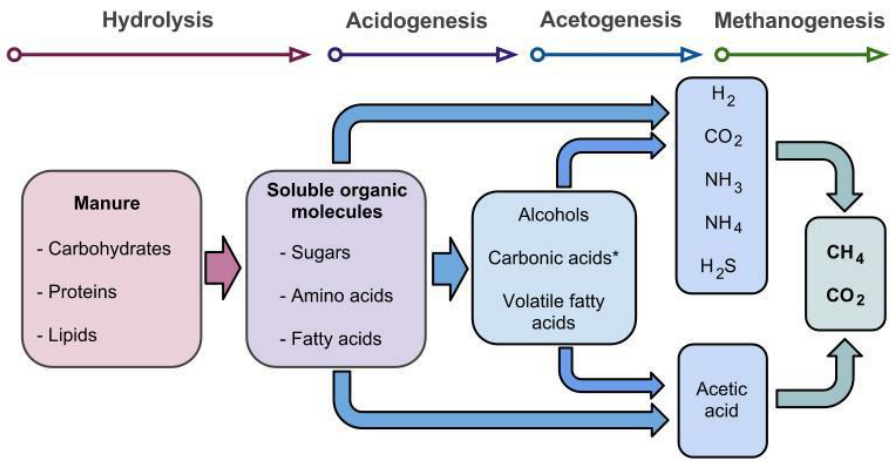

Figure 1: The anaerobic digestion pathway follows four major steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis.[1]

1.1.1 Hydrolysis

The first step in the anaerobic digestion process, hydrolysis is the cleavage of chemical bonds by the addition of water. The digester feedstock may be made up of many different components and materials, and thus there are many different versions of hydrolysis; carbohydrates, fats, and proteins are all broken down into smaller molecules by this initial step of anaerobic digestion.

In the case of a carbohydrate, polysaccharides (complex sugars) are broken down into monosaccharides. One example is the breakdown of lactose into galactose and glucose, given in figure 2[2].

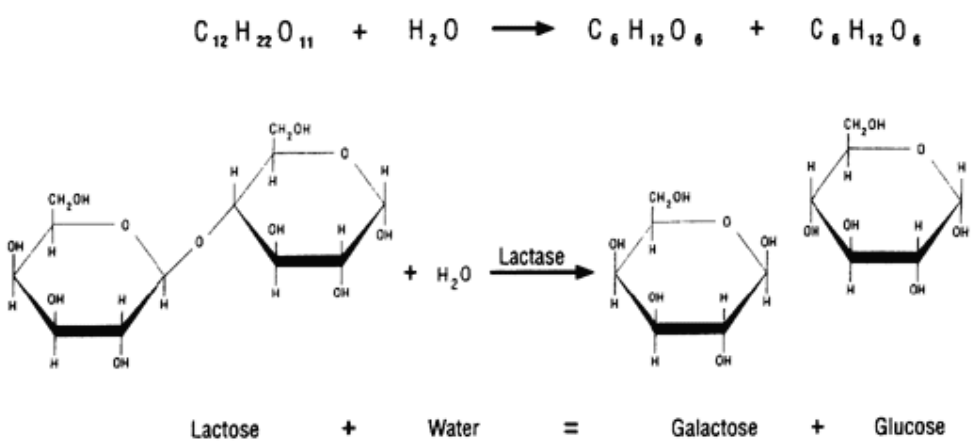

Figure 2[2]**:** Hydrolysis breaks down lactose, a polysaccharide, into galactose and glucose, monosaccharides.

In the case of lipids, usually triglycerides are split into three fatty acids and glycerol by the addition of three water molecules, as illustrated in figure 3[3].

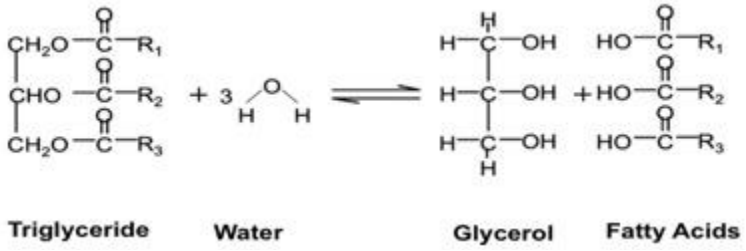

Figure 3[3]**:** Hydrolysis of a triglyceride results in glycerol and three fatty acids.

In the case of proteins, peptide bonds are broken to separate amino acids.[4, 5]

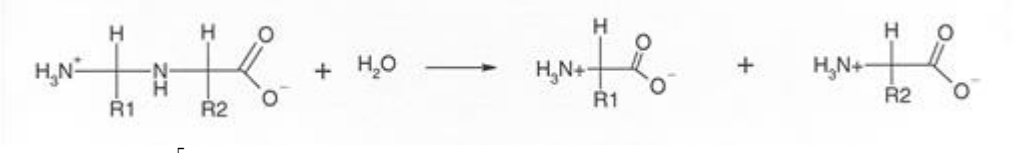

Figure 4[5]**:** Hydrolysis of a protein involves breaking a peptide bond to separate amino acids.

1.1.2 Acidogenesis

Acidogenic bacteria degrade the products of hydrolysis into volatile fatty acids. Some hydrogen, carbon dioxide, and acetic acid are also produced, which will skip the acetogenesis stage.[6] Acidogenesis represents the portion of figure 5 in which bacteria produce acetate and butyrate (volatile fatty acids) from glucose.

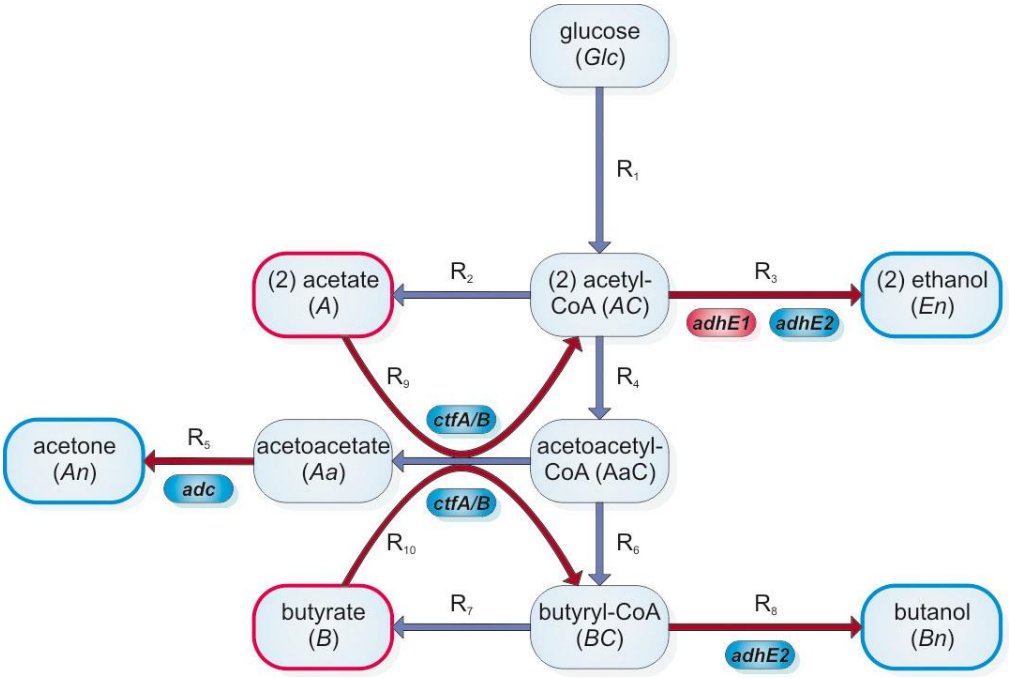

Figure 5[7]**:** During acidogenesis, bacteria produce acetate and butyrate (bordered with red edges). The fermentive pathway can also produce other by-products.

1.1.3 Acetogenesis

In the third step of anaerobic digestion, acetogenic bacteria consume precursors and produce acetate (acetic acid). One example of this process is the consumption of glucose, given in equation 1.[6]

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (1)$$

1.1.4 Methanogenesis

The final step of anaerobic digestion is the formation of methane by bacteria called methanogens. For the most part, the biological process here is the breakdown of acetic acid, given in equation 2, though other forms of the reaction can also produce methane via anaerobic digestion.

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (2)$$

1.2 Other Parameters that Influence Gas Production

Gas production from an anaerobic digester depends on the ability of bacteria to thrive inside the digester. The survival of bacteria depends on the temperature, pH, and physical conditions of the anaerobic digester.

1.2.1 Temperature

There are three anaerobic digestion operational temperature ranges. Psychrophilic digestion occurs at below 25 °C, or below room temperature. Mesophilic digestion occurs between 25 and 45 °C, while thermophilic digestion occurs above 45 °C[8]. In general, higher temperatures result in higher biogas production. Further, rapid temperature changes can upset bacterial activity, so for experimental studies, it is important that temperature is held constant[9].

1.2.2 pH

The survival of methanogenic bacteria also depends on the acidity of the environment that they are in: methanogenesis requires a near-neutral pH (between 6.5 and 7.5). A decrease in pH can inhibit gas production and can lead to further accumulation of acids[10].

1.2.3 Mixing and Other Physical Conditions

Contact between bacteria and the slurry that they are consuming is vital to the anaerobic digestion process. One way to maximize this contact is to keep the digester thoroughly mixed at all times.

Methanogens naturally live inside the stomachs of animals, and attach to the stomach lining as a way to secure a safe habitat with a steady supply of food. When placed inside of a man-made anaerobic digester, instead of floating around in the slurry, the bacteria attach to surfaces while being exposed to the flow of digestible material[11]. Some anaerobic digester designs address this issue by creating internal structures so that bacteria can attach to them and be exposed to more digestible material. Otherwise, mixing is an important design parameter in maximizing anaerobic digestion performance because it allows enhanced contact between bacteria and the material being consumed.

1.3 History and Use of Anaerobic Digestion

The generation of combustible gas from decomposing organic matter has been known for decades. In 1776, Volta determined that the amount of organic material and the amount of gas produced were directly connected. John Dalton and Humphrey Davy established that the combustible gas was methane in 1804-1808. Anaerobic digestion was applied to a septic tank in 1881, and has since been applied to wastewater treatment at much larger scales. In developing countries, where energy production is generally scarcer and more expensive, anaerobic digestion may have more relevance in the absence of strong alternatives. Notably, India is credited for having built the first-ever anaerobic digester in 1897, using human waste to meet lighting needs. Intensive plant design and technology research began in the 1950s, and the application of anaerobic digestion has grown over time. The largest biogas program in the world is in China, where over 10 percent of rural households use biogas[12].

1.3.1 Applications and Scales

Anaerobic digesters are very useful in agricultural settings, given that they take inputs of agricultural products and produce energy and fertilizer which can both be used at these sites. They are also useful in industrial settings, where economies of scale can be realized by handling large throughputs of material. They can be designed to take in virtually any type of organic waste, including plant matter, animal excrement, and by-products of industrial processes. Anaerobic digesters range in size from as small as taking in the food scraps from one family to as large as entire wastewater treatment plants for a large city.

1.3.2 Case Study: ARTI

The Appropriate Rural Technologies Institute (ARTI) has developed a household-scale anaerobic digester that takes in kitchen scraps and produces biogas used for cooking. The main added benefits of this model are waste management in an area that does not have it (better sanitation, less pollution) and the reduction of cooking cost for families with low income. This is a low-cost model that uses cheap materials to achieve reduced initial costs and a shorter payback period. Because the feedstock for the ARTI model is not at all processed (as an alternative to using animal manure which has been processed inside the stomach of an animal), it has a higher biogas potential than most other applications. 100 liters of biogas is reported to produce 23 minutes of cooking time[13].

Figure 6[13]**:** The ARTI anaerobic digester design, which converts a feedstock of kitchen scraps to biogas used for cooking, targets the application of developing world communities.

1.3.3 Case Study: Deer Island Wastewater Treatment Plant

The Deer Island Wastewater Treatment Plant, run by the Massachusetts Water Resources Authority, serves over 1 million people in the greater Boston area. The anaerobic digesters on this site use sewage waste as a feedstock, and produce biogas that is used in boilers to produce steam and electricity. Because it is a net energy consumer, the primary function of the Deer Island Wastewater Treatment Plant is to "protect Boston Harbor against pollution from Metropolitan Boston's sewer systems."[14] However, the plant does provide enough energy for a majority of the heating needs of the facilities on the island, as well as approximately 3 megawatts of electricity[14].

Figure 7: The Deer Island Wastewater Treatment Plant uses sewage waste from the greater Boston area to produce steam heating and electricity.

1.3.4 Case Study: Brinson Farms

Brinson Farms, in Prentiss, MS has an anaerobic digestion system specifically designed for chicken litter. About 1600 tons of waste is produced per year, and mixed with water to reach 5% solids concentration. This farm has the potential to produce about 11,250,000 cubic feet of biogas each year that supports a 65 kW generator. In addition, the fertilizer value of the effluent liquid is high due to a favorable fraction of Nitrogen, Phosphorous, and Potassium (NPK).[15]

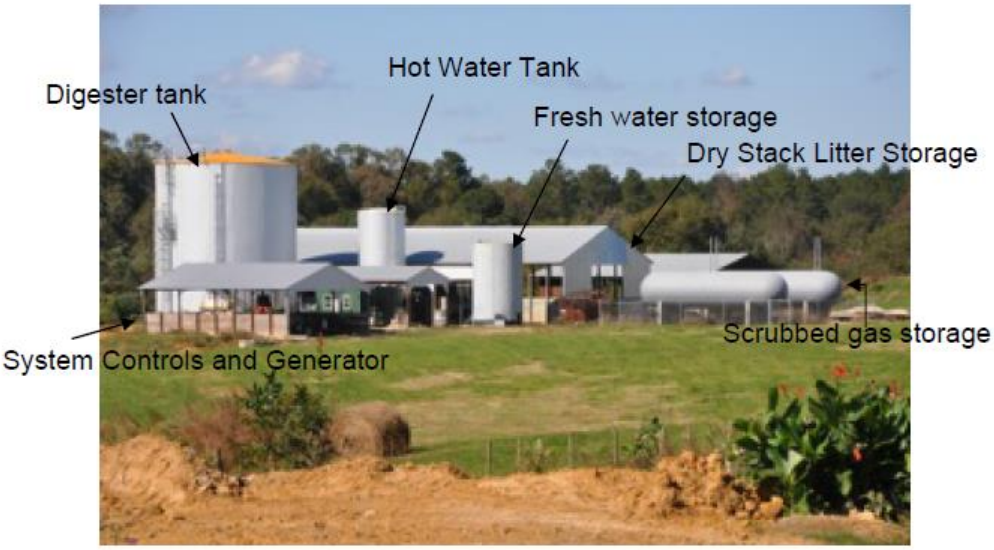

Figure 8[15]**:** Brinson Farms, in Prentiss, MS, has an anaerobic digestion system designed for chicken manure that takes in 1600 tons of waste and supports a 65 kW generator.

1.3.5 Other Case Studies

Several other examples have been compiled by MIT D-Lab and are given below in table 1. This demonstrates the wide variety of scales and applications of anaerobic digesters.

Table 1[16]**:** Anaerobic digester case studies that demonstrate the wide variety of scales and applications of anaerobic digesters.

Description	Location	Feedstock/Input	Digester Size	Energy Output
Central Biogas Supply System	Beijing, Fangshan District, China	Cow dung	$1{,}100\ m^3$ digester capacity, 44 tons of cow dung per day (1000 cows)	$2{,}000\ m^3$ biogas used for cooking fuel
Power Generation	Beijing, Yanqing Deqingyuan, China	Poultry Manure	Four $3000\ m^3$ tanks	Two generators of 1064 kW
Clean Development Mechanism	Minas Gerais, Brazil	Pig Manure	500 pigs	$12{,}500\ m^3$ biogas per day
Small Scale USAID Project	Bahia, Brazil	Goat Manure	Small - $700 construction cost	Biogas for lighting and cooking
Polyethylene Tube Biodigester	Santa Fe de Guatuso, Costa Rica	Cow and pig manure	$8.5\ m^3$, $300 construction cost	Biogas for cooking stoves
Chiquita Brands	Guapiles, Costa Rica	Food waste (bananas, papayas, mangos, other fruit)	Industrial scale	Electricity
ARTI household digester	Pune, South India	Food waste from kitchens	$1\ m^3$ digester capacity	Cooking gas
Toilet-to-methane system	Shirdi, Maharashtra (India)	Human waste	30,000-50,000 people	Electricity generation and methane for cooking stoves
Wastewater Treatment	Oakland, CA	Municipal sewage waste	Large scale	Electricity used at wastewater treatment facility

2. Literature Review and Scope of this Project

2.1 Literature Review of Anaerobic Digestion Modeling

The IWA Anaerobic Digestion Model 1 (ADM1) is one of the most comprehensive anaerobic digestion models[17]. The highly structured model includes multiple steps describing chemical and physical processes; it considers the four steps of hydrolysis, acidogenesis, acetogenesis, and methanogenesis, and how those steps differ for input carbohydrates, proteins, and lipids. The differential and algebraic equation set has 26 dynamic state concentration variables and 8 implicit algebraic variables per reactor. It is highly accurate but requires input of many parameters and a high level of complexity.

Polit et al use a mass-balance model to calculate output gaseous flow rates[18]. This paper attempts to find a balance between complicated models based on differential equations and "black box" models derived entirely from data. However, the model includes "fuzzy" logic to include pH and temperature dependence and match modeling to real-world data.

Wu et al developed a 3-D numerical simulation model based on conservation of mass, conservation of energy, and species transport that predicts biogas production from plug-flow anaerobic digesters[19]. Their work uses a first-order kinetic model that considers the ratio of carbon, hydrogen, and oxygen of the feedstock. This most basic model is useful for the initial development of the model of this project.

Mahar et al, in the analysis of waste agricultural biomass, considered a similar biochemical reaction to Wu et al for the prediction of methane potential of different waste inputs, but adding a term for nitrogen[20]. The biochemical reaction is not applied, however, to any time-dependent kinetic gas production predictions.

Wu et al also provides a review of many previous pieces of work. These include a model by Chen and Hashimoto that predicts gas production as a function of volatile solids, kinetic parameter, specific growth rate of bacteria, and temperature, but does not consider biochemical processes. Hill used this model and a computer analysis to determine maximum volumetric methane production, but did not use kinetics to model gas production over time. Other simple models address the effects of temperature, pH, nutrients, and toxins, but not kinetics of gas production based on biochemical reactions. Complex models such as ADM1 and a model produced by Minott include as many as 34 differential and algebraic equations or consider spatial dependence and fluid dynamics.

Yu et al give another review of anaerobic digestion models, comparing between "black box" models and comprehensive complex models[21]. The balance between these models given by this work is described in section 2.2.

2.2 Scope of this Project

One anaerobic digester design approach is to simply build a digester, put in a feedstock, and improve the use of the digester by trial and error. This method may apply to an individual in a rural household with few resources and an immediate need for a functioning digester, is largely employed by groups like ARTI.

Another design approach would be to create a comprehensive analysis of all possible parameters that impact the anaerobic digestion process, and run full simulations that consider every scenario to maximize the benefits under any conditions. This method may apply to a large company that plans to install many digesters at sites around the world and has resources of many engineers and large computational capacity.

This thesis project aims to create a model of the anaerobic digestion process that is an intermediate between the two approaches given above. It aims to identify the most significant parameters and otherwise simplify the process to reduce computation time and required input information. It makes most sense to apply this model at an intermediate scale, such as small farmers who have some but limited resources and want to improve performance of an anaerobic digester.

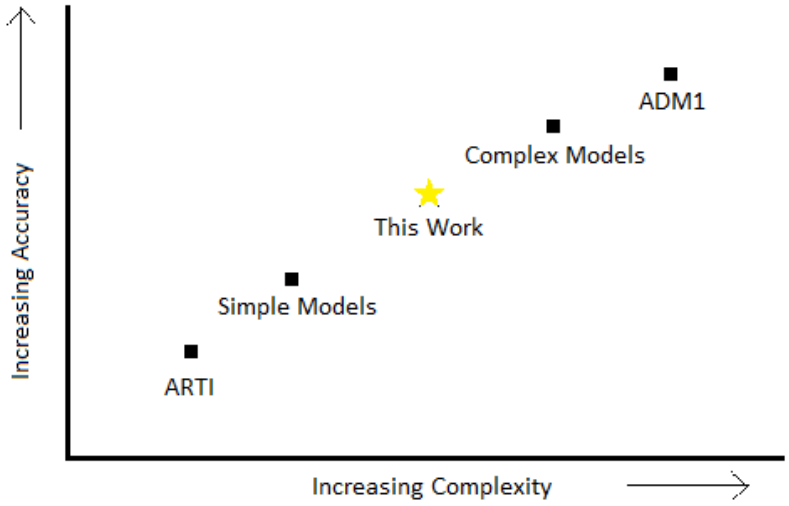

Figure 9: The scope of this project and how it fits in with other design approaches.

Chicken waste is selected as an immediate application of this model and experimental data is used for fitting the model to the real world. Because chicken waste has potential for higher biogas production than many other feedstocks, it is an attractive option for scaling up and making economically viable anaerobic digesters. It also makes sense as a choice for analysis of this model because there are many small-scale chicken farmers that could make use of the model.

3. Kinetic Model of Anaerobic Digestion

3.1 Purpose of this Model

This model attempts to strike a balance between simplicity and effective biogas prediction. The purpose is not to create an entirely comprehensive model that takes all factors into account and predicts biogas output to a very high level of precision. It can, however, predict biogas output over time, instead of other simple models that assume that a reaction goes to completion. This is useful because it informs how much biogas potential is being captured by an anaerobic digester based on how long a feedstock is held inside the digester, which is determined by size and feed rate.

3.2 Model Assumptions

The initial assumptions of this model are given in bullet form below.

- Constant temperature
- Constant digester volume
- Perfect mixing
- Ideal bacterial conditions, meaning full digestion
- Input waste consists of only C, H, and O
- Products of reaction include only CO_2 and CH_4
- No accumulation of ashes

3.3 Model

3.3.1 Basic Input-Output Model and Biochemical Equation

In the simplest case of a well-stirred single tank reactor, reactants A and B are put into the digester at a certain rate (in the model, this value is specified by a user input). Once in the digester, A and B break down into products C and D at a rate based on reaction coefficients. Some of A and B don't break down all the way, and leave through the outlet - the amount that leaves instead of being broken down depends upon digester size and feeding rate, which determine the residence time of the feedstock.

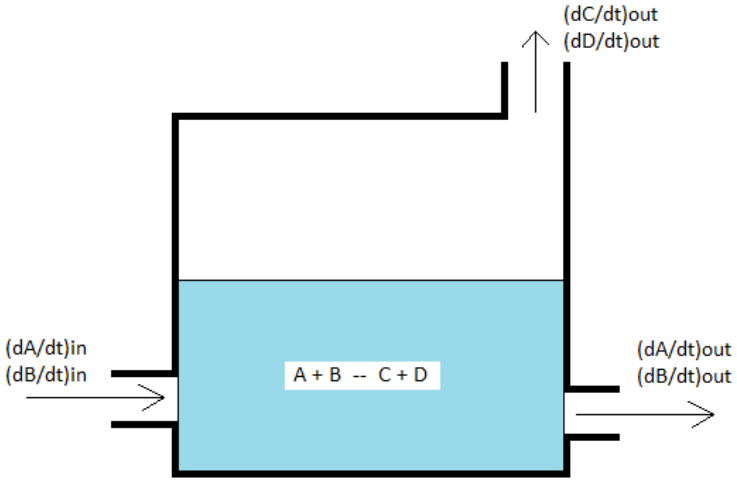

Figure 10: Basic input-output model of a well-stirred single tank reactor. This simple process is used for the kinetic model of this work.

The biochemical reaction equation used for this analysis is taken from Wu et al[19], and is reproduced in equation 3 below.

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \leftrightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 \quad (3)$$

Or

$$C_nH_aO_b + (C_1)H_2O \leftrightarrow (C_2)CO_2 + (C_3)CH_4 \quad (4)$$

With

$$C_1 = n - \frac{a}{4} - \frac{b}{2} \quad (5)$$

$$C_2 = \frac{n}{2} - \frac{a}{8} + \frac{b}{4} \quad (6)$$

$$C_3 = \frac{n}{2} + \frac{a}{8} - \frac{b}{4} \quad (7)$$

The biochemical reaction is automatically balanced and can be applied to any input with known relative ratios of carbon, hydrogen, and oxygen. The model assumes that these elements are the only components of the feedstock.

Table 2: Balance of biochemical reaction used in this model.

	Left	Right
C	n	n/2 + n/2 = n
H	a + 2*(n – a/4 – b/2) = 2n + a/2 - b	4*(n/2 + a/8 – b/4) = 2n + a/2 -b
O	b + (n – a/4 – b/2) = n –a/4 + b/2	2*(n/2 – a/8 + b/4) = n – a/4 + b/2

3.3.2 Differential Equations

A set of differential equations can describe the rate of accumulation of each component of the reaction. For example, the rate of change of concentration of "A" in the tank is equal to the rate of change of concentration due to new feedstock being added plus the rate of change of concentration due to material going to outlet plus the rate of change of concentration due to the biochemical reaction. The set of differential equations that follows from the simple equation (4) is given below.

$$\frac{d[A]}{dt} = \frac{d[A]}{dt}_{in} - \frac{d[A]}{dt}_{out} - k[A][B]^{C_1} \tag{8}$$

$$\frac{d[B]}{dt} = \frac{d[B]}{dt}_{in} - \frac{d[B]}{dt}_{out} - C_1 k[A][B]^{C_1} \tag{9}$$

$$\frac{d[C]}{dt} = \frac{d[C]}{dt}_{in} - \frac{d[C]}{dt}_{out} + C_2 k[A][B]^{C_1} \tag{10}$$

$$\frac{d[D]}{dt} = \frac{d[D]}{dt}_{in} - \frac{d[D]}{dt}_{out} + C_3 k[A][B]^{C_1} \tag{11}$$

The reaction rate constant k can be either determined experimentally or taken from literature. Theoretically, we can determine k from the Arrhenius equation:

$$k = Ce^{-E_a/RT} \tag{12}$$

For an initial approximation, Wu et al[19] gives an estimation of the value of k:

$$\mathrm{k} = 6.21 * 10^{-8} \left(\frac{mol}{L} * t\right)^{-1} \tag{13}$$

The value of k used in this model is determined by matching the model to the experiment initially by eye and more accurately by running a number of simulations.

3.3.3 Molar Ratios and Coefficient Calculations

The ultimate analysis selected by the user of the model is converted from mass ratios to molar ratios in order to determine the constants n, a, and b for the feedstock $C_nH_aO_b$. Ultimate analysis gives mass ratios C:H:O (in grams) which are then defined as variables $nbymass: abymass: bbymass$. Then, for molar masses of carbon (mm_{Carbon}), hydrogen (mm_H), amd oxygen (mm_O) we have:

$$\text{n} = \frac{nbymass}{mm_{Carbon}} = \frac{nbymass}{12.0107} \tag{14}$$

$$\text{a} = \frac{abymass}{mm_H} = \frac{abymass}{1.0079} \tag{15}$$

$$\text{b} = \frac{bbymass}{mm_O} = \frac{bbymass}{15.999} \tag{16}$$

The constants C_1, C_2, and C_3 are then calculated using equations 5, 6, and 7.

The molar masses of each reactant and product can then also be calculated:

$$\begin{aligned} \text{mm}_\text{A} &= n * mm_{Carbon} + a * mm_H + b * mm_O \\ &= 12.0107n + 1.0079a + 15.999b \end{aligned} \tag{17}$$

$$\text{mm}_\text{B} = 2 * mm_H + mm_O = 18.0148 \frac{g}{mol} \tag{18}$$

$$\text{mm}_\text{C} = mm_{Carbon} + 2 * mm_O = 44.01 \frac{g}{mol} \tag{19}$$

$$\text{mm}_\text{D} = \text{mm}_\text{Carbon} + 4 * mm_H = 16.04 \frac{g}{mol} \tag{20}$$

3.3.4 Additional Parameters

Now the only other parameters needed for the model are the kinetic parameter k, the feeding and removal rates, and the initial conditions.

The kinetic parameter k is initially determined by eye to make the time scale of the reaction consistent with experimental data, and is later determined more accurately by running a number of simulations.

The feeding and removal rates of each component of the biochemical reaction must be given by the user. In some circumstances, the feeding rate may actually be continuous, such as in the case of a wastewater treatment plant. In other cases, feeding may happen at specific times, such as once per day or once per week, and to fit this model one option is to average the amount of feedstock put in and estimate it as continuous flow in. The user may input a continuous feeding rate ($\frac{dA}{dt}$) in units of grams per second, and the change in concentration due to this feeding rate is calculated using the molar mass of the component as well as the capacity of the digester ($C_{digester}$). Equation 21 gives an example of this calculation.

$$\frac{d[A]}{dt}_{in} = \frac{\frac{dA}{dt}}{mm_A * C_{digester}} \tag{21}$$

Another option would be for the user to input discrete amounts of feedstock at specific times, when the digester is fed during operation. Because the only products of the reaction are assumed to be carbon dioxide and methane, this would effectively mean that the digester would be filled with as much of the input feedstock as the digester has remaining capacity for after the previous material has been digested, and any extra material that is put in simply flows through and is not digested at all.

3.3.5 Initial Conditions

If the user inputs digester capacity, initial mass of water in grams (m_{water}), and initial mass of waste in grams (m_{waste}), the initial concentrations can be calculated using the molar masses of each component of the slurry (mm_{waste}, mm_{water}):

$$[A]_0 = \frac{m_{waste}}{mm_{waste} * C_{digester}} \tag{22}$$

$$[B]_0 = \frac{m_{water}}{mm_{water} * C_{digester}} \tag{23}$$

And because none of the reaction has been completed at the beginning of the simulation,

$$[C]_0 = [D]_0 = 0 \tag{24}$$

3.3.6 Simulation

The model updates for small time intervals the concentration of each component of the biochemical reaction based on the rate of change of each concentration calculated from equations 10-13. The updates are linear but given small enough time steps (1 second) the predicted gas output follows a smooth curve and the approximation gives useful results.

Because the model calculates the change in concentration of each gas in moles per liter, the mass of each gas (m_{CO_2}, m_{CH_4}) must be back-calculated from the predicted concentration of each reactant and product over time.

$$\mathrm{m}_{\mathrm{C0}_2} = C = [C] * mm_C * C_{digester} \tag{25}$$

$$\mathrm{m}_{\mathrm{CH}_4} = D = [D] * mm_D * C_{digester} \tag{26}$$

Described in section 7.1, two other parameters are added to match the model with real-world experimental results. First, there is a time delay (τ) before gas production begins in the start-up of an anaerobic digester, because some initial time is required before a sustainable microbial population can be established to start producing a significant amount of gas. Second, there is a limiting factor (f) that prevents the reaction from going to completion. Reactions rarely go entirely to completion, and in the case of anaerobic digestion, this limiting factor is a result of imperfect mixing, toxin accumulation, and pH and temperature effects. Instead of creating a model that considers all possible causes of these two adjustment parameters, the values of the parameters are selected to fit the data so that the model can remain simple and be used for other applications.

3.4 Application of Model to Chicken Waste

To apply this model to the specific feedstock of chicken waste, we need to know the chemical components of the waste as well as a reaction rate constant. The model considers only carbon, hydrogen, and oxygen as input elements, and the relative ratios of these elements can be taken from published values for ultimate analyses of chicken waste. Table 3 below lists ultimate analyses from a number of sources, and table 4 gives the final ratio of each element used for the model based on the published ultimate analyses.

Table 3: Published ultimate analyses of chicken waste.

Reference	C (%)	H (%)	O (%)	N (%)	S (%)	Ash (%)	Moisture (%)
Dayananda et al[22]	25.2	3.5	22.25	6.7	0.25	34.8	7.3
Bock Consulting[23]	27.2	3.7	23.1	2.7	0.3	15.7	27.4
Serio et al[24] (Broiler)	37.0	5.0	30.8	4.3	0.8	22.1	11.4
Serio et al[24] (Layer)	29.4	3.8	25.2	4.6	0.8	36.3	9.6

The composition of chicken waste depends on the type of chicken, the feed they are given, and the external conditions that they are in; for example, broilers produce waste with higher moisture content than layers. Because of the variation in waste composition for different types of chickens in different conditions, only one set of published values for ultimate analysis is used instead of averaging over published values. The moisture values obtained during experimental waste characterization (section 4.1.1) are closest to those of Bock Consulting[23], so in order to best match experimental data to the model, the ultimate analysis used for modeling is taken from this reference. It is assumed that if the moisture content of the waste is most closely matched to this ultimate analysis, the other values will also be most accurate if all parameters of the same literature source are used. The ultimate analysis used for modeling is reproduced in table 4.

Table 4: Ratio of elements used for modeling.

Element	C	H	O
Ratio	27.2	3.7	23.1

The feedstock used for experiments in this work is pure chicken waste. In practice, most small farmers have bedding (typically sawdust) that naturally gets mixed into the waste and would be added to the feedstock that a farmer would put into a digester. This would effectively be co-digestion of multiple materials. The way to adjust the model to analyze this situation would be to input the total mass of each element by summing the mass of each element input based on the ultimate analysis of both components of the feedstock – both the chicken manure and the sawdust. In practice, the first steps of breaking down the bedding material takes longer than the initial steps of breaking down the manure; when displaced as effluent, a larger portion of the bedding would be undigested and would come out as part of the valuable fertilizer as the output of the digester.

3.5 Initial Modeling Results

Assuming the following parameters:

- reaction rate constant $k = 5 * 10^{-6}$
- initial amounts of 100 g of waste, 100 g of water
- digester capacity is 1 L
- feeding rate and removal rate are zero
- reaction goes to completion and is uninhibited by any limiting factors

the model gives the following curves:

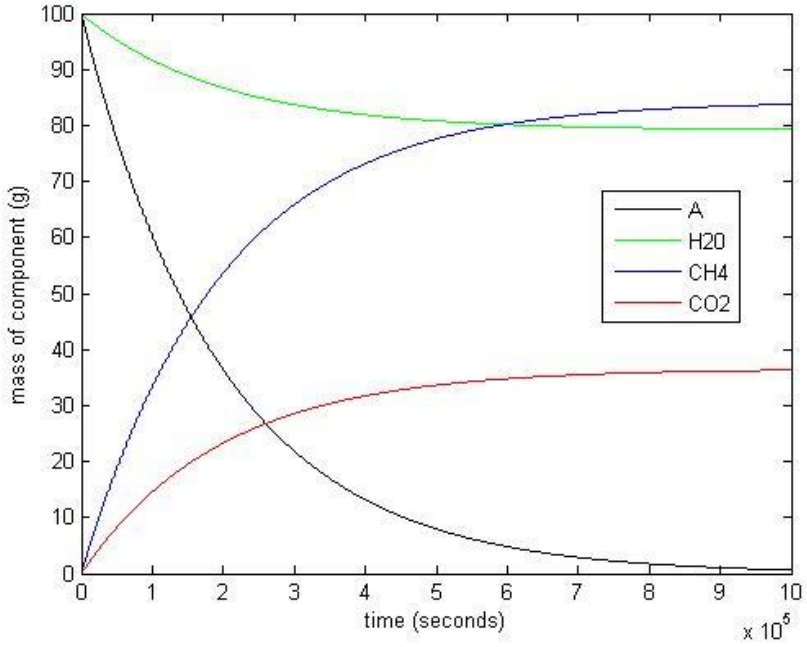

Figure 11: Initial modeling results with basic inputs.

These initial results are unlikely to match the true results because in practice no reaction goes to full completion and the model predicts ideal settings that are not found in the real world. This is why, later, the model is adjusted with a time delay (τ) and limiting factor (f) to adjust the ideal conditions to more realistic ones. However, this figure does demonstrate that the consumption of products and production of reactants follows exponential decay and logarithmic growth. It also shows that the reactant A (the feedstock) is consumed much more quickly than water. Water will likely not be the limiting reactant, but it is still important for diluting waste to prevent ammonia accumulation and for improving mixing capability of the digester.

From a design perspective for the farmer, this means after about 100 hours 80% of the methane that can be obtained is reached. So in a week of digestion all the methane is obtained. This makes sense as it motivates the farmer to clean the coop every two weeks: 10 days to cook, two days to unload and use the fertilizer, two days to clean the coop and reload the digester. Furthermore, if enough water is added to not only supply the reaction but to make it easy to empty the reactor into a sprayer for easy application of liquid fertilizer to fields.

4. Waste Characterization

The waste obtained for experimental evaluation was taken from NerdHerd Farm, a small farm in New Hampshire that raises various animals including chickens. Samples were collected and transported to MIT D-Lab, where they were stored in a fume hood until use. Samples were stored for less than a week before being used, a time that is similar to what would be expected in the practical use of an anaerobic digester placed locally on a chicken farm. The chicken waste contains small amounts of straw and other farmland material in quantities assumed to be negligible relative to the amount of pure chicken waste. A photo of the chicken waste is given in figure 12 below.

Figure 12: Chicken waste used for experiments are from NerdHerd Farm in New Hampshire. Small amounts of straw and other farmland material are assumed to be negligible relative to the quantity of chicken waste.

4.1 Solids Content

To evaluate the solids content of the chicken waste used for this experiment, samples are dried in a briquette oven at 175 degrees Fahrenheit for approximately two days. The waste is spread in a thin layer and pressed down slightly to maximize surface area to make the drying process faster. The mass of the waste is measured before and after drying using a Cen-Tech digital scale with measurements given to the nearest gram. All moisture is assumed to have evaporated, and the remaining percentage of mass represents the total solids content of the waste.

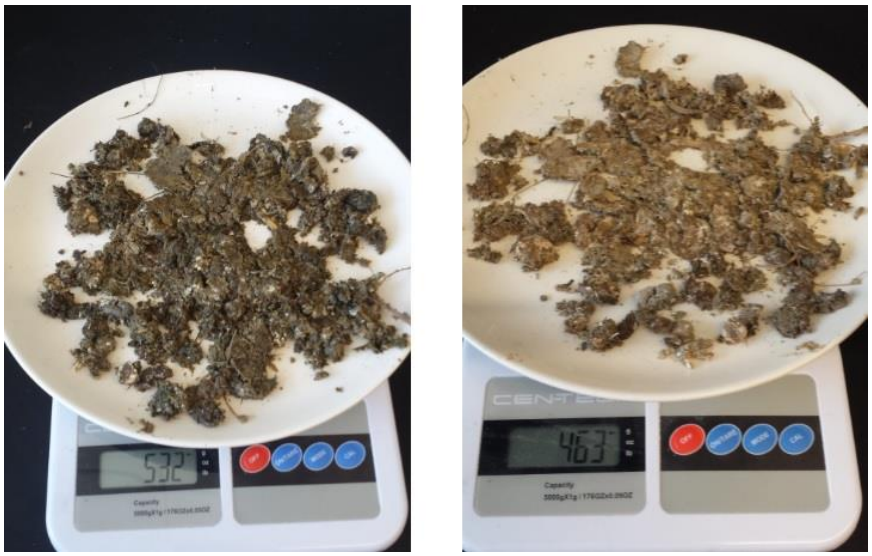

Figure 13: Chicken waste is dried to experimentally determine moisture content. The mass of the waste is measured before and after drying in a briquette oven to find the percentage of mass after drying (the solids content).

The measured values of the waste are given in table 5, and total solids is calculated as the ratio of mass after drying to mass before drying.

Table 5: Solids content measurements and calculations characterize the chicken waste solids content of 31 ± 1 %.

Mass before drying (g)	Mass after drying (g)	Total solids (%)
100	31	31%
100	30	30%
100	32	32%

The data gives a total solids content of 31 ±1%. This value is used to determine the ultimate analysis used for modeling (section 3.4) and in experimental design (section 6.2) to reduce the risk of excessive ammonia buildup by keeping the solids content of the slurry below 10 %.

4.2 Density Measurement

The density of the waste is measured by simply determining the volume of a given mass of waste. An Erlenmeyer flask is placed on a scale and initially filled with water. Waste is placed into the flask; its volume is determined by the amount of displaced liquid in the flask, and its mass is determined by the change in mass observed on the scale. The measurement is done three times, and measured values and calculation of density of the waste are given below. Density is calculated as the ratio of mass to volume, and is found to be $1.13 \pm .01 \frac{kg}{L}$.

Table 6: Density measurements and calculations find the chicken waste samples to have a density of 1.13 ± .01 kg/L.

Mass of sample (g)	Volume of sample (mL)	Density of sample (kg/L)
56	50	1.12
113	100	1.13
117	103	1.136

For a sense of accuracy, the same measurement was done to evaluate the density of the tap water that was mixed with the chicken waste to produce the slurry. Samples were evaluated with densities of $0.985, 1.00$, and $0.995 \frac{kg}{L}$ to give an average density of $0.99 \pm 0.01 \frac{kg}{L}$. The standard value for density of water is $1000 \frac{kg}{m^3} = 1 \frac{kg}{L}$.

5. Experimental Design Iterations

In order to verify predicted gas output from the kinetic model, this project includes experimental evaluation of the anaerobic digestion process. Chicken waste is collected from a small chicken farm and put into an anaerobic environment. Gas production is measured and used to adjust parameters of the model. Multiple iterations of the experiment are considered before a final design option is selected. The purpose of the experiment is to obtain real-world values of gas production over time. This can be used to adjust the time delay (τ) and limiting factor (f) in the kinetic model to match the model to the specific digester set-up used.

5.1 Experiment Iteration 1: Balloon Test

As a very simple initial experiment, waste is put into an enclosed tank with a balloon placed on top. Gas produced by the digestion process inflates the balloon. This is meant to be the most basic of experiments to demonstrate the fact that anaerobic digestion is a real phenomenon and that gas can truly be produced by simply placing chicken manure and water into an enclosed anaerobic environment and letting it sit for a period of time.

To avoid contamination from used Erlenmeyer flasks, the flasks are boiled in hot water prior to starting the experiment. 50 grams of chicken manure is mixed with 350 grams (yellow balloon) and 750 grams of water (blue balloon) in the two variations of the experiment. The flasks are then stored in a fume hood at room temperature.

Figure 14: Balloon anaerobic digester used as a baseline experiment to demonstrate that biogas can be produced by simply putting chicken manure and water into an enclosed anaerobic environment.

In this experiment, no quantitative data is collected. Qualitative observations are made to aid in design of future experiment iterations. After 19 days held at ambient conditions, gas production was observed. This is demonstrated by the pressure inside the balloon in figure 15.

Figure 15: Noticeable gas collection was observed for the balloon digestion experiment after 19 days.

Observations were made only sparsely (one observation every few days) and the balloon connected to the top of the Erlenmeyer flask was only marginally secure (the yellow balloon was found to have been ripped after a few days and was replaced). This experiment doesn't give data that can be used to adjust modeling parameters; however, the fact that gas is produced from this basic experiment does give some baseline reasoning that the process of anaerobic digestion does occur when simply mixing water and chicken manure in an enclosed container.

5.2 Experiment Iteration 2: Brass Through-Wall Fitting

To measure biogas produced by anaerobic digestion, one method is to create a small digester tank that remains enclosed for the duration of a batch process of anaerobic digestion. The experiment done for this iteration is modeled after lab-scale experiments by Mississippi State University, shown in figure 16.

Figure 16[15]**:** Anaerobic digester experimental setup used for laboratory tests at Mississippi State University.

In this experiment iteration, a 1 L polypropylene bottle is used as a sample digester tank. A brass through-wall fitting connects the tank to a pressure gauge, so that the amount of gas produced by the process can be measured. Teflon tape is used to create an air-tight seal between threaded connections, and a rubber washer is used to create an air-tight seal between the brass through-wall fitting and the top of the digester tank. Figure 17 demonstrates the parts used and the final construction of this experiment.

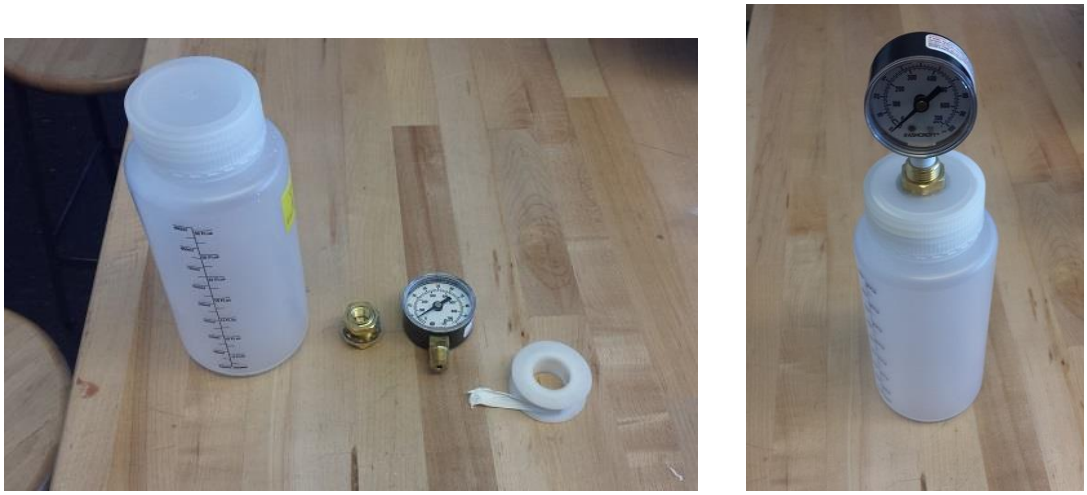

Figure 17: Parts used and final construction of a laboratory anaerobic digester using a brass through-wall fitting. The experiment is found to have a leak and future improved experiments are constructed.

Initially, 70 grams of chicken waste is mixed with 420 grams of water. The digester is stored inside a water bath with temperature held at 92.7 ± 0.4 degrees F, to keep the conditions in the middle of the mesophilic range.

Figure 18: The brass through-wall fitting experiment was held inside a water bath at a temperature of 92.7 ± 0.4 degrees F.

Before collecting data, the digester tank was held underwater (similar to figure 20) to see whether or not air can easily escape, which would produce bubbles. The digester was not observed to generate a significant amount of bubbles; still, the results of this dunk test are not conclusive because the test generally only works for significant leaks and would not clearly demonstrate a slow leak over time or a very small leak (which may be plugged from the pressure of being underwater).

Data was collected for three weeks, though no pressure buildup and thus no gas collection was observed inside the digester tank. Upon further examination of the experimental design, the rubber gasket used to create a seal was not uniformly pressed down on either side of the hole at the top of the digester tank. It is highly likely that the brass through-wall fitting was unable to create a reliable seal at the top of the tank, and this error is assumed to account for both exposure to atmospheric air and leaking of any gas produced by the slurry. Future experimental design options are thus pursued to alleviate the leaking concerns.

5.3 Experiment Iteration 3: Bulk Head Fitting

In order to address the issue of the leak at the connection between the air space in the tank and the pressure gauge used to measure gas production, a bulk head fitting is used in place of a brass through-wall fitting. It is a more reliable experimental design because the bulk head fitting is designed for creating tight seals while the brass through-wall fitting is meant for connecting pipes through a wall without regard for gas leaks outside of the pipe.

The experimental setup is identical to that of the brass through-wall fitting, except for the connection from the top of the digester tank to the pressure gauge. Initially, 70 grams of chicken waste is mixed with 420 grams of water inside of two different 1 L polypropylene bottles. The digester is stored inside a water bath with temperature held at 92.7 ± 0.4 degrees F, to keep the conditions in the middle of the mesophilic range.

5.3.1 Bulk Head Fitting Leak Tests

To test for air leaks, the digester is placed under water, similar to what was done for the brass through-wall fitting leak test, to see if bubbles are generated. No bubbles were observed, though once again, that does not guarantee an absence of slow leaks.

Figure 19: The bulk head fitting digester is placed under water to determine whether or not there are significant air leaks in the system.

To test the experimental setup more rigorously for leaks, another test is run to see if the experimental setup is able to hold pressure for an extended period of time. “Efferdent” tablets, normally purposed as denture cleaners, are placed into the digester and most of the remaining volume is filled with water. The tablets react in water and produce gas that is measured by the pressure gauge of the experimental setup.

Figure 20: "Efferdent" pills are placed into a bulk head digester to test whether pressure can be held by this experimental setup. This test raises concern for leaks of the bulk head fitting experiment.

The pressure inside the digester reached 27 psi after the reaction of the Efferdent pill and water was complete. Two days later, the pressure had fallen to 20 psi, and one day after that, the pressure had dropped to 10 psi. This experiment was unable to hold high pressure, but it is possible that the specific connections used for this experiment were slightly different than those used with anaerobic digestion experiments. The use of Teflon tape as a method of creating air tight seals is not perfectly consistent, and multiple attempts at the same seal may produce different results. Though this test showed a gas leak, if it were done again it may not have. The bulk head fitting experiment did produce quantitative results, but the Efferdent pill test clearly raises concerns about how reliable these results may be.

5.3.2 Bulk Head Fitting Experimental Data

Figure 19 displays the data collected from the two iterations of the bulk head fitting experiment. Noticeable gas production was observed, though data collection is sparse and so no gas production curve can be fit to the data with any reliable accuracy. In-depth calculations of predictions and results (with respect to amount of feedstock consumed and gas produced by mass) are not given here because a final design iteration is constructed and considered in more detail (section 6).

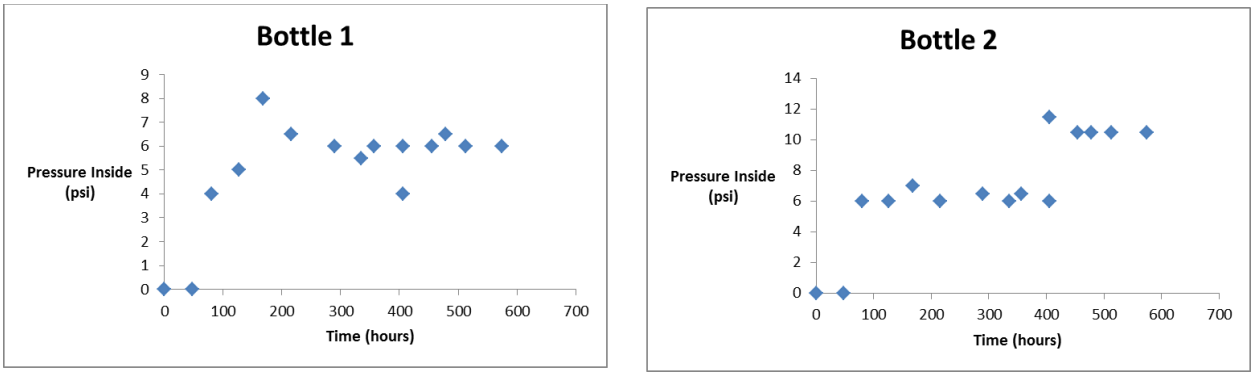

Figure 21: Data was collected for two iterations of the bulk head fitting experiment, with data values of gauge pressure (psi) over time.

5.3.3 Bulk Head Fitting Experiment Conclusions

The bulk head fitting experiment does give quantitative results, but the results are not used for adjusting the kinetic model because of a number of concerns. The digesters were able to hold pressure for an extended period of time, but the Efferdent pill test raises concern for gas leaks that may have affected the data collected. Further analysis of the experiment also raises questions about the aerobic initial conditions, the solubility of gases at elevated pressures, ammonia and other toxin accumulation, and imperfect mixing. These issues are described in more detail in section 5.4, and are considered before final experimental design iteration.

5.4 Experimental Design Issues

From the first three experimental iterations, concerns about leaks and other issues are raised; critical experimental design parameters are considered here.

5.4.1 Gas Leaks

Both the balloon digester and brass through-wall fitting digester experiments leaked gas. The bulk head fitting experiment was able to hold pressure for an extended period of time, but the Efferdent pill leak test raises concerns as to how air-tight the system is and how reliable the experimental data is. For final experimental design, it is important to be sure that no gas leaks can occur.

5.4.2 Aerobic Initial Conditions

In each of these first few experimental iterations, the digester has some volume of ambient air inside the digester before it is sealed. This means that the initial condition inside the digester includes oxygen and is not perfectly anaerobic. It is possible that initial gas production would then be a result of aerobic digestion; if this were the case, then the gas measured during the bulk head fitting experiment does not come from anaerobic digestion and definitely does not provide useful results. It is also possible that initial aerobic conditions make it impossible for anaerobic bacteria to survive long enough to produce significant gas. In this case, no anaerobic digestion would be measured. The potential for either of these two scenarios to occur makes it very important for oxygen to be removed from the digester during the initial setup of the experiment.

5.4.3 Imperfect Mixing

As explained in section 1.2.3, one important parameter to the digestion process is the extent to which anaerobic bacteria are able to come into contact with the slurry that they are consuming. This can be determined to a large extent by the extent of mixing of the digester system. However, the experiments done for this project include a limited amount of mixing. Mixing of the digesters is done by hand each time a data point is collected, which occurs during different intervals but with a minimum of a few hours between mixing instances. Thus the reaction kinetics and interaction between bacteria and slurry may not be what is initially predicted by modeling. This is why the kinetic reaction rate constant k is set to match the data of experimental results.

5.4.4 Ammonia Accumulation

According to Karaalp et al, because chicken manure is rich in Nitrogen, digestion of chicken manure as a single feedstock can be problematic because of ammonia toxicity, and different reports say that inhibition of the anaerobic digestion process occurs at an ammonia concentration of about 10 grams per liter, depending on the pH of the system. However, the study done by Karaalp et al concludes that there is minimal impact on productivity in the case of co-digestion or dilution of chicken manure to 10% dry matter[25]. To avoid potentially hazardous ammonia accumulation, it is then important in these experiments to maintain a solids content of the slurry below 10% - all experimental iterations did achieve this but there still could be a small impact in gas production caused by a limited amount of ammonia accumulation.

5.4.5 Solubility of Gases at Elevated Pressures

At higher pressures, gases become more soluble. Thus, there is some concern that once the pressure inside the digester tank becomes high enough, some of the gas produced is absorbed back into the slurry. This could affect the pressure measured inside the digester, and could affect the pH of the slurry which impacts the survival of bacteria.

To analyze the potential impact of solubility on gas collection, parameters from the final experimental design (see section 6) are used. If the experimental design is able to eliminate carbon dioxide from initial conditions, the initial partial pressure inside the digester tank is zero. Assuming that the experiment reaches a maximum of 10 psi (68.95 kPa) during data collection, the total number of moles of gas produced (carbon dioxide plus methane) is

$$\mathrm{n_{total}} = \frac{\mathrm{PV}}{\mathrm{RT}} = \frac{(68950\ Pa) * (.00155\ m^3)}{\left(8.314 \frac{J}{mol * K}\right) * (306.8\ K)} = 0.0419\ mols \tag{27}$$

If the output gas is made up of 30% (by volume) carbon dioxide, then the number of moles of carbon dioxide is 30% of this value

$$\mathrm{n_{CO_2}} = .3 * n_{total} = .0126\ mols \tag{28}$$

And the ideal gas law gives a partial pressure for CO2 of

$$\mathrm{P_{partial}} = \frac{\mathrm{nRT}}{V} = \frac{(.0126\ mols) * \left(8.314 \frac{J}{mol * K}\right) * (306.8\ K)}{(.00155\ m^3)} = 20.725\ kPa \tag{29}$$

According to Carroll et al[26], the solubility (in mole fraction) of carbon dioxide in water at a partial pressure of 50 kPa is $2.71 * 10^{-4}$. Because in this region solubility is linear, by interpolation the solubility of carbon dioxide (in mole fraction) in water at 20.725 kPa is $1.12 * 10^{-4}$. This gives a mass of CO2 of

$$\frac{1.12 * 10^{-4} mols\ CO_2}{mols\ of\ water\ in\ digester} * mm_{CO_2} * \frac{570\ g\ water}{mm_{H_2O}} = 0.16\ g\ CO_2 \tag{30}$$

Compared to the total mass of CO2, this is significant:

$$\text{mass of } CO_2 \text{ produced} = .0126\ mols * \frac{44.01\ g}{mol} = 0.55\ g\ CO_2 \tag{31}$$

This calculation says that the effect of solubility is significant. However, solubility varies with pressure, and pressure varies with gas production over time, so a solubility curve needs to be used to update the amount of gas accumulation during the simulation. Adding this effect into the kinetic model of this work adds a higher level of complexity than is the goal of the model; to incorporate the calculations into the kinetic model of gas production over time, much more computation is needed relative to what is already required. However, if the productivity of the bacteria is not significantly impacted by the absorption of carbon dioxide into the slurry, then the end result of increased solubility is to reduce the amount of pressure measured inside the anaerobic digester. This effect, along with other effects that are limiting gas production, is included in the limiting factor (*f*) that is used to match the model to experimental results. Therefore, while there is some concern for increased solubility of CO2, it is possible for this effect to also occur in standard use of anaerobic digesters and is accounted for by the limiting factor (*f*) of this model.

6. Final Experimental Design

The final experiment iteration addresses some concerns raised by initial rounds of experiments. In the final experimental design, 95 grams of chicken waste and 570 grams of water are put into a pump spray tank that is normally used for spray paint. It has inlet and outlet connections and a pressure gauge that makes it convenient for the purposes of this experiment. A system is designed to pump argon gas through the digestion tank to eliminate all atmospheric air and potential sources of oxygen at the beginning of experimental setup. The digester is kept in a water bath with temperature held at 92.7 ± 0.4 degrees Fahrenheit. A standard dial pressure gauge already attached to the pump spray tank is used for data collection, which is done over a period of 2 weeks.

6.1 Elimination of Atmospheric Air

To eliminate atmospheric air and the presence of oxygen at the beginning of the experiment, a cylinder of pressurized argon gas is used to flow argon through the digester tank. Argon gas is inert, and does not react with any other structures or gases in the chamber. Thus the initial condition of the digester tank is made anaerobic and there are no other negative effects from the replacement of gas.

The outlet of the tank is connected to an oxygen sensor so that the amount of oxygen held inside the tank can be measured as it is replaced by argon. Figure 22 provides a schematic of the flow of gas through the system.

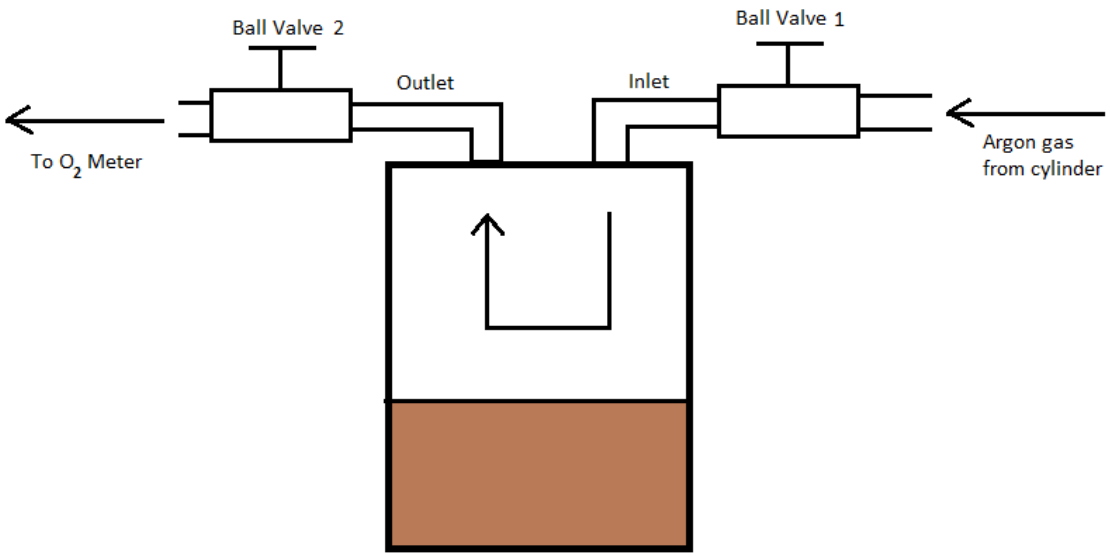

Figure 22: Argon gas is flown from the gas cylinder into the digester tank and is pulled out by the gas sensor.

Once the amount of oxygen measured by the oxygen sensor drops below 1 percent, both ball valves are closed so that the tank is not pressurized by incoming argon gas and a vacuum is not created by the gas measurement sensor pulling gas from the tank.

Figure 23: Argon gas is pumped through the digester tank until the amount of oxygen inside falls below 1 percent.

Figure 24 describes the interaction between the argon gas cylinder, the digester tank, and the gas sensor.

Figure 24: Argon gas is flown from the gas cylinder into the digester tank and is pulled out by the gas measurement sensor.

6.2 Experimental Parameters

The total volume that can be held inside the digester includes the volume of the inlet and outlet from the ball valves to the main tank as well as the space inside the tank. Though the capacity of the pump spray tank is listed as 2 quarts (1.89 liters), the measured value of the digester capacity is 2.21 liters, obtained by measuring input water with a graduated cylinder until the tank is full. The value of 2.21 liters is used as the digester capacity.

To begin the experiment, 95 g of chicken waste and 570 g of water are mixed together and put into the digester tank. After argon gas has been pumped through the tank, it is assumed to be completely filled with argon and is at atmospheric pressure (0 psi gauge pressure).

After the digester tank has been cleared of atmospheric air and valves have been closed, the tank is stored in a heated water bath. The temperature of the bath is controlled by an aquarium heater and made consistent throughout the bath by pumping the water through a water circulator. During the duration of the experiment, the temperature of the bath is found to remain at 92.7 $\pm$ 0.4 degrees Fahrenheit, which is near the middle of the mesophilic digestion temperature range.

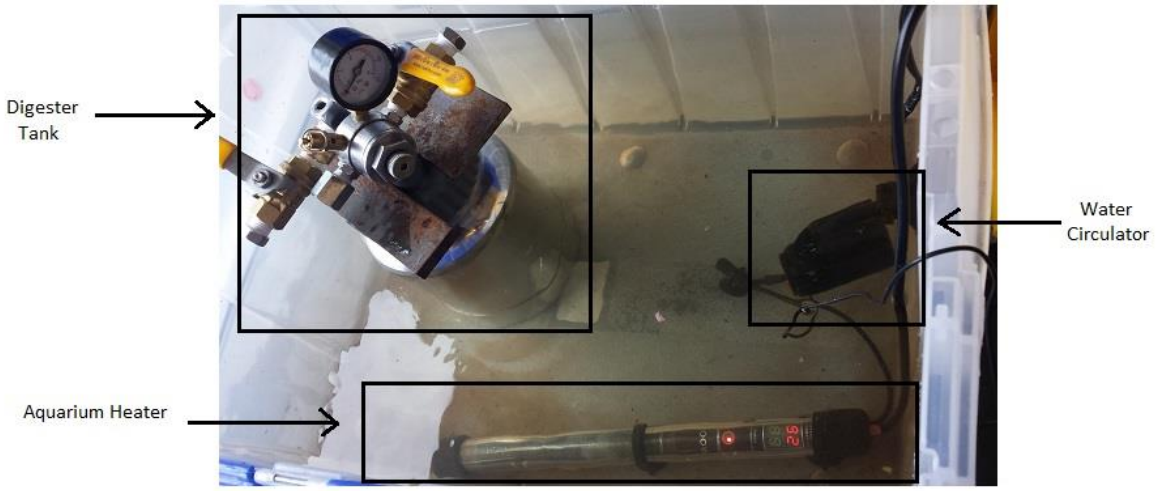

Figure 25: The digester is kept inside a water bath and held at an elevated temperature to simulate mesophilic digestion.

6.3 Expected Gas Production

The amount of chicken waste is chosen such that the expected gas production does not cause the pressure inside the digester tank to exceed 50 psi, the maximum rating of the pump spray tank. The expected pressure inside the tank is determined using the ideal gas law:

$$\mathrm{PV} = \mathrm{nRT} \tag{32}$$

All initial conditions are known except for the number of molecules in the tank, so this can be calculated from other known values. The initial volume left inside the tank for gas to accumulate is given by the amount and density of each type of initial input to the tank:

$$V = Initial\ volume\ of\ tank - Volume\ of\ waste - Volume\ of\ Water \tag{33}$$

$$V = Initial\ volume\ of\ tank - \frac{mass\ of\ waste}{density\ of\ waste} - \frac{mass\ of\ water}{density\ of\ water} \tag{34}$$

$$\mathrm{V} = 2.21\ \mathrm{L} - \frac{95\ \mathrm{g}}{1120\ \mathrm{g/L}} - \frac{570\ g}{1000\ g/L} = 1.555\ L = 0.001555\ m^3 \tag{35}$$

The other known values are:

$$P = 101.325\ kPa, R = 8.314\ \frac{J}{mol*K}\ , T = 306.9\ K \tag{36}$$

So the initial amount of gas inside the tank is:

$$\mathrm{n}_i = \frac{\mathrm{PV}}{\mathrm{RT}} = \frac{((101325\ Pa)*(0.001555\ m\text{^}3))}{(8.314\ \frac{J}{mol*K})*(306.9\ K)} = 0.0618\ mols \tag{37}$$

The predicted amount of gas produced is based on literature values. A number of references are given in table 7 for comparison.

Table 7: Biogas potential of chicken manure from different sources

Biogas Potential (units given by source)	Biogas potential (L/kg)	Reference
50 m^3 per wet tonne	50	Mississippi State Report[15]
75 m^3 per fresh ton	75	Karaalp et al[25]
35 m^3 per ton	35	Navickas[27]

Assuming that 1 kg of waste will produce approximately 50 L of biogas, and that the experiment uses 95 g of chicken waste, this gives an expected gas production of:

$$Expected\ gas\ production = 95\ g * \frac{50\ L}{kg} * \frac{1\ mol}{22.4\ L} = 0.212\ mols \tag{38}$$

Using the ideal gas law once again, the expected pressure inside the digester tank is calculated using the total moles, n_{total}, from the addition of both the initial condition and expected amount of gas production:

$$P_{expected} = \frac{(n_{total}\ * R * T)}{V} \tag{39}$$

$$P_{expected} = \frac{.274\ mols * 8.314 \frac{J}{mol * K} * 306.9\ K}{.00155\ m^3} = 451\ kPa \tag{40}$$

This is equivalent to 65 psi internal pressure, or 50psi gauge pressure, which is the limit of 50 psi that the pump spray tank is rated for.

The expected amount of gas produced by mass is:

$$0.212\ mols * 24.431 \frac{g}{mol} = 5.18\ g \tag{41}$$

6.4 Slurry Solids Content

Using the experimental calculation that the moisture content of the chicken waste is 70%, the percent solids of the slurry is

$$percent\ solids = \frac{mass\ of\ solids}{mass\ of\ slurry} * 100 \tag{42}$$

$$mass\ of\ solids = (95\ g\ waste)(30\%\ solids) + (570\ g\ water)(0\%\ solids) \tag{43}$$
$$= 28.5\ g$$

$$percent\ solids = \frac{28.5\ g}{95\ g + 570\ g} = 4.28\% \tag{44}$$

This value of 4.28% solids is expected to be a solution that is dilute enough to avoid issues of significant ammonia accumulation described in section 5.4.4.

6.5 Data Collection

Pressure is measured using a standard pressure gauge that comes with the Model RP8313 Air Paint Sprayer. The measured pressure inside the digester can be transformed into the amount of gas produced by using the molar mass of the gas along with the ideal gas law, previously stated in equation 19. The mass of the total gas produced is given by:

$$total\ gas\ produced = n_{total} * molar\ mass_{gas} \tag{45}$$

The molar mass is calculated with the assumption that 70% of the output gas is methane and 30% of the output gas is carbon dioxide.

$$molar\ mass_{gas} = .7 * molar\ mass_{CH_4} + .3 * molar\ mass_{CO_2} \tag{46}$$
$$= .7 * \left(16.04 \frac{g}{mol}\right) + .3 * \left(44.01 \frac{g}{mol}\right) = 24.431 \frac{g}{mol}$$

From the ideal gas law we know that:

$$n_{total} = \frac{PV}{RT} \tag{47}$$

So, by combining equations 44 and 46 we calculate:

$$total\ gas\ produced = \frac{PV}{RT} * molar\ mass_{gas} \tag{48}$$

With units of pressure in Pa, volume in m^3, R in $\frac{J}{m*K}$, T in kelvin, and molar mass in $\frac{g}{mol}$ to calculate gas production in grams. Using these calculations, total gas production by mass is determined and given in figure 26.

The final measurement of 9.75 psi (67.2 kPa) gives:

$$total\ gas\ produced = \frac{(67200\ Pa)\left(0.00155\ m^3\right)}{\left(8.314 \frac{J}{mol * K}\right)(306.9\ K)} * 24.431 \frac{g}{mol} \tag{49}$$

$$= 0.997\ g$$

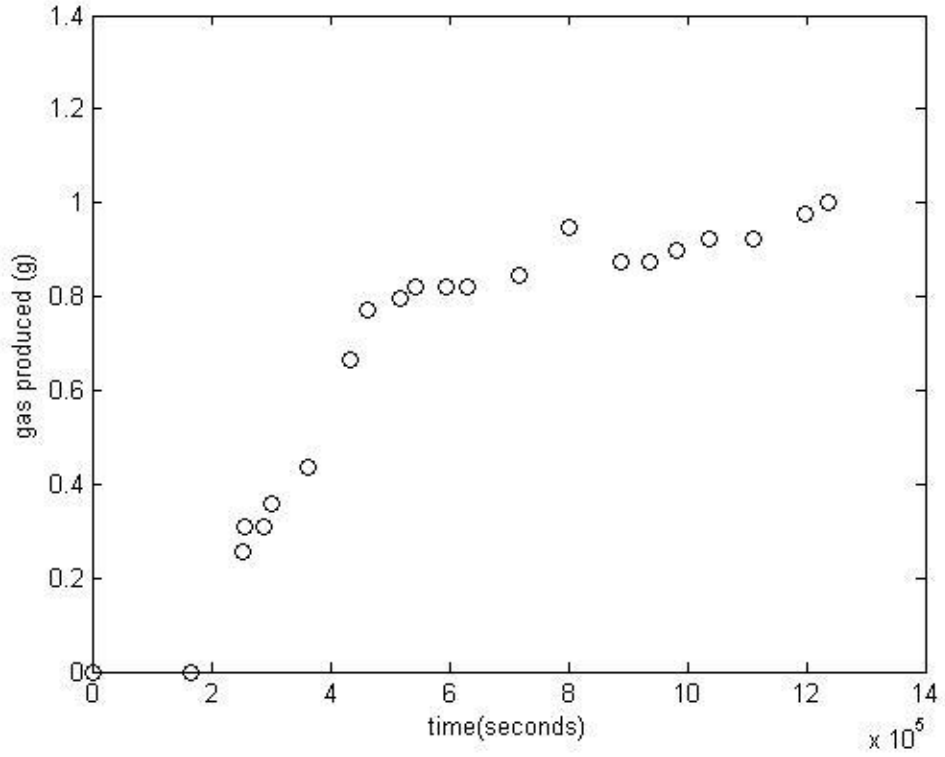

Figure 26: Experimental gas production over time. Pressure was experimentally measured, and the amount of gas was calculated using the ideal gas law.

7. Matching Model and Experiment

7.1 Time delay (τ) and limiting factor (f)

Because there is an initial time period during which a sustainable microbial population must be established to start producing gas, the model must be offset by a time delay (τ). The value of the time delay is determined experimentally, and is the amount of time that passes from the start of the experiment to when the digester begins to produce gas.

Another fitting parameter is a limiting factor (f) that accounts for the fact that the hypothetical potential of complete reaction will not be reached. Reactions rarely go entirely to completion, and in the case of anaerobic digestion, this limiting factor is a result of imperfect mixing, toxin accumulation, and pH and temperature effects. Instead of creating a model that considers all possible causes of this adjustment parameter, the value for f is taken as the ratio of total experimental gas production to the gas production that would occur under (unrealistic) ideal conditions.

By adjusting parameter values to match experimental results by eye, and taking experimental values of $\tau = 2 * 10^5 seconds$ and $f = .0085$, we can adjust the kinetic parameter k to give a reasonable fit of the model to the data. When $k = 5 * 10^{-6} \left(\frac{mol}{L} * seconds\right)^{-1}$, we obtain the curves given in figure 26.

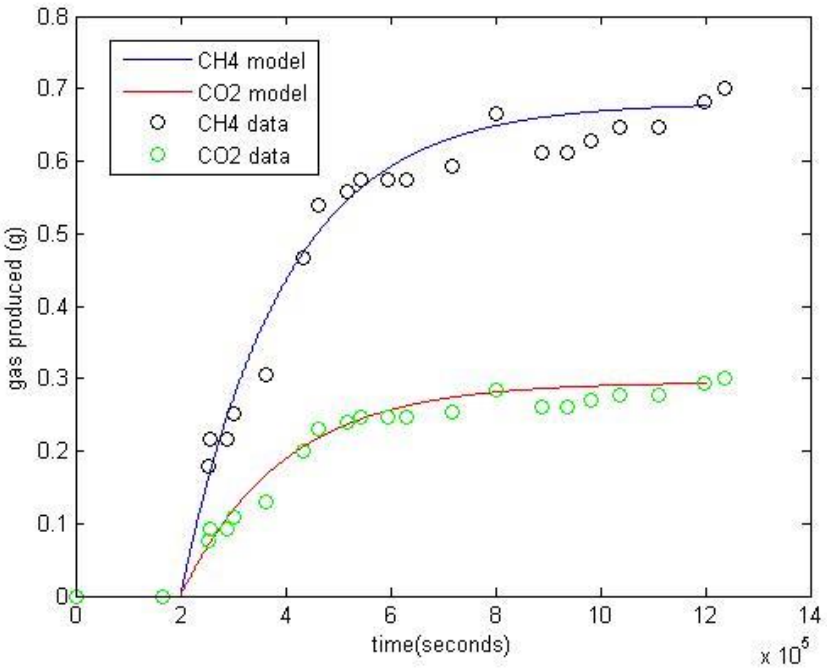

Figure 27: Initial matching of experimental data to the kinetic model.

7.2 *More Precise Value of Kinetic Constant*

To obtain a more precise value of k, the simulation is run for varying values of k near to the value used to match the experimental data by eye. To reduce computation time, only a handful of simulations are run and k is found to the nearest tenth; using the method of least squares to find a more exact value of k requires much more computational effort, which is not in the spirit of this model. The final value of the kinetic constant is found to be $k = 4.8\left(\frac{mol}{L} * seconds\right)^{-1}$. Using this value, the data matches more closely to the model, as shown in figure 27.

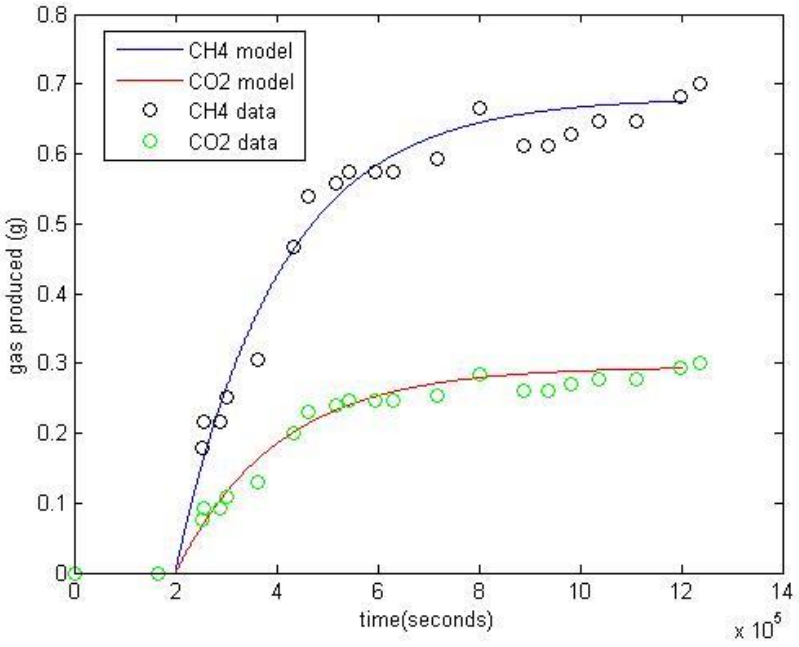

Figure 28: A refined value of $k = 4.8\left(\frac{mol}{L} * seconds\right)^{-1}$ matches data and experiment more closely.

8. Summary and Discussion

8.1 Application of This Model

This work provides a basic model that does not require many inputs or a large amount of computation time, but still considers biochemical processes to predict biogas output over time. This is useful for predicting results of an anaerobic digester given similar settings to those used in experiments of this project. It is also useful for predicting results of other settings if other experimental data is available to adjust parameters of time delay (τ), limiting factor (f), and the kinetic constant (k).

This model can also help a user determine the ideal digester sizing and feed rate for their anaerobic digester. This model predicts that the rate of gas production slows over time, and a user may identify a minimum gas production rate that is profitable or otherwise utilize the ability to determine the percentage of completion of the reaction at any time.

The model may also be applied to any number of feedstocks, as long as the user can input the ultimate analysis of the feedstock that includes mass ratios of carbon, hydrogen, and oxygen. Simplifications are made and the results for varying feedstocks and external conditions may vary, but the model provides baseline predictions that can aid basic digester design.

8.2 Future Work

This model does include a number of simplifications and could be made more complex without adding excessive computation time if done correctly. Some additional considerations that the model could be adjusted to include are:

- Temperature dependence of the kinetic constant k.
- Additional terms in the biochemical reaction used for analysis, such as the biochemical reaction used by Mahar et al[20] that includes a term for nitrogen.
- Further optimization of the kinetic constant k using the method of least squares or other optimization techniques.
- Inclusion of ashes in ultimate analysis can lead to a calculation of accumulation of ashes. This can tell a user how much of their digester capacity they are losing over time, which could inform how regularly the digester needs to be cleaned.
- In addition, the inputs and outputs can help with the design of digesters for small farms to help with ease of use and maximize total useful output which includes not only useful biogas by liquid fertilizer for easy application to fields.

9. Appendices

Appendix A: Glossary

Co-Digestion – the digestion of multiple materials as a feedstock for a digester. For example, a digester may co-digest chicken manure with sawdust.

Effluent – the residual slurry left at the end of the anaerobic digestion process, which is generally displaced by incoming feedstock.

Feedstock – the input to an anaerobic digester, which can be any organic matter. This project focuses on chicken manure as a feedstock.

Residence Time – the amount of time that material spends inside the digester before leaving the digester as effluent when displaced by new feedstock coming in.

Slurry – the mixture of a feedstock, water, and any other components that are contained inside an anaerobic digester during operation.

Appendix B: MATLAB Simulation Code

```
%% Kinetic Model
%

% kinetic coefficient
k = 4.8*10^-6 ;
% mass flow rate in (kg/day)
dAdtin = 0 ;
% masss flow rate out
dAdtout = 0 ;
% these are molar masses of each element
mm_carbon = 12.0107 ;
mm_hydrogen = 1.0079 ;
mm_oxygen = 15.999 ;

% For C_n H_a O_b + H20 -- CO2 + CH4
% These constants come from the ultimate analysis
% These constants dictate the coefficients of each term
nbymass = .272 ;
abymass = .037 ;
bbymass = .231 ;

% to get molar ratios we divide by molar mass
n = nbymass/mm_carbon ;
a = abymass/mm_hydrogen ;
b = bbymass/mm_oxygen ;

% These are the coefficients in front of each component of the reaction.
% C_n H_a O_b + c_1*H20 -- c_2*CO2 + c_3*CH4
c_1 = n - a/4 -b/2 ;
c_2 = n/2 -a/8 + b/4 ;
c_3 = n/2 + a/8 - b/4 ;

% These are the molar masses of each component
mm_A = mm_carbon*n + mm_hydrogen*a + mm_oxygen*b ;
mm_B = 2*mm_hydrogen + mm_oxygen ;
mm_C = mm_carbon + 2*mm_oxygen ;
mm_D = mm_carbon + 4*mm_hydrogen ;

% These are the masses of each component per mol of waste
m_A = mm_A ;
m_B = c_1*mm_B ;
m_C = c_2*mm_C ;
m_D = c_3*mm_D ;

ratio = m_C/(m_C + m_D)

% Initial conditions
% mass in g, capacity in L, volume of reaction in L
mass_of_waste = 95 ;
mass_of_water = 570 ;
density_of_waste = 1.13 ;
```

```
density_of_water = 1 ;
volume_of_reaction = (mass_of_waste/density_of_waste +
mass_of_water/density_of_water)/1000 ;
digester_capacity = 2.21 ;
Ahat_0 = mass_of_waste/mm_A/digester_capacity ;
Bhat_0 = mass_of_water/mm_B/digester_capacity ;
Chat_0 = 0 ;
Dhat_0 = 0;
dAhatdt_0 = -k*Ahat_0*(Bhat_0^(c_1)) ;
dBhatdt_0 = -k*Ahat_0*(Bhat_0^(c_1))*c_1 ;
dChatdt_0 = k*Ahat_0*(Bhat_0^(c_1))*c_2 ;
dDhatdt_0 = k*Ahat_0*(Bhat_0^(c_1))*c_3 ;

%% Can iterate this process for very small steps of time to approximate the
% new concentration of each component of the reaction

% Concentration of each component put into a row vector
tfinal = 1000000 ;
t = (1:tfinal) ;
Ahat = zeros(1,tfinal) ;
Bhat = zeros(1,tfinal) ;
Chat = zeros(1,tfinal) ;
Dhat = zeros(1,tfinal) ;

% Rate of concentration of each component put into a row vector
dAhatdt = zeros(1,tfinal) ;
dBhatdt = zeros(1,tfinal) ;
dChatdt = zeros(1,tfinal) ;
dDhatdt = zeros(1,tfinal) ;

% initial conditions put into the first index of the vectors
Ahat(1) = Ahat_0 ;
Bhat(1) = Bhat_0 ;
Chat(1) = Chat_0 ;
Dhat(1) = Dhat_0 ;
dAhatdt(1) = dAhatdt_0 ;
dBhatdt(1) = dBhatdt_0 ;
dChatdt(1) = dChatdt_0 ;
dDhatdt(1) = dDhatdt_0 ;

% simulation run for small time steps to give concentration over time
for i = 2:tfinal
    Ahat(i) = Ahat(i-1) + dAhatdt(i-1) ;
    Bhat(i) = Bhat(i-1) + dBhatdt(i-1) ;
    Chat(i) = Chat(i-1) + dChatdt(i-1) ;
    Dhat(i) = Dhat(i-1) + dDhatdt(i-1) ;

    dAhatdt(i) = -k*Ahat(i)*(Bhat(i)^(c_1)) ;
    dBhatdt(i) = -k*Ahat(i)*(Bhat(i)^(c_1))*c_1 ;
    dChatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1))*c_2 ;
    dDhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1))*c_3 ;

end
```

```
% mols converted to mass of gas produced
mols_of_c = Chat*digester_capacity ;
mols_of_d = Dhat*digester_capacity ;
mass_of_CO2 = mols_of_c*mm_C ;
mass_of_CH4 = mols_of_d*mm_D ;

% fitting factor used to adjust model to experiment
fitting_factor = .0085 ;
mass_of_CO2_fitted = mass_of_CO2*fitting_factor ;
mass_of_CH4_fitted = mass_of_CH4*fitting_factor ;
t_fitted = t + 2*10^5 ;

%% Now to add data and convert it to mass
time_h =
[0;46;70;71.5;80.5;83.5;101.25;120.5;128.5;144.25;150.75;165.25;175.5;199;222
.25;247.25;260.25;272.75;288.5;308.75;333.25;343.5] ;
time_s = time_h*3600 ;
pressure_psi =
[0;0;2.5;3;3;3.5;4.25;6.5;7.5;7.75;8;8;8;8.25;9.25;8.5;8.5;8.75;9;9;9.5;9.75]
;
pressure_Pa = 6894.757*pressure_psi ;
T = 307 ; %K ;
R = 8.314 ; %J/mol/K
V_L = digester_capacity - volume_of_reaction ; %Liters
V_m3 = V_L*10^-3 ; % m^3
mm_g = .7*mm_D + .3*mm_C ;
mass_of_CO2_data = (.3*V_m3*mm_g/(R*T))*pressure_Pa ;
mass_of_CH4_data = (.7*V_m3*mm_g/(R*T))*pressure_Pa ;

% plot data and model on same plot to observe how well they match
plot(t_fitted, mass_of_CO2_fitted,'b', t_fitted, mass_of_CH4_fitted, 'r',
time_s, mass_of_CH4_data, 'ko', time_s, mass_of_CO2_data, 'go')
xlabel('time(seconds)')
ylabel('gas produced (g)')
legend('CH4 model', 'CO2 model','CH4 data', 'CO2 data')
```

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